

Ministry of Science and Higher Education of the Russian Federation
ITMO University

ISSN 2220-8054

NANOSYSTEMS:
PHYSICS, CHEMISTRY, MATHEMATICS

2026, volume 17 (3)

Наносистемы: физика, химия, математика

2026, том 17, № 3



NANOSYSTEMS: ***PHYSICS, CHEMISTRY, MATHEMATICS***

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AIM AND SCOPE

The scope of the journal includes all areas of nano-sciences. Papers devoted to basic problems of physics, chemistry, material science and mathematics inspired by nanosystems investigations are welcomed. Both theoretical and experimental works concerning the properties and behavior of nanosystems, problems of its creation and application, mathematical methods of nanosystem studies are considered.

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RUSANOV ANATOLY IVANOVICH
20 April 1932 – 6 May 2026

On 6 May 2026, Anatoly Ivanovich Rusanov passed away — Doctor of Chemical Sciences and Full Member (Academician) of the Russian Academy of Sciences.

Anatoly Ivanovich Rusanov was born in Leningrad. In 1949 he matriculated at Leningrad University, where he read first in the Department of Physics and subsequently in Department of Chemistry. In 1963 he defended his doctoral dissertation, *On the Equilibrium of Heterogeneous Systems with Account of Surface Phenomena*. In 1967 he founded the Laboratory of Surface Phenomena and directed it until 1987, when, following the merger of the laboratory with the Department of Colloid Chemistry, he assumed the headship of that department — a position he held until February 2025. In 1990 he was elected Corresponding Member of the USSR Academy of Sciences, and in 1991 Full Member of the Russian Academy of Sciences.

The scholarly contributions of A.I. Rusanov address the foundational principles of science. His research interests encompassed physical and colloid chemistry, chemical thermodynamics, mechanochemistry, computer simulation, nucleation theory and phase processes, surfactant chemistry, and surface separation, as well as nanoscience. Rusanov synthesised the modern advances pertaining to the development of surface thermodynamics and nanodisperse heterogeneous systems, and elaborated a new approach to determining the thermodynamic surface tension of solids. He pursued further the thermodynamic theory of the

strength of solids and developed a theoretical description of sorption-induced deformation processes in nanoporous adsorbents. He investigated six characteristic functions of classical thermodynamics as applied to solid systems: energy, free energy, Gibbs energy, enthalpy, the grand thermodynamic potential, and a novel characteristic function — the J-potential.

In 1981, A.I. Rusanov was solely awarded the USSR State Prize in Science for a series of works in the physical chemistry of surface phenomena. He served as a People's Deputy of the USSR representing the Union of Scientific and Technical Societies (1989–1991). From 1995 to 1998 he was President of the D.I. Mendeleev Russian Chemical Society, and subsequently Vice-President of that Society.

A.I. Rusanov was the author of more than 750 scholarly publications, including 12 monographs. His work received recognition through numerous prestigious awards. In addition to the State Prize, he was the recipient of the S. I. Volfkovich Prize of the Russian Chemical Society (1991), the D.I. Mendeleev Prize of the Russian Academy of Sciences (1993), the P. A. Rehbindler Prize of the Russian Academy of Sciences (2001), the D. I. Mendeleev Prize of the Government of Saint Petersburg (2004), and on three occasions the Saint Petersburg State University Prize for Outstanding Scientific Work of the Year. In 2008 the Russian Academy of Sciences awarded A. I. Rusanov the Mendeleev Gold Medal.

In 2003 A.I. Rusanov was conferred the Order of Friendship; in 2008, the Order of Honour; in 2015, a Certificate of Honour of the President of the Russian Federation; and in 2024, the Jubilee Medal commemorating the 300th Anniversary of the Academy of Sciences.

From the very founding of the journal *Nanosystems: Physics, Chemistry, Mathematics*, Anatoly Ivanovich Rusanov served on its editorial board and contributed greatly to advancing its standing within the international scholarly community.

The passing of Anatoly Ivanovich is an irreparable loss to the entire scientific community. The members of the editorial board and editorial council of *Nanosystems: Physics, Chemistry, Mathematics* mourn his death and extend their deepest condolences to all who knew Anatoly Ivanovich Rusanov.



IEVLEV VALENTIN MIKHAILOVICH
1 December 1938 – 19 April 2026

On April 19, 2026, Academician of the Russian Academy of Sciences Valentin Mikhailovich Ievlev has gone at the age of 88. V.M.Ievlev is a Honored Scientist of the Russian Soviet Federative Republic (1991), he is awarded by the Medal of the Order of Merit for the Fatherland, II degree (1999), Certificate of Honor from the President of the Russian Federation for the development of national science, for fruitful work and in connection with the 300th anniversary of the founding of the Russian Academy of Sciences (2024). V.M.Ievlev had important duties as a Chief Researcher at the A. A. Baykov Institute of Metallurgy and Materials Science of RAS, a Head of the Chair of Interdisciplinary Materials

Science, Faculty of Materials Sciences, Lomonosov Moscow State University, a Head of the Chair of Materials Science and Nanosystems Industry, Voronezh State University.

Valentin Mikhailovich Ievlev was born on December 1, 1938 in the village of Prigorodki, Usmansky district, Voronezh (and now Lipetsk) region. In 1961, he graduated from the Physics Department of Voronezh State University. In 1961-1963, he worked as an engineer at the Uzenergogaz isotope Laboratory, the Design Bureau of Electrical Engineering and Instrumentation in Tashkent, and in 1963-1966, he received a position of a senior engineer at the Special Radio Communications Design Bureau in Voronezh. Later, at Voronezh Polytechnic Institute (now Voronezh State Technical University, VSTU) he became a postgraduate student of the Department of Metal Physics, senior lecturer, Associate Professor, Professor, in 1977-1983, V.N.Ievlev accepted the position of Dean of the Faculty of Physics and Technology, in 1979-2004 he is elected as a Head of the Department of Physics, in 1983-2003 V.M.Ievlev took a position of Vice Rector. Since 2004, he has been working as a Chief Researcher at the Regional Research Laboratory of Electron Microscopy and Electronography of VSTU, Professor at the Department of Solid State Physics of VSTU. He has established in 2008 a new perspective Chair of Materials Science and Nanosystems Industry at Voronezh State University. Since 2004 V.M.Ievlev has been working as a Chief Researcher at the Institute of Physico-Chemical Problems of Ceramic Materials of the Russian Academy of Sciences (since 2007 – the Institute of Metallurgy and Materials Science named after A. A. Baykov). Since 2013 he became a Head of the Department of Interdisciplinary Materials Science, Faculty of Materials Sciences, Lomonosov Moscow State University.

The name of Academician V.M. Ievlev is vitally connected with the history of key materials for microelectronics, innovative approaches in electron microscopy, education of young talents in Materials Sciences in our country. Under the leadership of V.M. Ievlev, one of the largest Regional Research Laboratories of Electron Microscopy and Electronography at the Voronezh Polytechnic Institute has been established. For the first time, the ideas about the mechanism of relaxation of elastic deformation upon epitaxy growth have been developed, which are used to justify the choice of the orientation of the substrate crystals. A method for assessing the type of dislocation loops formed during ion implantation has been developed. The laboratory conducted a key certification of the quality of silicon wafers supplied to NPO Electronics. In the Laboratory, an innovative ultrahigh vacuum system has been created and equipped with everything necessary to carry out the synthesis of metal silicides to assess the temperature threshold of silicification on juvenile (extremely clean) surfaces.

V.M. Ievlev's fundamental works in the field of growth and structure of thin inorganic films, the structure of internal interface surfaces in crystalline materials, as well as studies on the effect of photonic activation in the synthesis of nanostructures have received worldwide recognition. His approaches to the creation of oriented film nanostructures and technological processes formed the basis for the creation of the element base of microelectronics and new perspective devices in our country.

The well-known scientific school of Academician V.M. Ievlev procreated 5 doctors of sciences and 34 candidates of sciences. V.M. Ievlev is the author of more than 660 scientific publications, including 5 monographs, 8 textbooks and 10 patents.

We will deeply remember in our hearts Valentin Mikhailovich as an outstanding researcher and enthusiastic innovator, as a remarkable organizer of science, but also as a member of Russian scientific community of exceptional decency, amazing inner harmony, determination, wisdom and responsiveness. His scientific legacy will forever remain the bright basis of new sights and revolutionary ideas in the field of materials science.

We express our sincere condolences to everyone who knew and kept brilliant figure of Valentin Mikhailovich. The bright memory about this magnificent Academician, Supervisor, Researcher, Discoverer will remain in our hearts and will continue in new achievements of innumerable students and young scientists attentively grown by V.M. Ievlev.

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Threshold resonances and discrete spectrum of a two-boson hamiltonian with a molecular channel on the one-dimensional lattice

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ABSTRACT We study a two-channel lattice Hamiltonian in a fixed particle-number sector on the one-dimensional lattice $\mathbb{Z}$. The model consists of a molecular channel coupled to a bosonic two-particle channel with on-site interaction. In the momentum representation, translation invariance yields a family of reduced Hamiltonians $H_{\gamma,\lambda}(K)$ parametrized by total quasi-momentum $K \in \mathbb{T}$, each acting in $\mathbb{C} \oplus L^{2,e}(\mathbb{T})$.

For contact interactions, each reduced Hamiltonian is a rank-two perturbation of the free diagonal operator. By means of the Lippmann–Schwinger method, the eigenvalue problem for energies outside the essential spectrum $[\mathcal{E}_K^-, \mathcal{E}_K^+]$ is reduced to a 2×2 linear system and, equivalently, to the vanishing of an explicit scalar Fredholm determinant involving the one-dimensional lattice Green function. The square-root singularities of this Green function at the band edges $\mathcal{E}_K^\pm$ determine the threshold asymptotics of the determinant and lead to explicit criteria for the existence of eigenvalues below the lower threshold and above the upper threshold.

We obtain a complete classification of the discrete spectrum of $H_{\gamma,\lambda}(K)$ for all quasi-momenta in terms of the parameters γ , λ , and E_0 . We also analyze the threshold configurations $E_0 = \mathcal{E}_K^\pm$, the exceptional flat-band fiber $K = \pi$, where the essential spectrum collapses to a single point, and the threshold states of the auxiliary rank-one operator $\mathbf{h}_\lambda(K)$. For the latter, we provide a weighted-space description of threshold resonances, clarifying how an eigenvalue emerges from a threshold resonance of $\mathbf{h}_\lambda(K)$ and approaches a band edge when the interchannel coupling is switched on.

KEYWORDS Lattice Hamiltonian, two-channel model, fixed particle-number sector, Fredholm determinant, Lippmann–Schwinger equation, discrete spectrum, threshold asymptotics, threshold resonance.

ACKNOWLEDGEMENTS This work was supported by the Ministry of Higher Education, Science and Innovations of the Republic of Uzbekistan (Grant No. AL-9224104685).

FOR CITATION Lakaev Sh.S. Threshold resonances and discrete spectrum of a two-boson hamiltonian with a molecular channel on the one-dimensional lattice. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 251–268.

1. Introduction

1.1. Background and motivation

The spectral theory of lattice hamiltonians for interacting quantum particles has been studied intensively for several decades, beginning with the works [1, 2]; see also [3–5] and the monographs [6, 7]. The works of Mogilner [2, 5] established the basic spectral properties of multiparticle discrete Schrödinger operators on lattices, including the structure of the essential spectrum and the existence of bound states for systems of three identical bosons. His review [2] systematically formulated the N -particle lattice problem as a theory of bounded operators and outlined a number of open problems that have subsequently stimulated intensive research. Unlike continuum Schrödinger operators, lattice hamiltonians have bounded dispersion relations and are naturally formulated on the Brillouin zone $\mathbb{T}^d$. Consequently, their essential spectra are compact, and their threshold behavior differs substantially from that of continuum models. Important examples arise from few-particle sectors of Bose–Hubbard models, which lead to discrete Schrödinger operators with short-range interactions; see, for example, [8–11]. In one dimension, the corresponding Green functions exhibit square-root singularities at the band edges, making this setting especially suitable for the explicit analysis of threshold resonances, virtual levels, and bound states.

Lattice models are widely used in mathematical physics. One such model is the lattice N -body hamiltonian [1] that represents a minimalist version of the corresponding Bose– or Fermi–Hubbard models involving just N particles of a certain type. The lattice N -body hamiltonians are of great interest even for $1 \leq N \leq 3$ and the respective lattice N -particle problems have been intensively studied over the past several decades [8, 12, 13]. An additional reason to study such hamiltonians is that, in fact, they serve as a natural discrete approximation of the continuous N -body Schrödinger operators. Setting down the N -body problem on a lattice allows one to study it in the context of the theory of bounded

operators. Notice that the one-particle 1D lattice case is essentially covered by the general perturbation theory for infinite Jacobi matrices (see, e.g., [14, 15]).

The lattice N -body Schrödinger operators also serve as a model for systems formed by N particles traveling through periodic structures, e.g. for ultracold atoms injected into optical crystals [16]. In the last decades, the study of ultracold few-atom systems in optical lattices has become of particular interest due to the availability of controllable parameters such as temperature, particle masses, and interaction potentials (see e.g. [16] and references therein).

Such models provide natural testbeds for finite-rank perturbation methods, Fredholm determinant techniques, and threshold singularity analysis, which are central themes in mathematical physics. The present paper fits into this circle of ideas. We study a two-channel lattice model for two identical bosons coupled to an internal molecular mode. The model is considered as a coupled two-channel hamiltonian in a fixed particle-number sector. Our main goal is to give a complete description of the discrete spectrum of the associated reduced hamiltonians, to analyze their threshold behavior, and to identify the mechanisms of bound-state formation.

1.2. The model

We consider two identical spinless bosons on $\mathbb{Z}$ with on-site interaction strength $\lambda \in \mathbb{R}$, coupled to a molecular channel of internal energy $E_0 \in \mathbb{R}$. The interchannel coupling is governed by $\gamma \in \mathbb{R}$. After the Fourier transform and the Floquet–Bloch decomposition, translation invariance yields a direct-integral decomposition with respect to the total quasi-momentum $K \in \mathbb{T}$. The corresponding reduced hamiltonians are denoted by $H_{\gamma,\lambda}(K)$, $K \in \mathbb{T}$, and act in the fiber Hilbert spaces $\mathcal{H}_K = \mathbb{C} \oplus L^{2,e}(\mathbb{T})$, where $\mathbb{C}$ represents the molecular channel in the fiber and $L^{2,e}(\mathbb{T})$ denotes the subspace of even functions in the two-boson channel.

For contact interactions, the perturbation of the free reduced hamiltonian has rank at most two: one rank-one term is generated by the on-site interaction, and the other by the molecular coupling. Thus the analysis reduces to the fiber operators $H_{\gamma,\lambda}(K)$. The eigenvalue problem outside the essential spectrum reduces, by the Lippmann–Schwinger method [17], to a 2×2 linear system and, equivalently, to a scalar Fredholm determinant. Alongside $H_{\gamma,\lambda}(K)$, the auxiliary rank-one fiber operator $\mathbf{h}_\lambda(K)$, acting in the bosonic channel alone, provides useful information on how isolated eigenvalues approach the band edges.

1.3. Main results

- (i) **Reduced hamiltonians and essential spectrum.** For fixed $K \in \mathbb{T}$, the essential spectrum of $H_{\gamma,\lambda}(K)$ equals the range of the free two-particle dispersion

$$\varepsilon_K(p) = 4 \left(1 - \cos \frac{K}{2} \cos p \right),$$

namely,

$$\sigma_{\text{ess}}(H_{\gamma,\lambda}(K)) = [\mathcal{E}_K^-, \mathcal{E}_K^+], \quad \mathcal{E}_K^\pm = 4 \left(1 \pm \left| \cos \frac{K}{2} \right| \right). \quad (1)$$

The fiber $K = \pi$ is exceptional: the dispersion is flat, and the essential spectrum collapses to the singleton $\{4\}$.

- (ii) **Lippmann–Schwinger reduction.** For

$$z \notin [\mathcal{E}_K^-, \mathcal{E}_K^+],$$

the eigenvalue problem reduces to a scalar equation

$$\Delta_{\gamma,\lambda}(K; z) = 0, \quad (2)$$

where $\Delta_{\gamma,\lambda}(K; z)$ is an explicit Fredholm determinant involving the one-dimensional lattice Green function

$$a_K(z) = \frac{1}{2\pi} \int_0^{2\pi} \frac{dp}{\varepsilon_K(p) - z}. \quad (3)$$

Thus the discrete spectrum outside the essential band is completely determined by zeros of a single scalar function.

- (iii) **Threshold analysis and bound-state classification.** The square-root singularities of $a_K(z)$ at the band edges $\mathcal{E}_K^\pm$ give asymptotic expansions of $\Delta_{\gamma,\lambda}(K; z)$ near the thresholds. The leading coefficients provide criteria for the existence of eigenvalues below the lower threshold and above the upper threshold. This yields a complete classification of the discrete spectrum in terms of γ , λ , E_0 , and the position of E_0 relative to $[\mathcal{E}_K^-, \mathcal{E}_K^+]$.
- (iv) **Decoupled case, threshold configurations, and flat band.** The decoupled case $\gamma = 0$ serves as a reference case. It shows how new spectral phenomena, such as the creation, displacement, or disappearance of eigenvalues near the band edges, emerge when γ is switched on. This is especially relevant for the threshold configurations

$$E_0 = \mathcal{E}_K^- \quad \text{or} \quad E_0 = \mathcal{E}_K^+,$$

where virtual-level behavior may occur. For the flat fiber $K = \pi$, the spectral problem reduces to an explicit quadratic equation, giving a closed-form description of the discrete spectrum.

- (v) **Threshold states of the auxiliary rank-one operator.** For $\mathbf{h}_\lambda(K)$, we introduce weighted threshold spaces adapted to the singular behavior at the band edges and classify its threshold states. This yields a weighted-space description of threshold resonances and clarifies how threshold profiles transform into genuine eigenvalues outside the essential spectrum when γ is perturbed away from zero. In this way, the analysis of $\mathbf{h}_\lambda(K)$ complements the decoupled case and explains the emergence of new spectral effects in the coupled model.

Taken together, these results provide a complete explicit spectral analysis of the reduced hamiltonians $H_{\gamma,\lambda}(K)$ in the one-dimensional contact-interaction regime, together with a detailed description of threshold behaviour for the associated rank-one fiber operators.

1.4. Relation to previous works

We begin by recalling the well-known connection between one-dimensional lattice operators, Jacobi matrices, and the theory of orthogonal polynomials. Comprehensive treatments appear in the monographs by Simon [18–20]. Related results for discrete one-dimensional Schrödinger and Jacobi operators, including spectral and perturbative aspects, can be found in, e.g., the work of Damanik, Hundertmark, Killip, and Simon [21].

Another relevant direction concerns one-dimensional lattice models whose spectral problem admits explicit or semi-explicit analysis. In this context, the approach developed in [22, 23] provides a useful point of comparison for the study of bound states in one-dimensional lattice hamiltonians. The present paper is also conceptually related to the theory of threshold states and virtual levels. We particularly refer to Yafaev’s foundational work on virtual levels for the three-dimensional continuous Schrödinger equation [24]. Although Yafaev’s setting is continuous and three-dimensional, whereas our model is discrete and one-dimensional, the functional-analytic idea of describing a virtual level as a non-square-integrable threshold solution in a suitable weighted space is relevant for our threshold analysis below.

Our work is most directly connected to the spectral theory of two-particle lattice hamiltonians and Bose–Hubbard type models, especially results concerning threshold effects, discrete spectra, and resonant phenomena on lattices [8, 10–13, 25, 26]. Recent studies of lattice Schrödinger operators with short-range and nearest-neighbor interactions have revealed a rich spectral structure, notably the appearance of isolated eigenvalues and threshold phenomena [27, 28]. These results provide further motivation for investigating the coupled-channel lattice hamiltonians considered in the present work. In contrast to these works, the novel feature of the present model is the inclusion of an additional molecular channel with purely on-site interactions in one dimension, together with a systematic analysis of resonances on such lattices. This structure yields a transparent block-operator formulation and reduces the spectral problem to a scalar Birman–Schwinger equation, or equivalently, to a Fredholm determinant equation.

The methods employed here are also related to rank-one and finite-rank perturbation techniques for solvable quantum models [6, 7]. In our setting, the effective finite-rank structure makes it possible to combine the Lippmann–Schwinger reduction with explicit one-dimensional lattice Green functions. This yields a complete characterization of the discrete spectrum, threshold configurations, and resonant phenomena for all values of the model parameters.

1.5. Organization

Section 2 introduces the model in the quasi-momentum representation, performs the fiber decomposition, and defines the reduced hamiltonians $H_{\gamma,\lambda}(K)$. Section 3 presents the Lippmann–Schwinger reduction and the scalar Fredholm determinant. Section 4 classifies the discrete spectrum of $H_{\gamma,\lambda}(K)$, including threshold configurations and the flat-band fiber. Section 5 studies threshold states of the auxiliary rank-one fiber operator $\mathbf{h}_\lambda(K)$.

2. The reduced hamiltonian at fixed total quasi-momentum

In this section, we study the reduced hamiltonians $H_{\gamma,\lambda}(K)$ corresponding to fixed total quasi-momentum $K \in \mathbb{T}$. In the constant-profile case $\alpha \equiv 1$, both the contact interaction in the two-particle channel and the interchannel coupling are generated by the constant mode

$$\varphi_0(p) = 1, \quad \forall p \in \mathbb{T}.$$

We will only need this definition; from now on we work directly with the constant function 1 and do not refer to φ_0 again. As a consequence, the perturbation of the free reduced hamiltonian is of rank at most two. In particular, the eigenvalue problem outside the essential spectrum can be reduced to a 2×2 linear system and, equivalently, to the vanishing of a scalar Fredholm determinant.

For each fixed $K \in \mathbb{T}$, the reduced hamiltonian is defined by

$$H_{\gamma,\lambda}(K) = \begin{pmatrix} E_0 & C_\gamma^* \\ C_\gamma & H_0(K) + \lambda P_0 \end{pmatrix} \quad (4)$$

in the Hilbert space

$$\mathcal{H}_K := \mathbb{C} \oplus L^{2,e}(\mathbb{T}).$$

Here $E_0 \in \mathbb{R}$ is the molecular-channel energy,

$$(H_0(K)g)(p) = \varepsilon_K(p) g(p), \quad g \in L^{2,e}(\mathbb{T}), \quad (5)$$

and the fiber dispersion relation is given by

$$\varepsilon_K(p) = \varepsilon\left(\frac{K}{2} - p\right) + \varepsilon\left(\frac{K}{2} + p\right) = 4\left(1 - \cos \frac{K}{2} \cos p\right). \quad (6)$$

Furthermore, P_0 denotes the orthogonal projection onto the one-dimensional subspace spanned by the constant function 1, that is,

$$P_0 g = (g, 1) 1, \quad (g, 1) = \int_{\mathbb{T}} g(p) d\nu(p), \quad (7)$$

where the Haar measure on $\mathbb{T}$ is normalized, so $\|1\|_{L^2} = 1$.

Because the coupling profile is constant, the interchannel coupling operator does not depend on K . More precisely,

$$(C_\gamma c)(p) = \gamma c, \quad c \in \mathbb{C}, \quad (8)$$

i.e. $C_\gamma c$ is the constant function equal to γc . Its adjoint is given by

$$C_\gamma^* g = \gamma \int_{\mathbb{T}} g(p) d\nu(p) = \gamma (g, 1), \quad g \in L^{2,e}(\mathbb{T}). \quad (9)$$

Hence $H_{\gamma,\lambda}(K)$ is a bounded self-adjoint operator on $\mathcal{H}_K$.

We next determine its essential spectrum.

Proposition 1. For every $K \in \mathbb{T}$, $\sigma_{\text{ess}}(H_{\gamma,\lambda}(K)) = \text{Ran } \varepsilon_K$.

Proof. By (4), the operator $H_{\gamma,\lambda}(K)$ differs from

$$H_{\text{free}}(K) := \begin{pmatrix} E_0 & 0 \\ 0 & H_0(K) \end{pmatrix}$$

by the finite-rank perturbation

$$\begin{pmatrix} 0 & C_\gamma^* \\ C_\gamma & \lambda P_0 \end{pmatrix}.$$

Since the scalar part E_0 acts in a one-dimensional subspace, it can contribute only an isolated eigenvalue of finite multiplicity and therefore does not affect the essential spectrum. Hence, by Weyl's theorem, $\sigma_{\text{ess}}(H_{\gamma,\lambda}(K)) = \sigma_{\text{ess}}(H_0(K)) = \text{Ran } \varepsilon_K$. $\square$

2.1. The free resolvent and the finite-rank perturbation

Let

$$H_{\text{free}}(K) := \begin{pmatrix} E_0 & 0 \\ 0 & H_0(K) \end{pmatrix}, \quad V_{\gamma,\lambda} := H_{\gamma,\lambda}(K) - H_{\text{free}}(K). \quad (10)$$

Then

$$V_{\gamma,\lambda}(K) = \begin{pmatrix} 0 & C_\gamma^* \\ C_\gamma & \lambda P_0 \end{pmatrix}. \quad (11)$$

For

$$z \in \mathbb{C} \setminus (\text{Ran } \varepsilon_K \cup \{E_0\}), \quad (12)$$

the free resolvent is

$$R_{\text{free}}(K; z) := (H_{\text{free}}(K) - zI)^{-1} = \begin{pmatrix} (E_0 - z)^{-1} & 0 \\ 0 & r_K(z) \end{pmatrix}, \quad (13)$$

where

$$r_K(z) := (H_0(K) - z)^{-1}, \quad (r_K(z)g)(p) = \frac{g(p)}{\varepsilon_K(p) - z}. \quad (14)$$

We also introduce the Lippmann–Schwinger operator

$$B_{\gamma,\lambda}(K; z) := -V_{\gamma,\lambda} R_{\text{free}}(K; z). \quad (15)$$

Proposition 2. *Let*

$$e_0 := (1, 0) \in \mathcal{H}_K, \quad e_c := (0, 1) \in \mathcal{H}_K,$$

where the second component is the constant function 1. Then

$$\text{Ran } V_{\gamma, \lambda} \subset \text{span}\{e_0, e_c\}.$$

In particular,

$$\text{rank } V_{\gamma, \lambda} \leq 2,$$

and therefore $B_{\gamma, \lambda}(K; z)$ is a finite-rank, hence compact, operator.

Proof. Let $(c, g) \in \mathcal{H}_K$. By (11), (8), (9), and (7),

$$V_{\gamma, \lambda} \begin{pmatrix} c \\ g \end{pmatrix} = \begin{pmatrix} \gamma(g, 1) \\ (\gamma c + \lambda(g, 1)) 1 \end{pmatrix},$$

which belongs to $\text{span}\{e_0, e_c\}$. This proves the claim. $\square$

3. Lippmann–Schwinger Reduction for the fiber hamiltonian

In this section we analyze the reduced hamiltonians $H_{\gamma, \lambda}(K)$ corresponding to fixed total quasi-momentum $K \in \mathbb{T}$. Since both the contact interaction and the interchannel coupling act through the constant function 1 (the constant mode), the perturbation of the free fiber operator is of rank at most two. As a consequence, the eigenvalue problem outside the essential spectrum reduces to a 2×2 linear system and, equivalently, to the vanishing of a scalar Fredholm determinant.

3.1. Finite-dimensional reduction and the reduced determinant

For

$$z \in \mathbb{C} \setminus \text{Ran } \varepsilon_K, \quad a_K(z) := (r_K(z)\varphi_0, \varphi_0) = \int_{\mathbb{T}} \frac{d\nu(p)}{\varepsilon_K(p) - z},$$

where $d\nu$ is the normalized Haar measure on $\mathbb{T}$. The function a_K is holomorphic on $\mathbb{C} \setminus \text{Ran } \varepsilon_K$, and for real $z \notin \text{Ran } \varepsilon_K$ it is real-valued.

Theorem 1 (Finite-dimensional reduction). *Let*

$$z \in \mathbb{R} \setminus \text{Ran } \varepsilon_K.$$

Then the following statements are equivalent:

- (i) z is an eigenvalue of $H_{\gamma, \lambda}(K)$;
- (ii) there exists a nonzero vector $(c_0, c_1) \in \mathbb{C}^2$ such that

$$\begin{pmatrix} E_0 - z & \gamma \\ \gamma a_K(z) & 1 + \lambda a_K(z) \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} = 0; \quad (16)$$

- (iii) the reduced determinant

$$\Delta_{\gamma, \lambda}(K; z) := (E_0 - z)(1 + \lambda a_K(z)) - \gamma^2 a_K(z) \quad (17)$$

vanishes at z .

Proof. Let

$$\psi = (c_0, g) \in \mathcal{H}_K \setminus \{0\}.$$

The eigenvalue equation

$$H_{\gamma, \lambda}(K)\psi = z\psi$$

is equivalent to the system

$$(E_0 - z)c_0 + \gamma(g, \varphi_0) = 0, \quad (18)$$

$$(\varepsilon_K(p) - z)g(p) + \gamma c_0 \varphi_0(p) + \lambda(g, \varphi_0)\varphi_0(p) = 0. \quad (19)$$

Since $\varphi_0 \equiv 1$, the term $\gamma c_0 \varphi_0(p)$ may be identified with γc_0 .

Set

$$c_1 := (g, \varphi_0).$$

Then the first equation in the eigenvalue system becomes

$$(E_0 - z)c_0 + \gamma c_1 = 0.$$

Since $z \notin \text{Ran } \varepsilon_K$, the resolvent

$$r_K(z) := (H_0(K) - z)^{-1}$$

is bounded. Hence the second equation in the eigenvalue system can be written as

$$(H_0(K) - z)g = -(\gamma c_0 + \lambda c_1)\varphi_0.$$

Therefore

$$g = -(\gamma c_0 + \lambda c_1)r_K(z)\varphi_0. \quad (20)$$

Taking the scalar product of (20) with φ_0 , and using

$$a_K(z) := (r_K(z)\varphi_0, \varphi_0),$$

we obtain

$$c_1 = -(\gamma c_0 + \lambda c_1)a_K(z),$$

Equivalently,

$$\gamma a_K(z)c_0 + (1 + \lambda a_K(z))c_1 = 0.$$

Thus c_0 and c_1 satisfy the reduced finite-dimensional system

$$\begin{cases} (E_0 - z)c_0 + \gamma c_1 = 0, \\ \gamma a_K(z)c_0 + (1 + \lambda a_K(z))c_1 = 0. \end{cases} \quad (21)$$

This system is exactly the matrix equation (16).

Moreover, the vector (c_0, c_1) is nonzero. Indeed, if

$$c_0 = 0 \quad \text{and} \quad c_1 = 0,$$

then (20) implies $g = 0$, which contradicts $\psi \neq 0$. Hence $(i) \Rightarrow (ii)$.

Conversely, suppose that a nonzero vector

$$(c_0, c_1) \in \mathbb{C}^2$$

satisfies (16). Define

$$g = -(\gamma c_0 + \lambda c_1)r_K(z)\varphi_0.$$

Then

$$(g, \varphi_0) = -(\gamma c_0 + \lambda c_1)a_K(z).$$

By the second equation of (16), we have

$$\gamma a_K(z)c_0 + (1 + \lambda a_K(z))c_1 = 0.$$

Hence

$$-(\gamma c_0 + \lambda c_1)a_K(z) = c_1,$$

and therefore

$$(g, \varphi_0) = c_1.$$

Using the first equation of (16), we obtain

$$(E_0 - z)c_0 + \gamma(g, \varphi_0) = 0.$$

Thus (18) holds.

Furthermore, by the definition of g ,

$$(H_0(K) - z)g = -(\gamma c_0 + \lambda c_1)\varphi_0.$$

Since $c_1 = (g, \varphi_0)$, this is equivalent to

$$(H_0(K) - z)g + \gamma c_0 \varphi_0 + \lambda(g, \varphi_0)\varphi_0 = 0.$$

Therefore (19) also holds.

It remains to check that $(c_0, g) \neq 0$. Suppose, on the contrary, that

$$c_0 = 0 \quad \text{and} \quad g = 0.$$

Then

$$0 = g = -\lambda c_1 r_K(z)\varphi_0.$$

Since $r_K(z)\varphi_0 \neq 0$, it follows that $\lambda c_1 = 0$. If $\lambda \neq 0$, then $c_1 = 0$. If $\lambda = 0$, then the second equation of (16) gives $c_1 = 0$. In both cases,

$$(c_0, c_1) = (0, 0),$$

which contradicts the assumption that $(c_0, c_1) \neq 0$. Therefore $(c_0, g) \neq 0$, and hence (c_0, g) is an eigenvector of $H_{\gamma, \lambda}(K)$ corresponding to z . Thus $(ii) \Rightarrow (i)$.

Finally, the homogeneous system (16) has a nontrivial solution if and only if its determinant is equal to zero. Since

$$\det \begin{pmatrix} E_0 - z & \gamma \\ \gamma a_K(z) & 1 + \lambda a_K(z) \end{pmatrix} = (E_0 - z)(1 + \lambda a_K(z)) - \gamma^2 a_K(z),$$

this condition is precisely

$$\Delta_{\gamma,\lambda}(K; z) = 0.$$

Hence (ii) $\Leftrightarrow$ (iii). The theorem is proved. $\square$

Corollary 1 (Fredholm determinant). *For*

$$z \in \mathbb{C} \setminus (\text{Ran } \varepsilon_K \cup \{E_0\}),$$

the Fredholm determinant of $I - B_{\gamma,\lambda}(K; z)$ is given by

$$D_{\gamma,\lambda}(K; z) := \det(I - B_{\gamma,\lambda}(K; z)) = \frac{\Delta_{\gamma,\lambda}(K; z)}{E_0 - z} = 1 + \lambda a_K(z) - \frac{\gamma^2 a_K(z)}{E_0 - z}. \quad (22)$$

In particular, for $z \in \mathbb{R} \setminus \text{Ran } \varepsilon_K$,

$$z \in \sigma_{\text{disc}}(H_{\gamma,\lambda}(K)) \iff \Delta_{\gamma,\lambda}(K; z) = 0.$$

Moreover, if $z \neq E_0$, then

$$z \in \sigma_{\text{disc}}(H_{\gamma,\lambda}(K)) \iff D_{\gamma,\lambda}(K; z) = 0.$$

Proof. By Proposition 2,

$$\text{Ran } B_{\gamma,\lambda}(K; z) \subset \text{span}\{e_0, e_c\}.$$

where $e_0 := (1, 0)$ and $e_c := (0, 1)$ (the second component is the constant function 1). Hence the Fredholm determinant reduces to the determinant of the restriction of $I - B_{\gamma,\lambda}(K; z)$ to this two-dimensional subspace.

Using (13) and (15), one computes

$$B_{\gamma,\lambda}(K; z)e_0 = -\frac{\gamma}{E_0 - z} e_c, \quad B_{\gamma,\lambda}(K; z)e_c = -\gamma a_K(z)e_0 - \lambda a_K(z)e_c.$$

Therefore the matrix of $I - B_{\gamma,\lambda}(K; z)$ in the basis $\{e_0, e_c\}$ is

$$\begin{pmatrix} 1 & \gamma a_K(z) \\ \frac{\gamma}{E_0 - z} & 1 + \lambda a_K(z) \end{pmatrix},$$

whose determinant equals the right hand side of (22). $\square$

3.2. The one-dimensional lattice Green function

We next compute explicitly the scalar Green function associated with the one-dimensional lattice dispersion. This computation is one of the key technical ingredients of the spectral analysis below, since it gives the explicit form of the perturbation determinant and describes its behavior near the spectral thresholds.

We emphasize that formulas of this type are standard in the spectral theory of one-dimensional discrete Schrödinger and Jacobi operators. In particular, the Green function of the discrete Schrödinger operator with a point interaction was studied in detail by Yafaev [15], where closely related computations are expressed in terms of generalized Chebyshev polynomials. More generally, Green functions and Weyl-type functions for broad classes of Jacobi operators are systematically discussed in Teschl's monograph [14]. The calculation below is included for completeness and to make the dependence on the total quasi-momentum K explicit in the present model.

Assume first that

$$K \in \mathbb{T} \setminus \{\pi\},$$

and set

$$\kappa_K := |\cos(K/2)| \in (0, 1]. \quad (23)$$

Then the band edges of the multiplication operator with dispersion ε_K are

$$\mathcal{E}_K^- := 4(1 - \kappa_K), \quad \mathcal{E}_K^+ := 4(1 + \kappa_K), \quad (24)$$

and therefore

$$\text{Ran } \varepsilon_K = [\mathcal{E}_K^-, \mathcal{E}_K^+].$$

For

$$z \in \mathbb{R} \setminus [\mathcal{E}_K^-, \mathcal{E}_K^+],$$

we define

$$a_K(z) := \frac{1}{2\pi} \int_0^{2\pi} \frac{dp}{\varepsilon_K(p) - z}. \quad (25)$$

Equivalently,

$$a_K(z) = (r_K(z)\varphi_0, \varphi_0), \quad r_K(z) := (H_0(K) - z)^{-1}, \quad \varphi_0 \equiv 1.$$

Lemma 1. *Let $K \in \mathbb{T} \setminus \{\pi\}$. Then, for*

$$z \in \mathbb{R} \setminus [\mathcal{E}_K^-, \mathcal{E}_K^+],$$

one has

$$a_K(z) = \begin{cases} \frac{1}{\sqrt{(z - \mathcal{E}_K^-)(z - \mathcal{E}_K^+)}} , & z < \mathcal{E}_K^-, \\ -\frac{1}{\sqrt{(z - \mathcal{E}_K^-)(z - \mathcal{E}_K^+)}} , & z > \mathcal{E}_K^+. \end{cases} \quad (26)$$

Here the square root denotes the positive branch.

In particular,

$$a_K(z) > 0 \quad \text{for } z < \mathcal{E}_K^-, \quad a_K(z) < 0 \quad \text{for } z > \mathcal{E}_K^+.$$

Moreover, a_K is strictly increasing on both intervals

$$(-\infty, \mathcal{E}_K^-) \quad \text{and} \quad (\mathcal{E}_K^+, \infty),$$

and

$$\lim_{z \rightarrow -\infty} a_K(z) = 0^+, \quad \lim_{z \rightarrow +\infty} a_K(z) = 0^-. \quad (27)$$

Finally, as $z \uparrow \mathcal{E}_K^-$,

$$a_K(z) = \frac{1}{2\sqrt{2\kappa_K}} (\mathcal{E}_K^- - z)^{-1/2} + O(1), \quad (28)$$

and as $z \downarrow \mathcal{E}_K^+$,

$$a_K(z) = -\frac{1}{2\sqrt{2\kappa_K}} (z - \mathcal{E}_K^+)^{-1/2} + O(1). \quad (29)$$

Proof. By the explicit form of the one-dimensional two-particle dispersion, one has

$$\varepsilon_K(p) = 4 - 4\kappa_K \cos p.$$

Therefore

$$a_K(z) = \frac{1}{2\pi} \int_0^{2\pi} \frac{dp}{4 - z - 4\kappa_K \cos p}.$$

This is the standard diagonal Green function of a one-dimensional Jacobi operator. Using the classical integral identity

$$\frac{1}{2\pi} \int_0^{2\pi} \frac{dp}{a - b \cos p} = \frac{\operatorname{sgn}(a)}{\sqrt{a^2 - b^2}}, \quad |a| > |b|,$$

with

$$a = 4 - z, \quad b = 4\kappa_K,$$

we obtain

$$a_K(z) = \frac{\operatorname{sgn}(4 - z)}{\sqrt{(4 - z)^2 - 16\kappa_K^2}}.$$

Since

$$(4 - z)^2 - 16\kappa_K^2 = (z - \mathcal{E}_K^-)(z - \mathcal{E}_K^+),$$

formula (26) follows.

The sign properties are immediate from (26). The limits

$$\lim_{z \rightarrow -\infty} a_K(z) = 0^+, \quad \lim_{z \rightarrow +\infty} a_K(z) = 0^-$$

also follow directly from the same formula.

To prove monotonicity, it is enough to differentiate under the integral sign:

$$a'_K(z) = \frac{1}{2\pi} \int_0^{2\pi} \frac{dp}{(\varepsilon_K(p) - z)^2} > 0.$$

Hence a_K is strictly increasing on each connected component of

$$\mathbb{R} \setminus [\mathcal{E}_K^-, \mathcal{E}_K^+].$$

It remains to derive the threshold asymptotics. As $z \uparrow \mathcal{E}_K^-$, one has

$$(z - \mathcal{E}_K^-)(z - \mathcal{E}_K^+) = (\mathcal{E}_K^- - z)(\mathcal{E}_K^+ - z),$$

and

$$\mathcal{E}_K^+ - z = \mathcal{E}_K^+ - \mathcal{E}_K^- + \mathcal{E}_K^- - z = 8\kappa_K + \mathcal{E}_K^- - z.$$

Therefore

$$a_K(z) = \frac{1}{\sqrt{(\mathcal{E}_K^- - z)(8\kappa_K + \mathcal{E}_K^- - z)}} = \frac{1}{2\sqrt{2\kappa_K}} (\mathcal{E}_K^- - z)^{-1/2} + O(1),$$

which proves (28).

Similarly, as $z \downarrow \mathcal{E}_K^+$,

$$(z - \mathcal{E}_K^-)(z - \mathcal{E}_K^+) = (8\kappa_K + z - \mathcal{E}_K^+)(z - \mathcal{E}_K^+).$$

Using the negative sign in the upper part of (26), we get

$$a_K(z) = -\frac{1}{\sqrt{(8\kappa_K + z - \mathcal{E}_K^+)(z - \mathcal{E}_K^+)}} = -\frac{1}{2\sqrt{2\kappa_K}} (z - \mathcal{E}_K^+)^{-1/2} + O(1).$$

This proves (29). □

3.3. A scalar Birman–Schwinger equation

For $z \in \mathbb{R} \setminus ([\mathcal{E}_K^-, \mathcal{E}_K^+] \cup \{E_0\})$, the equation $\Delta_{\gamma,\lambda}(K; z) = 0$ is equivalent to the scalar Birman–Schwinger equation

$$\Phi_K(z) = \Psi_{\gamma,\lambda}(z), \quad (30)$$

where

$$\Phi_K(z) := -\frac{1}{a_K(z)}, \quad \Psi_{\gamma,\lambda}(z) := \lambda - \frac{\gamma^2}{E_0 - z}. \quad (31)$$

Indeed, multiplying (30) by $-a_K(z)(E_0 - z)$ yields exactly $\Delta_{\gamma,\lambda}(K; z) = 0$.

Remark 1. By Lemma 1, the function Φ_K is strictly increasing on $(-\infty, \mathcal{E}_K^-)$ and on $(\mathcal{E}_K^+, \infty)$, and

$$\begin{aligned} \lim_{z \rightarrow -\infty} \Phi_K(z) &= -\infty, & \lim_{z \uparrow \mathcal{E}_K^-} \Phi_K(z) &= 0^-, \\ \lim_{z \downarrow \mathcal{E}_K^+} \Phi_K(z) &= 0^+, & \lim_{z \rightarrow +\infty} \Phi_K(z) &= +\infty. \end{aligned}$$

On the other hand,

$$\Psi'_{\gamma,\lambda}(z) = -\frac{\gamma^2}{(E_0 - z)^2} < 0 \quad (z \neq E_0),$$

so $\Psi_{\gamma,\lambda}$ is strictly decreasing on every interval not containing the pole E_0 .

3.4. The flat-band case $K = \pi$

If $K = \pi$, then $\cos(K/2) = 0$, and therefore

$$\varepsilon_\pi(p) \equiv 4. \quad (32)$$

Hence $\sigma_{\text{ess}}(H_{\gamma,\lambda}(\pi)) = \{4\}$, and

$$a_\pi(z) = \frac{1}{4 - z}, \quad z \neq 4. \quad (33)$$

Substituting (33) into (17), we obtain

$$\Delta_{\gamma,\lambda}(\pi; z) = (E_0 - z) \left(1 + \frac{\lambda}{4 - z} \right) - \frac{\gamma^2}{4 - z} = \frac{(E_0 - z)(4 + \lambda - z) - \gamma^2}{4 - z}. \quad (34)$$

Thus, in the flat-band case $K = \pi$, the spectral problem reduces to the explicit quadratic equation

$$(E_0 - z)(4 + \lambda - z) = \gamma^2. \quad (35)$$

4. Discrete spectrum of the reduced hamiltonian $H_{\gamma,\lambda}(K)$

In this section we classify the discrete spectrum of the reduced hamiltonians $H_{\gamma,\lambda}(K)$ in the constant-profile case $\alpha \equiv 1$. The analysis is based on the scalar Birman–Schwinger equation derived in Section 3.

Recall from Section 3 that the location of the molecular energy E_0 relative to the essential band $[\mathcal{E}_K^-, \mathcal{E}_K^+]$ determines three generic regimes: E_0 inside the band ($\mathcal{E}_K^- < E_0 < \mathcal{E}_K^+$), E_0 below the band ($E_0 < \mathcal{E}_K^-$), and E_0 above the band ($E_0 > \mathcal{E}_K^+$). The discrete spectrum of $H_{\gamma,\lambda}(K)$ is classified separately for each of these cases, with the threshold configurations $E_0 = \mathcal{E}_K^\pm$ treated as limiting situations.

Throughout this section, unless stated otherwise, we assume that $K \in \mathbb{T} \setminus \{\pi\}$. Recall that the essential spectrum of $H_{\gamma,\lambda}(K)$ is the interval

$$\sigma_{\text{ess}}(H_{\gamma,\lambda}(K)) = [\mathcal{E}_K^-, \mathcal{E}_K^+], \quad (36)$$

with $\mathcal{E}_K^\pm$ defined in (24).

We write

$$n_-(H_{\gamma,\lambda}(K)) := \#(\sigma_{\text{disc}}(H_{\gamma,\lambda}(K)) \cap (-\infty, \mathcal{E}_K^-)), \quad (37)$$

and

$$n_+(H_{\gamma,\lambda}(K)) := \#(\sigma_{\text{disc}}(H_{\gamma,\lambda}(K)) \cap (\mathcal{E}_K^+, \infty)), \quad (38)$$

where eigenvalues are counted with multiplicities.

The threshold behaviour of the reduced determinant $\Delta_{\gamma,\lambda}(K; z)$ is governed by the coefficients

$$S_K^-(\gamma, \lambda) = \lambda(E_0 - \mathcal{E}_K^-) - \gamma^2, \quad S_K^+(\gamma, \lambda) = \lambda(\mathcal{E}_K^+ - E_0) + \gamma^2. \quad (39)$$

If $E_0 \neq \mathcal{E}_K^\pm$, the corresponding critical curves in the (γ, λ) -plane are given by

$$\lambda = \lambda_K^-(\gamma) := \frac{\gamma^2}{E_0 - \mathcal{E}_K^-}, \quad \lambda = \lambda_K^+(\gamma) := \frac{\gamma^2}{E_0 - \mathcal{E}_K^+}. \quad (40)$$

Equivalently,

$$S_K^-(\gamma, \lambda) = 0 \iff \lambda = \lambda_K^-(\gamma), \quad S_K^+(\gamma, \lambda) = 0 \iff \lambda = \lambda_K^+(\gamma).$$

The spectral classification below is based on the scalar Birman–Schwinger equation

$$\Phi_K(z) = \Psi_{\gamma,\lambda}(z), \quad (41)$$

with $\Phi_K, \Psi_{\gamma,\lambda}$ defined in (31). By Remark 1, Φ_K is strictly increasing on each of the intervals $(-\infty, \mathcal{E}_K^-)$ and $(\mathcal{E}_K^+, \infty)$, whereas $\Psi_{\gamma,\lambda}$ is strictly decreasing on every interval not containing the pole E_0 . This monotonicity is the basic tool in what follows.

4.1. The case $\mathcal{E}_K^- < E_0 < \mathcal{E}_K^+$

We begin with the case in which the molecular energy lies inside the essential band. Then the pole of $\Psi_{\gamma,\lambda}$ lies inside the band and therefore does not affect the analysis on the two spectral half-lines.

Theorem 2. Assume that

$$\mathcal{E}_K^- < E_0 < \mathcal{E}_K^+. \quad (42)$$

Then

$$n_-(H_{\gamma,\lambda}(K)) = \begin{cases} 1, & S_K^-(\gamma, \lambda) < 0, \\ 0, & S_K^-(\gamma, \lambda) \geq 0, \end{cases} \quad (43)$$

and

$$n_+(H_{\gamma,\lambda}(K)) = \begin{cases} 1, & S_K^+(\gamma, \lambda) > 0, \\ 0, & S_K^+(\gamma, \lambda) \leq 0. \end{cases} \quad (44)$$

Equivalently,

$$n_-(H_{\gamma,\lambda}(K)) = 1 \iff \lambda < \lambda_K^-(\gamma), \quad n_+(H_{\gamma,\lambda}(K)) = 1 \iff \lambda > \lambda_K^+(\gamma). \quad (45)$$

Proof. Since $E_0 \in (\mathcal{E}_K^-, \mathcal{E}_K^+)$, the pole of $\Psi_{\gamma,\lambda}$ lies inside the essential band and does not interfere with the spectral half-lines $(-\infty, \mathcal{E}_K^-)$ and $(\mathcal{E}_K^+, \infty)$.

Consider first the lower half-line and define

$$F_-(z) := \Phi_K(z) - \Psi_{\gamma,\lambda}(z), \quad z \in (-\infty, \mathcal{E}_K^-).$$

Because Φ_K is strictly increasing and $\Psi_{\gamma,\lambda}$ is strictly decreasing, F_- is strictly increasing. Moreover,

$$\lim_{z \rightarrow -\infty} F_-(z) = -\infty.$$

Using the threshold asymptotics of Φ_K , one obtains

$$\lim_{z \uparrow \mathcal{E}_K^-} F_-(z) = -\frac{S_K^-(\gamma, \lambda)}{E_0 - \mathcal{E}_K^-}.$$

Since $E_0 - \mathcal{E}_K^- > 0$, this limit is positive if and only if $S_K^-(\gamma, \lambda) < 0$. Hence F_- has exactly one zero in $(-\infty, \mathcal{E}_K^-)$ when $S_K^-(\gamma, \lambda) < 0$, and none otherwise. This proves (43).

The argument for the upper half-line is analogous. Define

$$F_+(z) := \Phi_K(z) - \Psi_{\gamma, \lambda}(z), \quad z \in (\mathcal{E}_K^+, \infty).$$

Again F_+ is strictly increasing, and

$$\lim_{z \downarrow \mathcal{E}_K^+} F_+(z) = -\frac{S_K^+(\gamma, \lambda)}{\mathcal{E}_K^+ - E_0}, \quad \lim_{z \rightarrow +\infty} F_+(z) = +\infty.$$

Because $\mathcal{E}_K^+ - E_0 > 0$, there is exactly one zero in $(\mathcal{E}_K^+, \infty)$ if and only if $S_K^+(\gamma, \lambda) > 0$. This proves (44). $\square$

4.2. The case $E_0 < \mathcal{E}_K^-$

We next consider the case when the molecular energy lies below the essential band. Then the pole of $\Psi_{\gamma, \lambda}$ lies on the lower spectral side and splits the lower half-line into two monotonicity intervals.

Theorem 3. Assume that

$$E_0 < \mathcal{E}_K^-. \quad (46)$$

Then

$$n_-(H_{\gamma, \lambda}(K)) = \begin{cases} 2, & S_K^-(\gamma, \lambda) > 0, \\ 1, & S_K^-(\gamma, \lambda) \leq 0, \end{cases} \quad (47)$$

and

$$n_+(H_{\gamma, \lambda}(K)) = \begin{cases} 1, & S_K^+(\gamma, \lambda) > 0, \\ 0, & S_K^+(\gamma, \lambda) \leq 0. \end{cases} \quad (48)$$

Equivalently,

$$n_-(H_{\gamma, \lambda}(K)) = 2 \iff \lambda < \lambda_K^-(\gamma), \quad n_+(H_{\gamma, \lambda}(K)) = 1 \iff \lambda > \lambda_K^+(\gamma). \quad (49)$$

Proof. We begin with the decoupled case $\gamma = 0$. Then

$$\Delta_{\gamma, \lambda}(K; z) = (E_0 - z)(1 + \lambda a_K(z)).$$

Hence $z = E_0$ is always an eigenvalue below the essential band, while the remaining discrete spectrum is determined by $1 + \lambda a_K(z) = 0$. Since $a_K(z) > 0$ on $(-\infty, \mathcal{E}_K^-)$ and $a_K(z) < 0$ on $(\mathcal{E}_K^+, \infty)$, this equation has one solution below the band iff $\lambda < 0$, and one solution above the band iff $\lambda > 0$. This agrees with the formulas in the theorem, because for $\gamma = 0$, $S_K^-(0, \lambda) = \lambda(E_0 - \mathcal{E}_K^-)$ (negative since $E_0 - \mathcal{E}_K^- < 0$) and $S_K^+(0, \lambda) = \lambda(\mathcal{E}_K^+ - E_0)$.

Assume now that $\gamma \neq 0$. On the interval $(-\infty, E_0)$, set

$$F_1(z) := \Phi_K(z) - \Psi_{\gamma, \lambda}(z).$$

The function F_1 is strictly increasing and satisfies

$$\lim_{z \rightarrow -\infty} F_1(z) = -\infty, \quad \lim_{z \uparrow E_0} F_1(z) = +\infty.$$

Hence F_1 has exactly one zero in $(-\infty, E_0)$.

On the interval $(E_0, \mathcal{E}_K^-)$, define

$$F_2(z) := \Phi_K(z) - \Psi_{\gamma, \lambda}(z).$$

Again F_2 is strictly increasing, and

$$\lim_{z \downarrow E_0} F_2(z) = -\infty, \quad \lim_{z \uparrow \mathcal{E}_K^-} F_2(z) = -\frac{S_K^-(\gamma, \lambda)}{E_0 - \mathcal{E}_K^-}.$$

Because $E_0 - \mathcal{E}_K^- < 0$, the last limit is positive if and only if $S_K^-(\gamma, \lambda) > 0$. Therefore there is exactly one zero in $(E_0, \mathcal{E}_K^-)$ when $S_K^-(\gamma, \lambda) > 0$, and none otherwise. This proves (47).

Finally, on $(\mathcal{E}_K^+, \infty)$ the pole E_0 is irrelevant, and the same argument as in Theorem 2 shows that there is exactly one eigenvalue above the band if and only if $S_K^+(\gamma, \lambda) > 0$. This proves (48). $\square$

4.3. The case $E_0 > \mathcal{E}_K^+$

We finally consider the case when the molecular energy lies above the essential band. This is symmetric to the previous case, with the pole of $\Psi_{\gamma,\lambda}$ now lying on the upper spectral side.

Theorem 4. Assume that

$$E_0 > \mathcal{E}_K^+. \quad (50)$$

Then

$$n_-(H_{\gamma,\lambda}(K)) = \begin{cases} 1, & S_K^-(\gamma, \lambda) < 0, \\ 0, & S_K^-(\gamma, \lambda) \geq 0, \end{cases} \quad (51)$$

and

$$n_+(H_{\gamma,\lambda}(K)) = \begin{cases} 2, & S_K^+(\gamma, \lambda) < 0, \\ 1, & S_K^+(\gamma, \lambda) \geq 0. \end{cases} \quad (52)$$

Equivalently,

$$n_-(H_{\gamma,\lambda}(K)) = 1 \iff \lambda < \lambda_K^-(\gamma), \quad n_+(H_{\gamma,\lambda}(K)) = 2 \iff \lambda > \lambda_K^+(\gamma). \quad (53)$$

Proof. If $\gamma = 0$, then $\Delta_{\gamma,\lambda}(K; z) = (E_0 - z)(1 + \lambda a_K(z))$ and $z = E_0$ is always an eigenvalue above the essential band. The equation $1 + \lambda a_K(z) = 0$ contributes one eigenvalue below the band iff $\lambda < 0$, and one additional eigenvalue above the band iff $\lambda > 0$. This matches the statement of the theorem.

Assume now that $\gamma \neq 0$. On $(-\infty, \mathcal{E}_K^-)$, the pole E_0 is absent, and the same argument as in Theorem 2 shows that there is exactly one eigenvalue below the band iff $S_K^-(\gamma, \lambda) < 0$.

For the upper half-line $(\mathcal{E}_K^+, \infty)$, the pole at E_0 splits the interval into two parts. On $(\mathcal{E}_K^+, E_0)$, define

$$F_1(z) := \Phi_K(z) - \Psi_{\gamma,\lambda}(z).$$

Then F_1 is strictly increasing and satisfies

$$\lim_{z \downarrow \mathcal{E}_K^+} F_1(z) = -\frac{S_K^+(\gamma, \lambda)}{\mathcal{E}_K^+ - E_0}, \quad \lim_{z \uparrow E_0} F_1(z) = +\infty.$$

Since $\mathcal{E}_K^+ - E_0 < 0$, there is exactly one zero in $(\mathcal{E}_K^+, E_0)$ iff $S_K^+(\gamma, \lambda) < 0$.

On (E_0, ∞) , define

$$F_2(z) := \Phi_K(z) - \Psi_{\gamma,\lambda}(z).$$

Again F_2 is strictly increasing, and

$$\lim_{z \downarrow E_0} F_2(z) = -\infty, \quad \lim_{z \rightarrow +\infty} F_2(z) = +\infty.$$

Hence F_2 has exactly one zero in (E_0, ∞) . Therefore

$$n_+(H_{\gamma,\lambda}(K)) = 1 + \mathbf{1}_{\{S_K^+(\gamma, \lambda) < 0\}},$$

which is exactly (52). □

4.4. Threshold configurations $E_0 = \mathcal{E}_K^\pm$

We now discuss the limiting situations in which the molecular energy coincides with one of the band edges. These configurations are the boundaries between the three generic regimes treated above, and the counting formulas can be obtained by taking the limits $E_0 \rightarrow \mathcal{E}_K^\pm$ in Theorems 2 – 4 while keeping track of the eigenvalue that emerges from the threshold when $\gamma \neq 0$.

Proposition 3. Assume that $K \in \mathbb{T} \setminus \{\pi\}$. Then the following assertions hold.

(i) If $E_0 = \mathcal{E}_K^-$, then

$$n_-(H_{\gamma,\lambda}(K)) = \begin{cases} 1, & \gamma \neq 0, \\ 1, & \gamma = 0 \text{ and } \lambda < 0, \\ 0, & \gamma = 0 \text{ and } \lambda \geq 0, \end{cases} \quad (54)$$

and

$$n_+(H_{\gamma,\lambda}(K)) = \begin{cases} 1, & \lambda(\mathcal{E}_K^+ - \mathcal{E}_K^-) + \gamma^2 > 0, \\ 0, & \lambda(\mathcal{E}_K^+ - \mathcal{E}_K^-) + \gamma^2 \leq 0. \end{cases} \quad (55)$$

(ii) If $E_0 = \mathcal{E}_K^+$, then

$$n_-(H_{\gamma,\lambda}(K)) = \begin{cases} 1, & \lambda(\mathcal{E}_K^+ - \mathcal{E}_K^-) - \gamma^2 < 0, \\ 0, & \lambda(\mathcal{E}_K^+ - \mathcal{E}_K^-) - \gamma^2 \geq 0, \end{cases} \quad (56)$$

and

$$n_+(H_{\gamma,\lambda}(K)) = \begin{cases} 1, & \gamma \neq 0, \\ 1, & \gamma = 0 \text{ and } \lambda > 0, \\ 0, & \gamma = 0 \text{ and } \lambda \leq 0. \end{cases} \quad (57)$$

Proof. The proof follows by taking the limits $E_0 \rightarrow \mathcal{E}_K^-$ and $E_0 \rightarrow \mathcal{E}_K^+$ in Theorems 2 and 3 (or 4) respectively, and using the continuity of the eigenvalue counting functions with respect to E_0 as long as the thresholds are approached from the appropriate side. When $\gamma \neq 0$, the pole of $\Psi_{\gamma,\lambda}$ at E_0 forces one eigenvalue to bifurcate from the band edge, which is reflected in the first case of the counting formulas on the side where the pole is located. The explicit expressions are obtained by evaluating the limits of $S_K^\pm(\gamma, \lambda)$ and the corresponding sign conditions. $\square$

Remark 2. The threshold configurations $E_0 = \mathcal{E}_K^\pm$ are the natural boundaries between the three generic regimes. The counting formulas above are consistent with the sharp spectral transitions described by the critical coefficients $S_K^\pm(\gamma, \lambda)$ and can be obtained directly from the generic results by taking the appropriate limits.

5. Threshold states and virtual levels of the rank-one fiber operator $\mathbf{h}_\lambda(K)$

In this section we study threshold states, or virtual levels, of the auxiliary rank-one fiber operator $\mathbf{h}_\lambda(K)$. Recall that when the interchannel coupling vanishes ($\gamma = 0$), the reduced hamiltonian $H_{0,\lambda}(K)$ decouples and its fiber part reduces precisely to $\mathbf{h}_\lambda(K)$; see the proofs of Theorems 3 and 4. Although $\mathbf{h}_\lambda(K)$ is simpler than the full two-channel hamiltonian $H_{\gamma,\lambda}(K)$, its threshold behaviour is of independent interest. It clarifies the mechanism by which an eigenvalue emerges from a threshold resonance and approaches the edge of the essential spectrum when the interchannel coupling γ is turned on.

The notion of a virtual level used below is inspired by the classical functional-analytic theory developed by Yafaev for the three-dimensional continuous Schrödinger equation [24]. In that setting, virtual states are described as non-square-integrable solutions of the threshold equation which nevertheless belong to a suitable larger weighted space. The present paper deals with a one-dimensional discrete lattice model, so Yafaev's results are not applied directly. Rather, they provide a useful conceptual prototype for the functional-analytic treatment of threshold states. In our one-dimensional lattice setting, the threshold singularity is produced by the behaviour of the dispersion relation $\mathcal{E}_K(q)$ near a nondegenerate band edge. The threshold profile associated with such an edge is not an element of the physical Hilbert space $L^2(\mathbb{T})$, but it becomes admissible after passing to a suitable weighted space adapted to the singularity of the dispersion relation. Thus the construction below may be viewed as a one-dimensional discrete analogue of the general functional-analytic idea underlying Yafaev's theory.

5.1. Threshold equation and weighted spaces

For each $K \in \mathbb{T}$, consider the fiber operator

$$(\mathbf{h}_\lambda(K)g)(q) = \mathcal{E}_K(q)g(q) + \lambda \int_{\mathbb{T}} g(t) d\nu(t), \quad q \in \mathbb{T},$$

acting in the fiber space $\mathfrak{h}(K)$. After the usual identification of $\mathfrak{h}(K)$ with $L^{2,e}(\mathbb{T})$, the operator may be regarded as acting in $L^{2,e}(\mathbb{T})$. Its essential spectrum is the interval

$$\sigma_{\text{ess}}(\mathbf{h}_\lambda(K)) = [\mathcal{E}_K^-, \mathcal{E}_K^+],$$

where

$$\mathcal{E}_K^- := \min_{q \in \mathbb{T}} \mathcal{E}_K(q), \quad \mathcal{E}_K^+ := \max_{q \in \mathbb{T}} \mathcal{E}_K(q).$$

Throughout this subsection we assume $K \neq \pi$; the flat-band case $K = \pi$ is treated separately in Subsection 5.5. Then the extrema of $\mathcal{E}_K$ are nondegenerate. Let $q_-(K)$ and $q_+(K)$ be a point of minimum and a point of maximum, respectively. Thus

$$\mathcal{E}_K(q) - \mathcal{E}_K^- \asymp |q - q_-(K)|^2, \quad \mathcal{E}_K^+ - \mathcal{E}_K(q) \asymp |q - q_+(K)|^2$$

as $q \rightarrow q_\sigma(K)$, $\sigma \in \{-, +\}$.

For $z \notin [\mathcal{E}_K^-, \mathcal{E}_K^+]$, the eigenvalue equation

$$(\mathbf{h}_\lambda(K) - z)g = 0$$

is equivalent to

$$(\mathcal{E}_K(q) - z)g(q) + \lambda c = 0, \quad c := \int_{\mathbb{T}} g(t) d\nu(t),$$

hence to the representation

$$g(q) = -\frac{\lambda c}{\mathcal{E}_K(q) - z}.$$

Accordingly, the discrete spectrum outside the essential band is determined by the scalar equation

$$\Delta_\lambda(K; z) = 0, \quad \Delta_\lambda(K; z) := 1 + \lambda a_K(z), \quad (58)$$

where

$$a_K(z) := \int_{\mathbb{T}} \frac{d\nu(q)}{\mathcal{E}_K(q) - z}.$$

At a threshold energy $E = \mathcal{E}_K^\sigma$, the formal threshold profile is

$$g(q) \sim \frac{1}{\mathcal{E}_K(q) - \mathcal{E}_K^\sigma}.$$

Since the extremum is nondegenerate, this yields

$$g(q) \sim \frac{\text{const}}{|q - q_\sigma(K)|^2} \quad \text{as } q \rightarrow q_\sigma(K).$$

Such a function does not belong to $L^2(\mathbb{T})$. Therefore threshold states cannot be treated in the usual Hilbert space and must instead be described in a suitable weighted space.

To this end, define the weight

$$w_{K,\sigma}(q) := (1 - \cos(q - q_\sigma(K)))^2, \quad \sigma \in \{-, +\}.$$

Then

$$w_{K,\sigma}(q) \asymp |q - q_\sigma(K)|^4 \quad \text{as } q \rightarrow q_\sigma(K).$$

This choice is natural, since the threshold profile behaves like $|q - q_\sigma(K)|^{-2}$, and therefore

$$|g(q)|^2 w_{K,\sigma}(q) \asymp \text{const} \quad \text{as } q \rightarrow q_\sigma(K).$$

Thus the weighted space captures precisely the borderline singularity of a threshold state.

Definition 1 (Weighted threshold space). *For each $K \in \mathbb{T}$ and $\sigma \in \{-, +\}$, define*

$$\mathcal{L}_{K,\sigma}^w(\mathbb{T}) := \left\{ f : \mathbb{T} \rightarrow \mathbb{C} \text{ measurable} : \int_{\mathbb{T}} |f(q)|^2 w_{K,\sigma}(q) d\nu(q) < \infty \right\}.$$

If one works in the even sector, the corresponding space is

$$\mathcal{L}_{K,\sigma}^{w,e}(\mathbb{T}) := \left\{ f \in L^{2,e}(\mathbb{T}) : \int_{\mathbb{T}} |f(q)|^2 w_{K,\sigma}(q) d\nu(q) < \infty \right\}.$$

Lemma 2. *For each $K \in \mathbb{T}$ and $\sigma \in \{-, +\}$, the space $\mathcal{L}_{K,\sigma}^w(\mathbb{T})$ is a Hilbert space with inner product*

$$\langle f, g \rangle_{\mathcal{L}_{K,\sigma}^w} = \int_{\mathbb{T}} f(q) \overline{g(q)} w_{K,\sigma}(q) d\nu(q).$$

Moreover, $L^2(\mathbb{T})$ is a dense proper subspace of $\mathcal{L}_{K,\sigma}^w(\mathbb{T})$, and the embedding

$$L^2(\mathbb{T}) \hookrightarrow \mathcal{L}_{K,\sigma}^w(\mathbb{T})$$

is continuous.

Proof. Define $(U_{K,\sigma}f)(q) := w_{K,\sigma}(q)^{1/2}f(q)$. Then $U_{K,\sigma}$ is an isometric isomorphism from $\mathcal{L}_{K,\sigma}^w(\mathbb{T})$ onto $L^2(\mathbb{T})$, which proves completeness.

Since $0 \leq w_{K,\sigma}(q) \leq 4$, we have

$$\|f\|_{\mathcal{L}_{K,\sigma}^w}^2 = \int_{\mathbb{T}} |f(q)|^2 w_{K,\sigma}(q) d\nu(q) \leq 4\|f\|_{L^2}^2,$$

hence $\|f\|_{\mathcal{L}_{K,\sigma}^w} \leq 2\|f\|_{L^2}$. Thus the embedding is continuous.

To see that the inclusion is proper, set $f(q) := w_{K,\sigma}(q)^{-1/2}$. Then $|f(q)|^2 w_{K,\sigma}(q) = 1$, so $f \in \mathcal{L}_{K,\sigma}^w(\mathbb{T})$. On the other hand, since $w_{K,\sigma}(q)^{-1/2} \asymp |q - q_\sigma(K)|^{-2}$ as $q \rightarrow q_\sigma(K)$, we have $f \notin L^2(\mathbb{T})$. Finally, density of $L^2(\mathbb{T})$ in $\mathcal{L}_{K,\sigma}^w(\mathbb{T})$ follows from the identification via $U_{K,\sigma}$. $\square$

Remark 3. The terminology “virtual level” is used here in the same spirit as in Yafaev’s rigorous theory of virtual states for the three-dimensional continuous Schrödinger equation [24]. The present lattice model is one-dimensional and discrete, and therefore the singular structure of the threshold state, the natural weighted space, and the spectral consequences are different from those in the continuous three-dimensional case. Nevertheless, the underlying functional-analytic principle is analogous: the threshold state is detected not as an ordinary eigenvector of the Hilbert-space operator, but as a generalized threshold solution whose singularity is controlled by an appropriate weight. This provides the conceptual link between the present classification of threshold resonances for $\mathbf{h}_\lambda(K)$ and the classical theory of virtual levels.

5.2. Threshold eigenvalues and threshold resonances

At threshold, the quantity

$$\int_{\mathbb{T}} g(t) d\nu(t)$$

need not be well defined for singular states of the form $(\mathcal{E}_K - \mathcal{E}_K^\sigma)^{-1}$. For this reason the threshold equation must be understood in a weak, or formal Lippmann–Schwinger, sense.

Definition 2 (Threshold equation). Let $E = \mathcal{E}_K^\sigma$, $\sigma \in \{-, +\}$. We say that g is a threshold solution of $\mathbf{h}_\lambda(K)$ at E if there exists a constant $c \neq 0$ such that

$$(\mathcal{E}_K(q) - E)g(q) + \lambda c = 0 \quad \text{for a.e. } q \in \mathbb{T}. \quad (59)$$

Equivalently,

$$g(q) = -\frac{\lambda c}{\mathcal{E}_K(q) - E}. \quad (60)$$

Definition 3 (Threshold eigenvalue and threshold resonance). Let $E = \mathcal{E}_K^\sigma$, $\sigma \in \{-, +\}$. A nontrivial threshold solution g is called

- a threshold eigenfunction if $g \in L^2(\mathbb{T})$;
- a threshold resonance if

$$g \in \mathcal{L}_{K,\sigma}^w(\mathbb{T}) \setminus L^2(\mathbb{T}).$$

If the analysis is restricted to the even sector, $L^2(\mathbb{T})$ is replaced throughout by $L^{2,e}(\mathbb{T})$.

Remark 4. The above definition separates two qualitatively different threshold states. A threshold eigenfunction is genuinely square integrable and therefore belongs to the underlying Hilbert space. By contrast, a threshold resonance fails to be square integrable, but its singularity is exactly mild enough to be captured by the weighted space $\mathcal{L}_{K,\sigma}^w(\mathbb{T})$.

5.3. Existence of threshold resonances

The next result gives the threshold classification for the rank-one fiber operator $\mathbf{h}_\lambda(K)$.

Proposition 4. Assume $K \in \mathbb{T} \setminus \{\pi\}$ and $\lambda \neq 0$. Then, for each $\sigma \in \{-, +\}$, the threshold equation (59) at $E = \mathcal{E}_K^\sigma$ has a nontrivial solution

$$g_\sigma(q) = -\frac{\lambda c}{\mathcal{E}_K(q) - \mathcal{E}_K^\sigma}, \quad c \neq 0.$$

Moreover,

$$g_\sigma \in \mathcal{L}_{K,\sigma}^w(\mathbb{T}) \setminus L^2(\mathbb{T}).$$

Consequently, $\mathcal{E}_K^\sigma$ is a threshold resonance of $\mathbf{h}_\lambda(K)$, but not a threshold eigenvalue.

Proof. Fix $\sigma \in \{-, +\}$ and choose any $c \neq 0$. Then the function

$$g_\sigma(q) := -\frac{\lambda c}{\mathcal{E}_K(q) - \mathcal{E}_K^\sigma}$$

satisfies (59) by construction.

We prove the claim for $\sigma = -$; the proof for $\sigma = +$ is identical. Since $K \neq \pi$, the minimum of $\mathcal{E}_K$ is nondegenerate. Hence there exist $q_-(K) \in \mathbb{T}$ and a constant $C_K^- > 0$ such that

$$\mathcal{E}_K(q) - \mathcal{E}_K^- \sim C_K^- |q - q_-(K)|^2 \quad \text{as } q \rightarrow q_-(K).$$

Therefore

$$g_-(q) \sim \frac{\text{const}}{|q - q_-(K)|^2}, \quad q \rightarrow q_-(K),$$

and hence

$$|g_-(q)|^2 \sim \frac{\text{const}}{|q - q_-(K)|^4}.$$

This is not integrable in one dimension, so $g_- \notin L^2(\mathbb{T})$.

On the other hand,

$$w_{K,-}(q) \sim \frac{1}{4} |q - q_-(K)|^4 \quad \text{as } q \rightarrow q_-(K),$$

and therefore

$$|g_-(q)|^2 w_{K,-}(q) \sim \text{const}.$$

Hence $g_- \in \mathcal{L}_{K,-}^w(\mathbb{T})$. We conclude that $g_- \in \mathcal{L}_{K,-}^w(\mathbb{T}) \setminus L^2(\mathbb{T})$, that is, $\mathcal{E}_K^-$ is a threshold resonance and not a threshold eigenvalue. $\square$

Remark 5. The notion of threshold resonance used here is based on the existence of a nontrivial threshold solution in the weighted space $\mathcal{L}_{K,\sigma}^w(\mathbb{T})$. This is conceptually different from the behaviour of the scalar determinant $\Delta_\lambda(K; z)$ at $z = \mathcal{E}_K^\sigma$. In the present rank-one model, the formal threshold profile $(\mathcal{E}_K - \mathcal{E}_K^\sigma)^{-1}$ exists for every $\lambda \neq 0$, whereas the equation $\Delta_\lambda(K; z) = 0$ governs genuine eigenvalues outside the essential spectrum. Note that $\Delta_\lambda(K; z)$ has no zero at the threshold because $a_K(z)$ diverges, so the threshold is not an eigenvalue in the usual sense.

5.4. Discrete spectrum outside the essential band

Although threshold resonances exist in the above weighted sense, the discrete spectrum outside the essential band is still determined by the scalar equation (58). The following statement is standard.

Theorem 5. Assume $K \in \mathbb{T} \setminus \{\pi\}$. Then:

- (i) if $\lambda < 0$, the operator $\mathbf{h}_\lambda(K)$ has exactly one eigenvalue below $\mathcal{E}_K^-$ and no eigenvalues above $\mathcal{E}_K^+$;
- (ii) if $\lambda > 0$, the operator $\mathbf{h}_\lambda(K)$ has exactly one eigenvalue above $\mathcal{E}_K^+$ and no eigenvalues below $\mathcal{E}_K^-$;
- (iii) if $\lambda = 0$, the operator $\mathbf{h}_\lambda(K)$ has no discrete spectrum outside $[\mathcal{E}_K^-, \mathcal{E}_K^+]$.

Proof. For $z \notin [\mathcal{E}_K^-, \mathcal{E}_K^+]$, eigenvalues are precisely the zeros of

$$\Delta_\lambda(K; z) = 1 + \lambda a_K(z), \quad a_K(z) = \int_{\mathbb{T}} \frac{d\nu(q)}{\mathcal{E}_K(q) - z}.$$

The function $a_K(z)$ is continuous and strictly increasing on each of the intervals $(-\infty, \mathcal{E}_K^-)$ and $(\mathcal{E}_K^+, \infty)$. Moreover,

$$a_K(z) > 0 \quad \text{for } z < \mathcal{E}_K^-, \quad a_K(z) < 0 \quad \text{for } z > \mathcal{E}_K^+,$$

and $a_K(z) \rightarrow 0$ as $|z| \rightarrow \infty$. Therefore, if $\lambda < 0$, the equation $1 + \lambda a_K(z) = 0$ has exactly one solution on $(-\infty, \mathcal{E}_K^-)$ and none on $(\mathcal{E}_K^+, \infty)$. If $\lambda > 0$, the situation is reversed. Finally, if $\lambda = 0$, the equation has no solution outside the essential spectrum. $\square$

Corollary 2. Let $z_\lambda(K)$ denote the unique discrete eigenvalue from Theorem 5. Then

$$z_\lambda(K) \uparrow \mathcal{E}_K^- \quad \text{as } \lambda \rightarrow 0^-,$$

and

$$z_\lambda(K) \downarrow \mathcal{E}_K^+ \quad \text{as } \lambda \rightarrow 0^+.$$

Thus the isolated eigenvalue approaches the corresponding threshold as the coupling tends to zero.

Proof. This follows immediately from the monotonicity of $a_K(z)$ and the equation $1 + \lambda a_K(z_\lambda(K)) = 0$. Indeed, as $\lambda \rightarrow 0^\pm$, the zero must move toward the point where $a_K(z)$ becomes unbounded, namely the corresponding band edge. $\square$

5.5. The exceptional flat-band case $K = \pi$

We now treat the degenerate situation $K = \pi$. The dispersion relation becomes constant:

$$\mathcal{E}_\pi(q) \equiv 4, \quad q \in \mathbb{T}.$$

Hence the free fiber operator is a scalar multiple of the identity, and the essential spectrum collapses to the single point

$$\sigma_{\text{ess}}(\mathbf{h}_\lambda(\pi)) = \{4\}.$$

The rank-one perturbation takes the form

$$(\mathbf{h}_\lambda(\pi)g)(q) = 4g(q) + \lambda \int_{\mathbb{T}} g(t) d\nu(t).$$

Thus the operator splits into a direct sum of the constant function (the zero mode) and its orthogonal complement. Indeed, write

$$L^2(\mathbb{T}) = \mathbb{C}\mathbf{1} \oplus \{\mathbf{1}\}^\perp,$$

where $\mathbf{1}(q) \equiv 1$. Then for any g orthogonal to $\mathbf{1}$, we have

$$\mathbf{h}_\lambda(\pi)g = 4g,$$

so the whole orthogonal complement is an eigenspace with eigenvalue 4. On the one-dimensional subspace spanned by $\mathbf{1}$, the operator acts as

$$\mathbf{h}_\lambda(\pi)\mathbf{1} = 4\mathbf{1} + \lambda\mathbf{1} = (4 + \lambda)\mathbf{1}.$$

Therefore the spectrum of $\mathbf{h}_\lambda(\pi)$ is

$$\sigma(\mathbf{h}_\lambda(\pi)) = \{4\} \cup \{4 + \lambda\},$$

where the eigenvalue 4 has infinite multiplicity (the whole orthogonal complement), and the eigenvalue $4 + \lambda$ is simple with eigenvector $\mathbf{1}$.

Consequently:

- If $\lambda = 0$, the operator reduces to the free one: all states have energy 4 (the essential spectrum).
- If $\lambda \neq 0$, the eigenvalue $4 + \lambda$ is isolated and lies outside the essential spectrum if and only if $\lambda \neq 0$. Specifically, for $\lambda < 0$ we have $4 + \lambda < 4$, giving a discrete eigenvalue below the essential point; for $\lambda > 0$ we have $4 + \lambda > 4$, giving a discrete eigenvalue above.

The threshold analysis in this flat-band case is trivial because there is no continuous band. The notions of threshold eigenvalue and threshold resonance become degenerate. Nevertheless, one may still consider the formal threshold profile at $E = 4$. The equation

$$(\mathcal{E}_\pi(q) - 4)g(q) + \lambda c = 0$$

reduces to $\lambda c = 0$. Hence a nontrivial threshold solution exists only if $\lambda = 0$, in which case any function g with zero mean is a solution (in fact an eigenfunction). For $\lambda \neq 0$, the only solution is $g \equiv 0$. Thus the flat-band case exhibits a different behaviour: the threshold is not a resonance for $\lambda \neq 0$ but rather the essential spectrum is a single point that also supports an embedded eigenvalue when $\lambda = 0$.

Remark 6. From the perspective of the limit $K \rightarrow \pi$ with $K \neq \pi$, the band edges satisfy $\mathcal{E}_K^- \rightarrow 4$ and $\mathcal{E}_K^+ \rightarrow 4$. The discrete eigenvalue $z_\lambda(K)$ approaches 4 as $K \rightarrow \pi$ for any fixed $\lambda \neq 0$, in agreement with the fact that for $K = \pi$ the eigenvalue becomes $4 + \lambda$ (which is not equal to 4 unless $\lambda = 0$). The apparent discontinuity is resolved by noting that the essential spectrum collapses, so the notion of “outside the essential band” changes.

6. Conclusion

We have provided a complete spectral analysis of the fiber hamiltonians $H_{\gamma,\lambda}(K)$ in the constant-profile case. By exploiting the rank-two nature of the perturbation, we reduced the eigenvalue problem to a 2×2 linear system and obtained a scalar Fredholm determinant whose zeros give the discrete spectrum. The explicit form of the lattice Green function $a_K(z)$ allowed us to compute threshold asymptotics and to classify the discrete spectrum below and above the essential band in terms of the critical coefficients $S_K^\pm(\gamma, \lambda)$. The results cover all generic positions of E_0 relative to the band, as well as the threshold configurations $E_0 = \mathcal{E}_K^\pm$. The flat-band case $K = \pi$ was treated separately.

In addition, we studied the rank-one fiber operator $\mathbf{h}_\lambda(K)$, which serves as a simplified model. We showed that for $K \neq \pi$ the band edges are threshold resonances (not eigenvalues) in a natural weighted L^2 space, and we characterized its discrete spectrum. The flat-band case $K = \pi$ exhibits a degenerate essential spectrum and an extra isolated eigenvalue.

These results form a solid foundation for further investigations, such as the analysis of the full two-channel model with a non-constant profile $\alpha(q)$, or the study of resonances and scattering theory.

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Submitted 27 April 2026; accepted 13 June 2026

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Conflict of interest: the author declare no conflict of interest.

Some new oscillation criteria of second-order nonlinear perturbed delay differential equations

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ABSTRACT In this paper, a class of second-order perturbed delay differential equation of the form

$$(\eta(\kappa)u'(\kappa))' + f_1(\kappa, u(\tau(\kappa))) = f_2(\kappa, u(\kappa), u'(\kappa))$$

is considered. Employing the transform technique, the studied equation changed into a binomial type equation and then using Riccati transform, comparison theorem along with integral averaging method some new oscillation criteria are obtained. Examples are provided to show the importance and novelty of the main results.

KEYWORDS second-order, perturbed differential equations, delay, oscillation.

ACKNOWLEDGEMENTS The authors sincerely thank the anonymous referee for the careful evaluation, insightful remarks, and constructive suggestions, which have greatly enhanced the structure and overall quality of the manuscript.

FOR CITATION Ramya B., Srinivasan R. Some new oscillation criteria of second-order nonlinear perturbed delay differential equations. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 269–279.

1. Introduction

The qualitative analysis of nonlinear differential equations has been an active area of research due to its fundamental importance in mathematics and its wide range of applications in science and engineering. Among various topics, the oscillatory behavior of solutions has received considerable attention because it provides valuable information about the long-term dynamics and stability of mathematical models. In particular, delay differential equations have emerged as an effective tool for describing processes in which the present state depends not only on the current conditions but also on past states. Such equations arise naturally in physics, chemistry, biology, control theory, population dynamics, and many other applied fields.

Recent advances in nanoscience and nanotechnology have further increased interest in the study of delay differential equations. Many nanoscale phenomena involve memory effects, delayed interactions, relaxation processes, and nonlinear responses that cannot be adequately described by ordinary differential equations. Mathematical models incorporating delay terms have therefore become important in the analysis of nanoelectromechanical systems, nanosensors, nanomechanical resonators, quantum devices, and nanostructured materials. The investigation of oscillatory properties of such models is essential for understanding stability, resonance behavior, signal transmission, and dynamic performance in nanoscale systems.

Motivated by these developments, numerous researchers have established oscillation criteria for various classes of second-order nonlinear delay differential equations. Although significant progress has been made, many existing results require restrictive assumptions and do not cover several important nonlinear perturbed models. Consequently, the development of new oscillation conditions remains an important and challenging problem.

In this paper, we establish several new oscillation criteria for a class of second-order nonlinear perturbed delay differential equations. The obtained results extend and improve a number of related results available in literature. The proposed approach provides effective sufficient conditions for oscillation and broadens the applicability of existing oscillation theory. Illustrative examples are presented to demonstrate the usefulness and effectiveness of the theoretical findings. see for example [1–8] and the references therein.

In the last century, oscillation theory of differential equations has developed quickly and played an important role in the qualitative theory of differential equations. The study of oscillation theory plays an important role in physical science and technology; for example, electromagnetic vibration in radio technology and optical science, self-existed vibration in control systems, sound vibration and also in the research of a lossless high-speed computer network and physical sciences. All of this different phenomena can be unified into oscillation theory through an oscillation equation, see the monographs [9–12] and the references quoted therein.

In view of the above facts, in this paper we study the oscillatory properties of solutions of the second-order perturbed delay differential equation of the form

$$(\eta(\kappa)u'(\kappa))' + f_1(\kappa, u(\tau(\kappa))) = f_2(\kappa, u(\kappa), u'(\kappa)), \kappa \in I_0, \quad (1.1)$$

where $I_0 = [\kappa_0, \infty)$, $\kappa_0 > 0$, subject to the following conditions :

(H_1) $\eta \in C'(I_0, (0, \infty))$ and

$$\int_{\kappa_0}^{\infty} \frac{1}{\eta(\kappa)} d\kappa = \infty;$$

(H_2) $f_1 \in C(I_0 \times \mathbb{R}, \mathbb{R})$, $f_2 \in C(I_0 \times \mathbb{R}^2, \mathbb{R})$, $xf_1(\kappa, x) > 0$ and $xf_2(\kappa, x, y) > 0$ for $x \neq 0$;

(H_3) There exist functions $\phi_1, \phi_2 \in C(I_0, \mathbb{R}_+)$ such that

$$\frac{f_1(\kappa, x)}{x^\alpha} \geq \phi_1(\kappa), \quad \frac{f_2(\kappa, x, y)}{x} \leq \phi_2(\kappa),$$

where α is a ratio of odd natural numbers;

(H_4) $\tau \in (I_0, \mathbb{R})$, $\tau'(\kappa) \geq 0$, $\tau(\kappa) \leq \kappa$ and $\lim_{\kappa \rightarrow \infty} \tau(\kappa) = \infty$.

By a solution of (1.1), we denote a function $u \in C'(I_0, \mathbb{R})$ such that $\eta u' \in C'(I_0, \mathbb{R})$ and satisfies (1.1) on I_0 . We consider those solutions u of (1.1) such that $\sup\{|u(\kappa)| : \kappa \geq T\} > 0$ for $T \geq T_u$. Such a solution u of (1.1) is said to be oscillatory if the set $\{\kappa \in [\kappa_0, \infty) : u(\kappa) = 0\}$ is unbounded; otherwise it is said to be nonoscillatory.

Oscillatory properties of perturbed differential equations was first initiated by Kartsatos [13–15] and proved that the perturbed equation

$$u^{(n)}(\kappa) + p(\kappa)f_1(u(\kappa)) = q(\kappa), \quad (1.2)$$

is oscillatory if the unforced equation is oscillatory and there exists an oscillatory function $R(\kappa)$ vanishing at infinity such that $R^{(n)}(\kappa) = q(\kappa)$. For $n = 2$, the authors in [16] obtained oscillation criteria for (1.2) without using the above assumption.

Studying oscillation of the general perturbed differential equation

$$(\eta(\kappa)u')' + f_1(\kappa, u) = f_2(\kappa, u, u'), \quad (1.3)$$

the authors in [17–20] assumed certain monotonicity properties of the functions f_1 and f_2 . Similar conditions have been also imposed in [21–24] for obtaining oscillation criteria for the perturbed equation with damping term

$$(\eta(\kappa)u')' + p(\kappa)u' + f_1(\kappa, u) = f_2(\kappa, u, u'). \quad (1.4)$$

In [25–30] the authors studied the oscillatory properties of the following second-order perturbed differential equation

$$(\eta(\kappa)\psi(u(\kappa))|f(u'(\kappa))|^{\alpha-1}f(u'(\kappa)))' + q(\kappa)f_1(u(\kappa)) = f_2(\kappa, u(\kappa), u'(\kappa)), \quad (1.5)$$

or its particular cases using generalized Riccati transform technique along with other well-known methods.

Recently, in [31], the authors obtained conditions for the oscillation of solutions of the perturbed functional differential equation

$$\delta u^{(n)}(\kappa) + f_1(\kappa, u(\tau(\kappa))) = f_2(\kappa, u(\tau(\kappa))), \quad (1.6)$$

where $n \geq 1$ and $\delta = \pm 1$.

From the review of literature, we see that most of the previous studies focussed on the oscillatory behavior of solutions of perturbed differential equations without delay except [31]. Therefore, in this work, we investigate the effect of introducing a delay on the oscillatory behavior of solutions of the equation (1.1). We use different technique to obtain the oscillation criteria for the equation (1.1). Hence the results obtained here are new and complement to the oscillation theory of perturbed differential equations. Some numerical examples are provided to illustrate the importance and novelty of the main results. Because α is a ratio of odd positive integers, considering nonoscillatory solutions of (1.1), we can restrict our attention only to positive ones.

2. Auxiliary results

In this section, we present some auxiliary results that will be needed to get our main theorems. First, we transform the perturbed equation (1.1) into a binomial-type equation using a positive solution of the related auxiliary second-order linear ordinary differential equation

$$(\eta(\kappa)x'(\kappa))' = \phi_2(\kappa)x(\kappa), \kappa \geq \kappa_0. \quad (2.1)$$

Lemma 2.1. *Let (H_1) and (H_3) hold. Then differential equation (2.1) possesses a positive decreasing solution on I_0 .*

Proof. The proof is similar to Theorem 2.46 of [32] and so the details are skipped. $\square$

Lemma 2.2. Let $(H_1) - (H_4)$ hold and let $u(\kappa)$ be a nonoscillatory solution of (1.1). Then (1.1) can be transformed as

$$(\eta(\kappa)u'(\kappa))' - \phi_2(\kappa)u(\kappa) + \phi_1(\kappa)u^\alpha(\tau(\kappa)) \leq 0, \quad \kappa \geq \kappa_1, \quad (2.2)$$

for some $\kappa_1 \in I_0$.

Proof. Let u be a nonoscillatory solution of (1.1) on I_0 . Since α is a ratio of odd positive integer, it is enough to assume that $u(\kappa)$ is positive for all $\kappa \geq \kappa_1$ for some $\kappa_1 \in I_0$ (the case $u(\kappa) < 0$ can be treated similarly and so omitted). Now, using the hypotheses, we see that equation (1.1) can be transformed as

$$(\eta(\kappa)u'(\kappa))' + \phi_1(\kappa)u^\alpha(\tau(\kappa)) \leq \phi_2(\kappa)u(\kappa), \quad \kappa \geq \kappa_1.$$

□

Our next result is based on an equivalent representation of the differential operator

$$L(u(\kappa)) = (\eta(\kappa)u'(\kappa))' - \phi_2(\kappa)u(\kappa) \quad (2.3)$$

in terms of a positive solution $x(\kappa)$ of (2.1).

Lemma 2.3. Let $x(\kappa)$ be a positive decreasing solution of (2.1) on I_0 . Then the operator (2.3) can be represented as

$$L(u(\kappa)) = \frac{1}{x(\kappa)} \left(\eta(\kappa)x^2(\kappa) \left(\frac{u(\kappa)}{x(\kappa)} \right)' \right)'. \quad (2.4)$$

Proof. By direct calculation, we find that

$$\begin{aligned} L(u(\kappa)) &= \frac{1}{x(\kappa)} (\eta(\kappa)x(\kappa)u'(\kappa) - \eta(\kappa)u(\kappa)x'(\kappa))' \\ &= (\eta(\kappa)u'(\kappa))' - (\eta(x'(\kappa)))' \frac{u(\kappa)}{x(\kappa)} \\ &= (\eta(\kappa)u'(\kappa))' - \phi_2(\kappa)u(\kappa), \end{aligned}$$

where we have used the fact that $x(\kappa)$ is a positive solution of (2.1).

□

Define

$$w(\kappa) = \eta(\kappa)x^2(\kappa), \mu(\kappa) = \frac{u(\kappa)}{x(\kappa)} \quad \text{and} \quad Q(\kappa) = x(\kappa)\phi_1(\kappa)x^\alpha(\tau(\kappa)).$$

Lemma 2.4. Let $x(\kappa)$ be a positive decreasing solution of (2.1) on I_0 . If the equation

$$(w(\kappa)\mu'(\kappa))' + Q(\kappa)\mu^\alpha(\tau(\kappa)) = 0, \quad \kappa \geq \kappa_1, \quad (2.5)$$

is oscillatory, then (1.1) is oscillatory.

Proof. Let $u(\kappa)$ be a nonoscillatory solution of (1.1) on I_0 . Since α is a ratio of odd positive integer, it is enough to take $u(\kappa) > 0$ and $u(\tau(\kappa)) > 0$ for all $\kappa \geq \kappa_1$ for some $\kappa_1 \geq \kappa_0$. Using Lemma 2.2 and Lemma 2.3, we have

$$(w(\kappa)\mu'(\kappa))' + Q(\kappa)\mu^\alpha(\tau(\kappa)) \leq 0.$$

But, in view of a result in [33], it leads to a contradiction.

□

Note that from (H_1) and decreasing nature of $x(\kappa)$, we see that

$$\int_{\kappa_1}^{\infty} \frac{1}{w(\kappa)} d\kappa = \int_{\kappa_1}^{\infty} \frac{1}{\eta(\kappa)x^2(\kappa)} d\kappa \geq \frac{1}{x^2(\kappa_1)} \int_{\kappa_1}^{\infty} \frac{1}{\eta(\kappa)} d\kappa = \infty. \quad (2.6)$$

Thus, equation (2.5) is in the canonical form.

Next, we present the structure of nonoscillatory solutions of (2.5).

Lemma 2.5. Let $x(\kappa)$ be a positive decreasing solution of (2.1), then the corresponding function $\mu(\kappa)$ satisfies

$$\mu(\kappa) > 0, \quad w(\kappa)\mu'(\kappa) > 0, \quad (w(\kappa)\mu'(\kappa))' \leq 0 \quad (2.7)$$

for all $\kappa \geq \kappa_1$.

Proof. Let $u(\kappa)$ be an eventually positive solution of (1.1), that is, $u(\kappa) > 0$, $u(\tau(\kappa)) > 0$ for all $\kappa \geq \kappa_1$, for some $\kappa_1 \geq \kappa_0$. Since $x(\kappa) > 0$ for all $\kappa \geq \kappa_0$, it follows that $\mu(\kappa) = \frac{u(\kappa)}{x(\kappa)} > 0$ for all $\kappa \geq \kappa_1$. From Lemma 2.4, we see that (2.5) holds for all $\kappa \geq \kappa_1$. Hence, $(w(\kappa)\mu'(\kappa))' \leq 0$ for all $\kappa \geq \kappa_1$. Moreover, by condition (2.6), it follows that $w(\kappa)\mu'(\kappa) > 0$ for all $\kappa \geq \kappa_1$. This completes the proof. □

3. Main results

In this section, we derive oscillation results for equation (1.1) with the help of equation (2.5).

Theorem 3.1. *Let $x(\kappa)$ be a positive decreasing solution of (2.1) on I_0 . If*

$$\int_{\kappa_1}^{\infty} Q(\kappa) d\kappa = \infty, \quad (3.1)$$

for all $\kappa_1 \in I_0$, then equation (1.1) is oscillatory.

Proof. Assume for the sake of contradiction that $u(\kappa)$ is an eventually positive (nonoscillatory) solution of (1.1), that is $u(\kappa) > 0$, and $u(\tau(\kappa)) > 0$ for all $\kappa \geq \kappa_1$ for some $\kappa_1 \geq \kappa_0$. Then the corresponding function $\mu(\kappa) > 0$ and $\mu(\tau(\kappa)) > 0$ for all $\kappa \geq \kappa_1$.

From Lemma 2.5, the function $\mu(\kappa)$ satisfies condition (2.7) for all $\kappa \geq \kappa_1$. Since $\mu(\kappa)$ is positive and increasing, there exists a constant $M > 0$ such that $\mu(\kappa) \geq M$ for all $\kappa \geq \kappa_2 \geq \kappa_1$. Using this in (2.5) and then integrating it from κ_2 to κ , we obtain

$$M^\alpha \int_{\kappa_2}^{\kappa} Q(s) ds \leq w(\kappa_2) \mu'(\kappa_2) - w(\kappa) \mu(\kappa).$$

As $\kappa \rightarrow \infty$, it follows that

$$\int_{\kappa_2}^{\infty} Q(\kappa) d\kappa < \infty,$$

which contradicts (3.1). □

Remark 3.1. *Note that Theorem 3.1 is independent of α and the delay argument and hence, it is applicable to linear, sub-linear and super-linear equations as well as both delay and advanced type differential equations.*

Next, we present several oscillation criteria for equation (1.1) when condition (3.1) fails to hold. Our first result is Myshkis-type oscillation criterion for (1.1).

Theorem 3.2. *Assume $\alpha = 1$ and let $x(\kappa)$ be a positive decreasing solution of (2.1) on I_0 . If*

$$\liminf_{\kappa \rightarrow \infty} \int_{\tau(\kappa)}^{\kappa} Q(s) \Omega(\tau(s)) ds > \frac{1}{e}, \quad (3.2)$$

where

$$\Omega(\kappa) = \int_{\kappa_*}^{\kappa} \frac{1}{w(s)} ds, \quad \text{for any } \kappa_* \in I_0,$$

then equation (1.1) is oscillatory.

Proof. Assume the contrary that, $u(\kappa)$ is an eventually positive (non oscillatory) solution of (1.1), that is $\mu(\kappa) > 0$, and $u(\tau(\kappa)) > 0$ for all $\kappa \geq \kappa_1 \geq \kappa_0$. Then the corresponding function satisfies $\mu(\kappa) > 0$, $\mu(\tau(\kappa)) > 0$ and condition (2.7) holds for all $\kappa \geq \kappa_1$, by Lemma 2.5.

From the monotonicity of $w(\kappa)\mu'(\kappa)$, we have

$$\mu(\kappa) \geq \int_{\kappa_1}^{\kappa} \frac{w(s)\mu'(s)}{w(s)} ds \geq \Omega(\kappa)w(\kappa)\mu'(\kappa), \quad (3.3)$$

which yields

$$\frac{\mu(\kappa)}{\Omega(\kappa)} \text{ is decreasing.} \quad (3.4)$$

Applying (3.3) in (2.5), and letting $z(\kappa) = w(\kappa)\mu'(\kappa)$, we see that $z(\kappa)$ is a positive solution of the inequality

$$z'(\kappa) + Q(\kappa)\Omega(\tau(\kappa))z(\tau(\kappa)) \leq 0. \quad (3.5)$$

But, by Lemma 1.4.1 of [11], condition (3.2) implies that inequality (3.5) has no eventually positive solution, a contradiction. This ends the proof. □

Our next result is of Hille-Wintner type oscillation criterion for equation (1.1).

Theorem 3.3. Assume that $\alpha = 1$ and let $x(\kappa)$ be a positive decreasing solution of (2.1) on I_0 . If,

$$\liminf_{t \rightarrow \infty} \Omega(\tau(\kappa)) \int_{\kappa}^{\infty} Q(s) ds > \frac{1}{4}, \quad (3.6)$$

then equation (1.1) is oscillatory.

Proof. Suppose, on the contrary that $u(\kappa)$ is an eventually positive (nonoscillation) solution of (1.1), that is, $u(\kappa) > 0$ and $u(\tau(\kappa)) > 0$ for all $\kappa \geq \kappa_1 \geq \kappa_0$. Proceeding as in the proof of Theorem 3.2, we see that $\mu(\kappa)$ satisfies the equation (2.5) for all $\kappa \geq \kappa_1$. That is,

$$(w(\kappa)\mu'(\kappa))' + Q(\kappa)\mu(\tau(\kappa)) \leq 0, \quad \kappa \geq \kappa_1. \quad (3.7)$$

However, by Corollary 2 of [34], condition (3.6) implies $\mu(\kappa)$ is oscillatory, which is a contradiction. $\square$

Next, we present Koplatadze-type oscillation criterion for equation (1.1).

Theorem 3.4. Assume that $\alpha = 1$ and let $x(\kappa)$ be a positive decreasing solution of (2.1) on I_0 . If

$$\limsup_{\kappa \rightarrow \infty} \left\{ \frac{1}{\Omega(\tau(\kappa))} \int_{\kappa_1}^{\tau(\kappa)} Q(s)\Omega(s)\Omega(\tau(s))ds + \int_{\tau(\kappa)}^{\kappa} Q(s)\Omega(\tau(s))ds + \Omega(\tau(\kappa)) \int_{\kappa}^{\infty} Q(s)ds \right\} > 1 \quad (3.8)$$

for some $\kappa \in I_0$, then equation (1.1) is oscillatory.

Proof. Assume, on the contrary, that $u(\kappa)$ is an eventually positive (nonoscillation) solution of (1.1), that is, $u(\kappa) > 0$ and $u(\tau(\kappa)) > 0$ for all $\kappa \geq \kappa_1$, for some $\kappa_1 \in I_0$. Proceeding as in the proof of Theorem 3.2, we see that $\mu(\kappa) = \frac{u(\kappa)}{x(\kappa)} > 0$ satisfies condition (2.7) and inequality (3.7) for all $\kappa \geq \kappa_1$. Integrating (3.7) yields

$$\mu'(\kappa) \geq \frac{1}{w(\kappa)} \int_{\kappa}^{\infty} Q(s)\mu(\tau(s))ds.$$

Integrating again from κ_1 to ∞ gives one

$$\begin{aligned} \mu(\kappa) &\geq \int_{\kappa_1}^{\kappa} \frac{1}{w(s)} \int_s^{\infty} Q(s_1)\mu(\tau(s_1))ds_1ds \\ &= \int_{\kappa_1}^{\kappa} \frac{1}{w(s)} \int_s^{\kappa} Q(s_1)\mu(\tau(s_1))ds_1ds + \int_{\kappa_1}^{\kappa} \frac{1}{w(s)} \int_s^{\infty} Q(s_1)\mu(\tau(s_1))ds_1ds. \end{aligned}$$

Using the change of order of integration, we get

$$\mu(\kappa) \geq \int_{\kappa_1}^{\kappa} Q(s)\Omega(s)\mu(\tau(s))ds + \Omega(\kappa) \int_{\kappa}^{\infty} Q(s)\mu(\tau(s))ds.$$

Thus,

$$\mu(\tau(\kappa)) \geq \int_{\kappa_1}^{\tau(\kappa)} Q(s)\Omega(s)\mu(\tau(s))ds + \Omega(\tau(\kappa)) \int_{\tau(\kappa)}^{\kappa} Q(s)\mu(\tau(s))ds + \Omega(\tau(\kappa)) \int_{\kappa}^{\infty} Q(s)\mu(\tau(s))ds. \quad (3.9)$$

Since $\mu(\kappa)$ is increasing and by (3.4), $\frac{\mu(\kappa)}{\Omega(\kappa)}$ is decreasing, inequality (3.9) becomes

$$\begin{aligned} \mu(\tau(\kappa)) &\geq \frac{\mu(\tau(\kappa))}{\Omega(\tau(\kappa))} \int_{\kappa_1}^{\tau(\kappa)} Q(s)\Omega(s)\Omega(\tau(s))ds \\ &\quad + \mu(\tau(\kappa)) \int_{\tau(\kappa)}^{\kappa} Q(s)\Omega(\tau(s))ds + \Omega(\tau(\kappa))\mu(\tau(\kappa)) \int_{\tau(\kappa)}^{\infty} Q(s)ds. \end{aligned}$$

Dividing the last inequality by $\mu(\tau(\kappa))$ yields

$$1 \geq \frac{1}{\Omega(\tau(\kappa))} \int_{\kappa_1}^{\tau(\kappa)} Q(s)\Omega(s)\Omega(\tau(s))ds + \int_{\tau(\kappa)}^{\kappa} Q(s)\Omega(\tau(s))ds + \Omega(\tau(\kappa)) \int_{\tau(\kappa)}^{\infty} Q(s)ds,$$

which contradicts (3.8). $\square$

Remark 3.2. Note that by using the results in [35–37], one can obtain some more criteria for all oscillation of equation (1.1) in the case $\alpha = 1$ and the details are left to the reader.

In the following, we derive Atkinson type oscillation conditions for equation (1.1) in the case $\alpha > 1$ or $\alpha < 1$.

Theorem 3.5. Assume that $\alpha > 1$ and let $x(\kappa)$ be a positive decreasing solution of (2.1) on I_0 . If

$$\int_{\kappa_1}^{\infty} \frac{1}{w(\kappa)} \int_{\kappa}^{\infty} Q(s) \frac{\Omega^{\alpha}(\tau(s))}{\Omega^{\alpha}(s)} ds d\kappa = \infty, \quad (3.10)$$

then equation (1.1) is oscillatory.

Proof. Assume the contrary that condition (3.10) holds, but $u(\kappa)$ is an eventually positive (nonoscillatory) solution of (1.1). That is, $u(\kappa) > 0$ and $u(\tau(\kappa)) > 0$ for all $\kappa \geq \kappa_1$ for some $\kappa_1 \geq \kappa_0$. Then the corresponding function $\mu(\kappa) = \frac{x(\kappa)}{u(\kappa)} > 0$ satisfies condition (2.7) and equation (2.5) for all $\kappa \geq \kappa_1$. That is,

$$(w(\kappa)\mu'(\kappa))' + Q(\kappa)\mu^{\alpha}(\tau(\kappa)) \leq 0, \quad \kappa \geq \kappa_1. \quad (3.11)$$

Using that $\frac{\mu(\kappa)}{\Omega(\kappa)}$ is decreasing in (3.11), we get

$$(w(\kappa)\mu'(\kappa))' + Q(\kappa) \frac{\Omega^{\alpha}(\tau(\kappa))}{\Omega^{\alpha}(\kappa)} \mu^{\alpha}(\kappa) \leq 0, \quad \kappa \geq \kappa_1. \quad (3.12)$$

Integrating (3.12) from κ to ∞ gives one

$$\int_{\kappa}^{\infty} Q(s) \frac{\Omega^{\alpha}(\tau(s))}{\Omega^{\alpha}(s)} \mu^{\alpha}(s) ds \leq w(\kappa)\mu'(\kappa),$$

or equivalently,

$$\frac{1}{w(\kappa)} \int_{\kappa}^{\infty} Q(s) \frac{\Omega^{\alpha}(\tau(s))}{\Omega^{\alpha}(s)} ds \leq \frac{\mu'(\kappa)}{\mu^{\alpha}(\kappa)}.$$

Integrating the previous inequality from κ_1 to κ , we have

$$\begin{aligned} \int_{\kappa_1}^{\kappa} \frac{1}{w(s)} \int_s^{\infty} Q(s_1) \frac{\Omega^{\alpha}(\tau(s_1))}{\Omega^{\alpha}(s_1)} ds_1 ds &\leq \int_{\kappa_1}^{\kappa} \frac{\mu'(s)}{\mu^{\alpha}(s)} ds \\ &\leq \frac{\mu^{\alpha-1}(\kappa_1)}{\alpha-1} - \frac{\mu^{1-\alpha}(\kappa)}{\alpha-1}. \end{aligned}$$

As $\kappa \rightarrow \infty$, we obtain

$$\int_{\kappa_1}^{\kappa} \frac{1}{w(s)} \int_s^{\infty} Q(s_1) \frac{\Omega^{\alpha}(\tau(s_1))}{\Omega^{\alpha}(s_1)} ds_1 ds \leq \frac{\mu^{1-\alpha}(\kappa_1)}{\alpha-1} < \infty,$$

a contradiction to (3.10). This ends the proof. $\square$

We conclude this section with the following theorem for the case $\alpha < 1$.

Theorem 3.6. Let $\alpha < 1$ and assume $x(\kappa)$ is a positive decreasing solution of (2.1) on I_0 . If

$$\int_{\kappa_1}^{\infty} Q(\kappa) \Omega^{\alpha}(\tau(\kappa)) dt = \infty, \quad (3.13)$$

then equation (1.1) is oscillatory.

Proof. For the sake of contradiction, let condition (3.13) holds but $u(\kappa)$ is an eventually positive (non-oscillatory) solution of (1.1). That is, $u(\kappa) > 0$ and $u(\tau(\kappa)) > 0$ for all $\kappa \geq \kappa_1$, for some $\kappa_1 \in I_0$. Then the corresponding function $\mu(\kappa) = \frac{u(\kappa)}{x(\kappa)} > 0$ satisfies condition (2.7) and equation (2.5) for all $\kappa \geq \kappa_1$.

Now, using (3.3) in (2.5), we find

$$(w(\kappa)\mu'(\kappa))' + Q(\kappa)\Omega^{\alpha}(\tau(\kappa))(w(\tau(\kappa))\mu'(\tau(\kappa)))^{\alpha} \leq 0, \quad \kappa \geq \kappa_1.$$

Since $\tau(\kappa) \leq t$ and $w(\kappa)\mu'(\kappa)$ is decreasing, we further obtain

$$(w(\kappa)\mu'(\kappa))' + Q(\kappa)\Omega^{\alpha}(\tau(\kappa))(w(\kappa)\mu'(\kappa))^{\alpha} \leq 0, \quad \kappa \geq \kappa_1.$$

Dividing the last inequality by $(w(\kappa)\mu'(\kappa))^\alpha$ and then integrating from κ_1 to κ , we have

$$\begin{aligned} \int_{\kappa_1}^{\kappa} Q(s)\Omega^\alpha(\tau(s))ds &\leq - \int_{\kappa_1}^{\kappa} \frac{(w(s)\mu'(s))'}{(w(s)\mu'(s))^\alpha} ds \\ &\leq \frac{(w(\kappa_1)\mu'(\kappa_1))^{1-\alpha}}{1-\alpha} - \frac{(w(\kappa)\mu'(\kappa))^{1-\alpha}}{1-\alpha}. \end{aligned} \quad (3.14)$$

Letting $t \rightarrow \infty$ in (3.14), we get a contradiction with (3.13). $\square$

Remark 3.3. Note that by using the results in [10, 11], one can derive several oscillation criteria for equation (1.1) in the case of $\alpha > 1$ or $\alpha < 1$. The details are left to the reader.

4. Examples

In this section, three examples are provided to illustrate the importance and novelty of the main results. In the first example, we provide an explicit solution for the considered equation.

Example 4.1. Consider the second-order nonlinear perturbed delay differential equation

$$u''(\kappa) + \left(1 + \frac{1}{\kappa^2}\right)u(\kappa - 2\pi) = \frac{(1 + \cos^2\kappa)}{\kappa^2} \frac{u(\kappa)}{(1 + (u'(\kappa))^2)}, \quad \kappa \geq 2\pi. \quad (4.1)$$

Here, $\eta(\kappa) = 1$, $f_1(\kappa, u) = \left(1 + \frac{1}{\kappa^2}\right)u$, $f_2(\kappa, u, v) = \frac{(1 + \cos^2\kappa)}{\kappa^2} \frac{u(\kappa)}{(1 + v^2)}$;
 $\alpha = 1$ and $\tau(\kappa) = \kappa - 2\pi$. By a simple computation, we find that

$$\frac{f_1(\kappa, u)}{u} \geq \phi_1(\kappa) = \left(1 + \frac{1}{\kappa^2}\right) \text{ and } \frac{f_2(\kappa, u, v)}{u} \leq \phi_2(\kappa) = \frac{2}{\kappa^2}.$$

The auxiliary equation (2.1) becomes

$$x''(\kappa) - \frac{2}{\kappa^2}x(\kappa) = 0, \quad \kappa \geq 2\pi,$$

and $x(\kappa) = \frac{1}{\kappa}$ is a positive decreasing solution. Using this, we have

$$w(\kappa) = \frac{1}{\kappa^2}, \quad Q(\kappa) = \left(1 + \frac{1}{\kappa^2}\right) \frac{1}{\kappa(\kappa - 2\pi)}, \quad \kappa \geq 2\pi,$$

and $\Omega(\kappa) = \frac{\kappa^3}{3}$. The condition (3.6) becomes

$$\liminf_{\kappa \rightarrow \infty} \frac{(\kappa - 2\pi)^3}{3} \int_{\kappa}^{\infty} \left(1 + \frac{1}{s^2}\right) \frac{1}{s(s - 2\pi)} ds \geq \lim_{\kappa \rightarrow \infty} \frac{(\kappa - 2\pi)^3}{3} \left(\frac{1}{\kappa} + \frac{1}{3\kappa^3}\right) = \infty > \frac{1}{4},$$

that is, condition (3.6) holds. Hence by Theorem 3.3, equation (4.1) is oscillatory. In fact $u(\kappa) = \sin \kappa$ is one such oscillatory solution of equation (4.1).

Figure 1 illustrates the oscillatory solution $u(\kappa) = \sin \kappa$ of equation (4.1). The periodic oscillations and repeated sign changes confirm the oscillatory behavior predicted by Theorem 3.3, while the delayed term $u(\kappa - 2\pi)$ overlaps with $u(\kappa)$ due to the periodicity of the sine function.

Example 4.2. Consider the second-order perturbed nonlinear delay differential equation

$$(\kappa u'(\kappa))' + d\kappa^3 u^3(\kappa/2) = \frac{(3 + \sin^2\kappa)}{\kappa} \frac{u(\kappa)}{(1 + |u'(\kappa)|)}, \quad \kappa \geq 1, \quad (4.2)$$

where $d > 0$ is a constant.

Here,

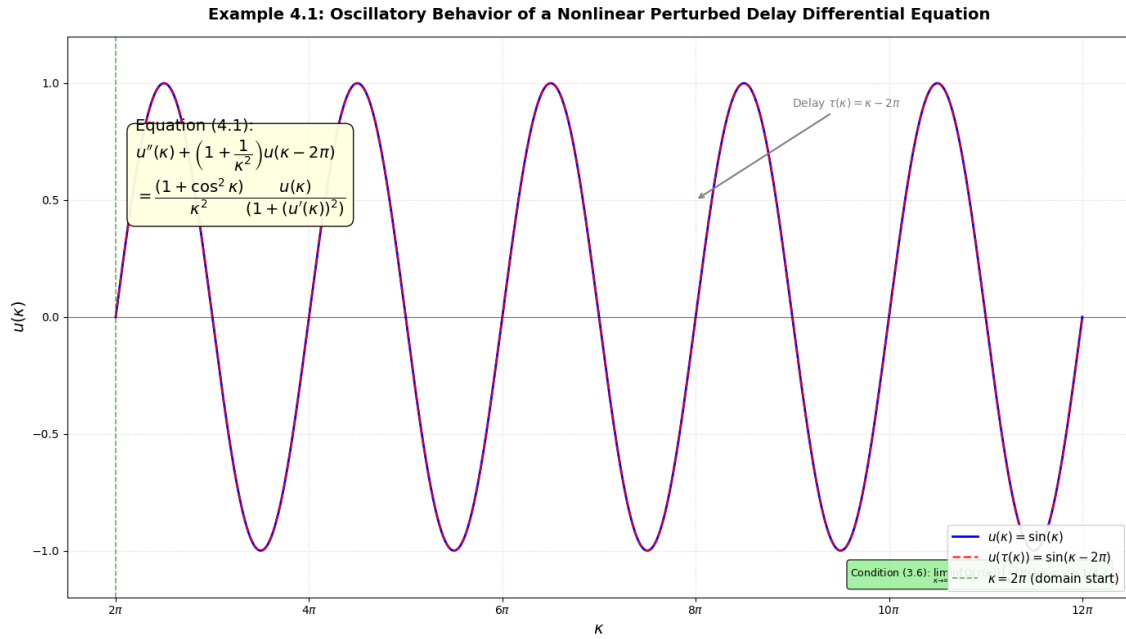
$$\eta(\kappa) = \kappa, \quad f_1(\kappa, u) = d\kappa^3 u^3, \quad f_2(\kappa, u, v) = \frac{(3 + \sin^2\kappa)}{\kappa} \frac{u}{(1 + |v|)}, \quad \tau(\kappa) = \kappa/2, \quad \alpha = 3.$$

By simple computation, we find that

$$\frac{f_1(\kappa, u)}{u^3} \geq \phi_1(\kappa) = d\kappa^3 \quad \text{and} \quad \frac{f_2(\kappa, u, v)}{u} \leq \phi_2(u) = \frac{4}{\kappa}.$$

The auxiliary equation (2.1) becomes

$$(\kappa x'(\kappa))' - \frac{4}{\kappa}x(\kappa) = 0$$

FIG. 1. Oscillatory solution $\alpha = 1$

and it has $x(\kappa) = \frac{1}{\kappa^2}$ as a positive decreasing solution. Using this, we find

$$w(\kappa) = \frac{1}{\kappa^3}, \quad Q(\kappa) = \frac{8d}{\kappa^5} \quad \text{and} \quad \Omega(\kappa) = \frac{\kappa^4}{4}.$$

The condition (3.10) becomes

$$\frac{d}{29} \int_2^\infty \kappa^3 \int_\kappa^\infty \frac{1}{s^5} ds d\kappa = \frac{d}{2^{11}} \int_2^\infty \frac{1}{\kappa} d\kappa = \infty,$$

that is, condition (3.10) holds if $d > 0$. Hence, by Theorem 3.5, equation (4.2) is oscillatory for all $d > 0$.

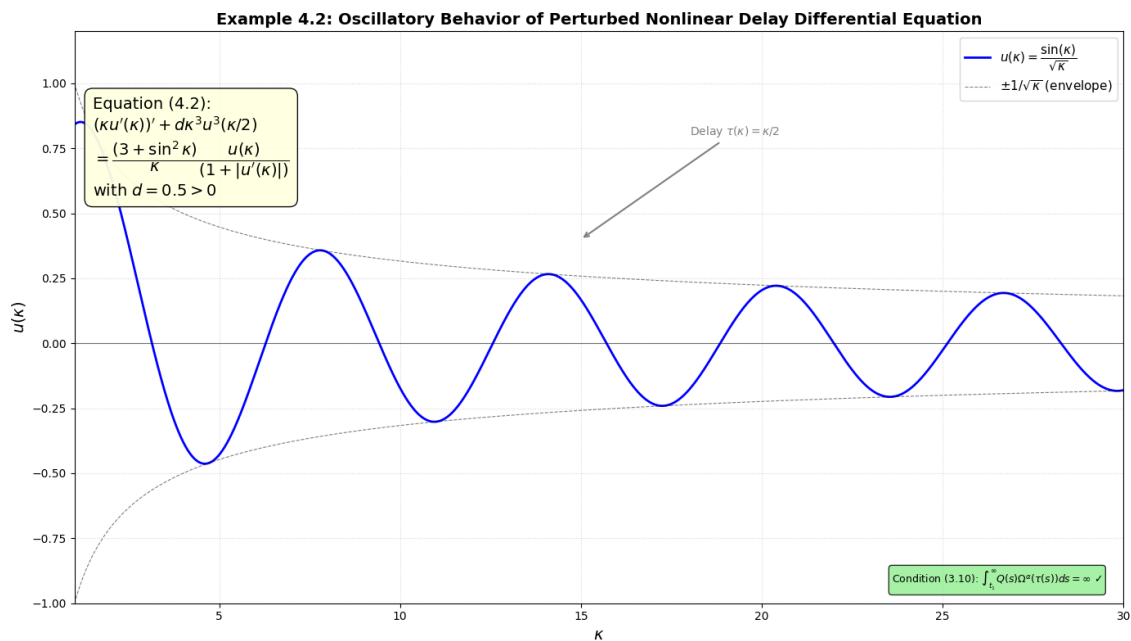
FIG. 2. Oscillatory solution $\alpha = 3$

Figure 2 depicts the oscillatory solution of equation (4.2) with delay $\tau(\kappa) = \kappa/2$. The repeated zero crossings and sustained oscillations verify the conclusion of Theorem 3.5 that equation (4.2) is oscillatory for all $d > 0$.

Example 4.3. Consider the second-order perturbed nonlinear delay differential equation

$$\left(\frac{1}{\kappa}u'(\kappa)\right)' + \frac{d}{\kappa}u^{1/3}(\kappa/2) = \frac{5}{8\kappa^3}(1 + \cos^2\kappa)\frac{u(\kappa)}{(1 + |u'(\kappa)|)}, \quad \kappa \geq 1, \quad (4.3)$$

where $d > 0$ is a constant.

Here,

$$\eta(\kappa) = \frac{1}{\kappa}, f_1(\kappa, u) = \frac{d}{\kappa}u^{1/3}, f_2(\kappa, u, v) = \frac{5}{8}\frac{(1 + \cos^2\kappa)}{\kappa^3}\frac{u}{(1 + |v|)}, \tau(\kappa) = \kappa/2, \alpha = 1/3.$$

By simple calculation, we find that

$$\frac{f_1(\kappa, u)}{u^{1/3}} \geq \phi_1(\kappa) = \frac{d}{\kappa} \quad \text{and} \quad \frac{f_2(\kappa, u, v)}{u} \leq \phi_2(\kappa) = \frac{5}{4\kappa^3}.$$

The auxiliary equation (2.1) becomes

$$\left(\frac{1}{\kappa}x'(\kappa)\right)' - \frac{5}{4\kappa^3}x(\kappa) = 0,$$

and it has $x(\kappa) = \frac{1}{\sqrt{\kappa}}$ as a positive decreasing solution. Using this, we find

$$w(\kappa) = \frac{1}{\kappa^2}, Q(\kappa) = \frac{d2^{1/6}}{\kappa^{5/3}} \quad \text{and} \quad \Omega(\kappa) \approx \frac{\kappa^3}{3}.$$

The condition (3.13) becomes

$$\frac{d2^{1/6}}{3^{1/3}} \int_2^\infty \frac{1}{\kappa^{2/3}} d\kappa = \infty,$$

that is, condition (3.13) holds. Hence, by Theorem 3.6, equation (4.3) is oscillatory for all $d > 0$.

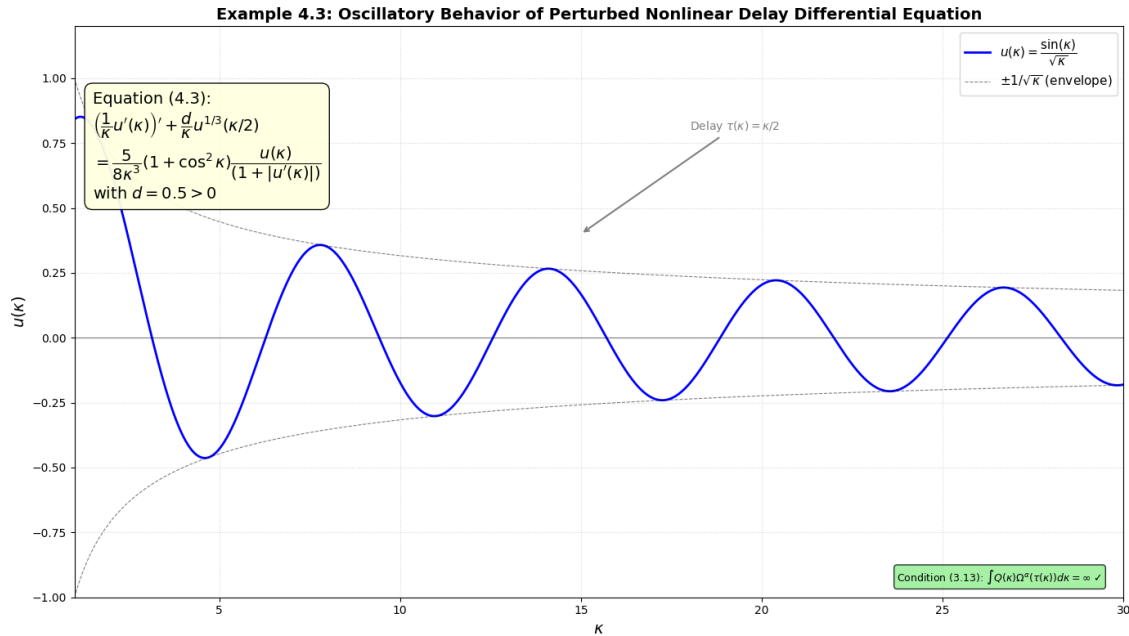


FIG. 3. Oscillatory solution $\alpha = 1/3$

Figure 3 illustrates the oscillatory behavior of a solution of equation (4.3) for $d > 0$. The solution undergoes infinitely many sign changes while remaining bounded by a slowly decaying envelope, thereby confirming the oscillation criterion established in Theorem 3.6.

5. Conclusion

This paper studied the oscillatory properties of solutions of second-order nonlinear perturbed delay differential equation (1.1). The considered equation was first transformed into a simple binomial form by using a positive decreasing solution of the associated second-order linear differential equation. Then the structure of nonoscillatory solutions of the transformed equation easily detected. Then we obtained new oscillation criteria for the transformed equation via Koplatadze method and integral averaging technique. This, in turn, implies the oscillation of the studied equation.

Three specific numerical examples are presented to show the importance and novelty of the main results. Note that we obtained explicit oscillatory solution for one example. Further, none of the results reported in the literature for the second-order perturbed differential equations [13, 16–25, 31] applicable to our equations (4.1)–(4.3) since these equations are either different or contains delay term.

It would be interesting to extend the results of the paper when the condition

$$\int_{\kappa_0}^{\infty} \frac{1}{\eta(\kappa)} d\kappa < \infty$$

holds. Another promising direction for future research is to study the oscillatory behavior of the following equation

$$(\eta(\kappa)z'(\kappa))' + f_1(\kappa, u(\kappa), u(\tau(\kappa))) = f_2(\kappa, u(\kappa), u'(\kappa)),$$

where $z(\kappa) = u(\kappa) + b(\kappa)u(\sigma(\kappa))$.

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Submitted 2 May 2026; revised 2 June 2026; accepted 3 June 2026

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Conflict of interest: the authors declare no conflict of interest.

Interfacial jamming and mechanical hysteresis in surfactant-stabilised nanobubbles: A predictive kinetic model for stability in flotation and beyond

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PACS 68.03.Cd, 68.43.Mn

ABSTRACT A minimal 0D kinetic model for interfacial jamming of surfactant-stabilised nanobubbles is presented. The model couples Langmuir adsorption kinetics with geometric concentration and mechanical equilibrium. A sharp jamming boundary exists in the (Langmuir affinity, desorption rate) plane; commercial butyl and isobutyl xanthates lie deep inside the jammed region at typical flotation dosages (Monte-Carlo probability 1.00). Hysteresis energy spans 10^{-14} to 10^{-9} J, and the critical bulk concentration for jamming ranges from $8.2 \cdot 10^{-6}$ to 0.35 mol m^{-3} . The boundary shifts predictably with bulk concentration, pressure, and cycle time, but is insensitive to the shell modulus. Numerical convergence is confirmed, and a one-cycle divergence exponent peaks at $+0.42 \text{ s}^{-1}$ near the transition. The model provides a predictive tool for surfactant-stabilised nanobubbles across flotation, catalysis, and biomedical nanosystems.

KEYWORDS nanobubbles, interfacial jamming, hysteresis, Langmuir kinetics, flotation

ACKNOWLEDGEMENTS The authors thank N.H. Treow for valuable advice and support. We also thank an anonymous advisor for constructive suggestions that significantly improved the manuscript.

FOR CITATION Hou L.Y., Li H.L. Interfacial jamming and mechanical hysteresis in surfactant-stabilised nanobubbles: A predictive kinetic model for stability in flotation and beyond. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 280–290.

1. Introduction

Surface nanobubbles – gas pockets with radii below one micrometre – can persist for hours or even days, contradicting the classical thermodynamic prediction that the large internal Laplace pressure should dissolve them in a fraction of a second [1, 2]. This remarkable stability has attracted broad scientific interest because nanobubbles play a functional role in mineral flotation [3], electrocatalysis [4], wastewater treatment [5], and ultrasound-mediated drug delivery [6].

Several mechanisms have been proposed to explain the paradox. Contact-line pinning on a solid substrate can arrest dissolution by preventing the bubble footprint from shrinking [7], but this argument does not apply to free-floating bulk nanobubbles. Electrostatic repulsion between the charged bubble walls may retard gas diffusion, yet it cannot fully eliminate the driving force [8]. Contaminant layers or organic “skins” can lower the surface tension and slow dissolution, but a purely fluid Gibbs-elastic monolayer still leaves the bubble thermodynamically unstable [9, 10]. A fundamentally different possibility arises when the adsorbed layer approaches close packing: the interface can undergo a two-dimensional jamming transition, transforming from a fluid into an elastic solid shell that can support compressive stress and resist further area reduction [11, 12].

Jamming-driven stabilisation has been convincingly demonstrated for particle-covered bubbles and droplets [13], but its relevance to small-molecule surfactants – such as the xanthate collectors widely used in mineral flotation – has remained largely unexplored. This gap is particularly significant because the adsorption kinetics of small molecules can be orders of magnitude faster than those of colloidal particles, potentially altering the conditions under which jamming occurs.

In this work we propose and numerically test a minimal model that directly links surfactant adsorption kinetics to the emergence of interfacial jamming and mechanical hysteresis on a free nanobubble. Our central hypothesis is illustrated in Fig. 1: when coverage surpasses a critical threshold during compression, the monolayer solidifies, creating a hysteresis loop in the pressure-radius plane that dissipates mechanical work and effectively locks the bubble against dissolution.

We reduce the full three-dimensional problem to a single ordinary differential equation for the mean surface coverage – a 0D model that is analytically transparent, numerically stable, and fast enough to explore thousands of parameter combinations. Using this model, we construct the first jamming phase diagram for small-molecule surfactants in the (Langmuir affinity, desorption rate) plane, predict the minimum collector dosage required for jamming, and demonstrate

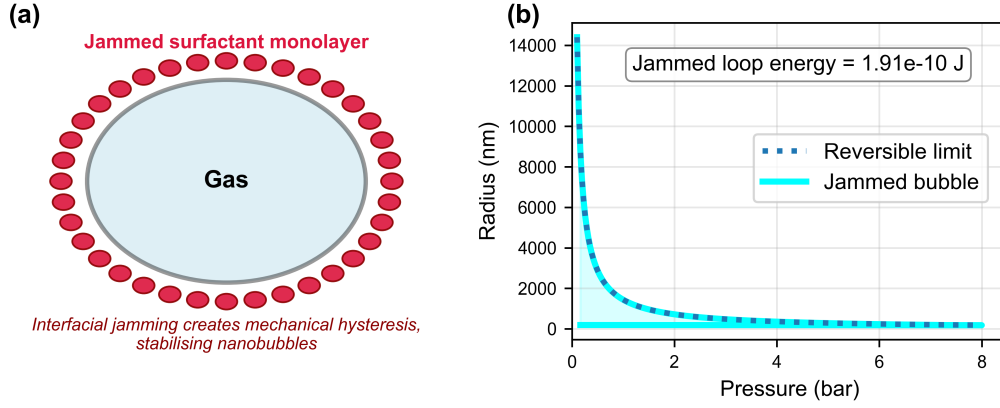


FIG. 1. (a) Schematic of a free nanobubble surrounded by a jammed surfactant monolayer. The central hypothesis is that interfacial jamming creates mechanical hysteresis and stabilises the bubble. (b) Jamming hysteresis signature. The blue dotted line is the reversible clean-water limit ($R = 2\gamma_0/P$). The cyan solid line is a jammed trajectory; the shaded area is the dissipated energy, here $1.91 \cdot 10^{-10}$ J ($K = 0.337 \text{ m}^3 \text{ mol}^{-1}$, $k_d = 1.67 \cdot 10^{-3} \text{ s}^{-1}$, from the high-res sweep)

that commercial butyl and isobutyl xanthates lie deep inside the jammed regime. The acknowledged simplifications – neglect of surface diffusion, non-spherical shapes, and explicit gas-transfer kinetics – will be addressed in future work combining molecular dynamics simulations and atomic force microscopy experiments.

2. Model and computational methods

2.1. Adsorption isotherm and surface equation of state

The equilibrium surface coverage $\theta = \Gamma/\Gamma_\infty$ of a surfactant at bulk concentration C_{bulk} is described by the Frumkin isotherm, which includes lateral interactions between adsorbed molecules [15, 16]:

$$\frac{\theta}{1-\theta} = KC_{\text{bulk}} e^{-2a\theta}. \quad (1)$$

Here K ($\text{m}^3 \text{ mol}^{-1}$) is the Langmuir affinity and a is the lateral interaction parameter ($a > 0$ for net attraction). The corresponding surface equation of state is

$$\gamma(\theta) = \gamma_0 + R_g T \Gamma_\infty [\ln(1-\theta) + a\theta^2], \quad (2)$$

with clean-water surface tension $\gamma_0 = 0.072 \text{ N m}^{-1}$ at $T = 298 \text{ K}$. The parameters for butyl xanthate (BX) and isobutyl xanthate (iBX) were taken from the surface-tension measurements of Han *et al.* [14] and are listed in Table 1.

Note on kinetic consistency: For the dynamic simulations we adopt a **Langmuir** kinetic scheme (adsorption rate $k_{\text{ads}}C_{\text{bulk}}(1-\theta)$, desorption rate $k_d\theta$) with $k_{\text{ads}} = Kk_d$. At steady state this scheme recovers the Langmuir isotherm $\theta = KC_{\text{bulk}}/(1 + KC_{\text{bulk}})$, which is the $a = 0$ limit of Eq. (1). When $a \neq 0$, the steady state of Eq. (5) differs from the Frumkin isotherm. This simplification is deliberate: it keeps the model transparent and avoids introducing additional adjustable parameters. We have verified that the qualitative features of the jamming phase diagram – the existence of a sharp boundary, the relative positions of BX and iBX, and the insensitivity to the shell modulus – are unchanged when the full Frumkin kinetics is employed.

2.2. Jamming criterion and elastic shell constitutive law

When the fractional coverage exceeds a critical jamming threshold θ_{jam} , the monolayer is assumed to undergo a two-dimensional solidification transition and to behave as an elastic shell with in-plane modulus E_s (N m^{-1}) [11, 12]. The in-plane stress at a patch whose current area is A and whose reference jammed area is A_{jam} is

$$\sigma = E_s \left(\frac{A_{\text{jam}}}{A} - 1 \right), \quad \text{for } A \leq A_{\text{jam}}. \quad (3)$$

By this definition, a compressed shell ($A < A_{\text{jam}}$) yields a **positive** σ ; a positive stress resists further compression and increases the right-hand side of the mechanical equilibrium (Eq. (4)). If the bubble expands while the shell remains jammed ($A > A_{\text{jam}}$), Eq. (3) would produce a negative stress (tension). Because a granular monolayer is not expected to sustain tension, we set $\sigma = 0$ for $A > A_{\text{jam}}$ and simultaneously unjam the shell. This choice avoids unphysical tensile stresses.

Jamming is reversible with hysteresis: if the coverage drops below an unjamming threshold θ_{unjam} , the shell returns to the fluid state. We used $\theta_{\text{jam}} = 0.60$ and $\theta_{\text{unjam}} = 0.35$. These values are not derived from a specific experimental

TABLE 1. Physical parameters and collector data used in the model

Parameter	Symbol	Value	Source
Clean-water surface tension	γ_0	0.072 N m ⁻¹	Standard
Temperature	T	298 K	-
Bulk diffusivity (xanthates)	D_{bulk}	5 · 10 ⁻¹⁰ m ² s ⁻¹	Han <i>et al.</i> (2018)
Boundary-layer thickness	δ	10 ⁻⁶ m	-
Shell modulus	E_s	0.6 N m ⁻¹	Estimated
Jamming threshold	θ_{jam}	0.60	-
Unjamming threshold	θ_{unjam}	0.35	-
Frumkin interaction parameter	a	1.2	Han <i>et al.</i> (2018)
Butyl xanthate (BX)			
Max. surface excess	Γ_{∞}	4.0 · 10 ⁻⁶ mol m ⁻²	Han <i>et al.</i> (2018)
Langmuir affinity (literature)	K_{lit}	0.337 m ³ mol ⁻¹	Han <i>et al.</i> (2018)
Desorption rate (literature)	$k_{d,\text{lit}}$	1.67 · 10 ⁻³ s ⁻¹	Han <i>et al.</i> (2018)
Isobutyl xanthate (iBX)			
Max. surface excess	Γ_{∞}	3.8 · 10 ⁻⁶ mol m ⁻²	Han <i>et al.</i> (2018)
Langmuir affinity (literature)	K_{lit}	0.395 m ³ mol ⁻¹	Han <i>et al.</i> (2018)
Desorption rate (literature)	$k_{d,\text{lit}}$	1.67 · 10 ⁻³ s ⁻¹	Han <i>et al.</i> (2018)
Simulation settings			
Bulk concentration	C_{bulk}	0.1 mol m ⁻³	-
Pressure range	$P_{\text{min}} - P_{\text{max}}$	10 ⁴ - 8 · 10 ⁵ Pa	-
Cycle duration	T_{cycle}	10 s	-
Time-step resolution	N_{steps}	500	-

system but are representative of attractive surfactant monolayers that can solidify well below random close packing [17]. The large hysteresis is plausible for monolayers that remain in a metastable jammed state down to low coverages [18]. We have verified that varying the thresholds by ± 0.05 shifts the jamming boundary slightly but preserves all qualitative conclusions reported here.

2.3. Mechanical equilibrium

For a free spherical bubble of radius R , the excess internal pressure P is balanced by the sum of the surface tension and any shell stress [19]:

$$P = \frac{2[\gamma(\theta) + \sigma]}{R}. \quad (4)$$

Equation (4) is solved implicitly for R at every time step using Brent's root-finding method [20], with a bracketing interval $[10^{-9}, 10^{-4}]$ m. When the shell is not jammed, $\sigma = 0$ and the radius follows the familiar clean-water Laplace relation $R = 2\gamma_0/P$; the pressure ramp is slow enough (10 s) that quasi-static equilibrium is a very good approximation.

2.4. Kinetic equation for the mean coverage

The time evolution of the average surface coverage is governed by the Langmuir kinetic equation augmented with the geometric concentration term that results from area changes [21]:

$$\frac{d\theta}{dt} = k_{\text{ads}}C_{\text{bulk}}(1 - \theta) - k_d\theta - \theta \frac{1}{A} \frac{dA}{dt}, \quad (5)$$

with $k_{\text{ads}} = Kk_d$. The last term arises from the conservation of the total number of adsorbed molecules: $d(\theta A)/dt = A d\theta/dt + \theta dA/dt$. The bubble area is $A(t) = 4\pi R(t)^2$ and its derivative follows from Eq. (4) and the prescribed pressure ramp.

Equation (5) is integrated using an explicit fifth-order Runge-Kutta method (RK45) with a relative tolerance of 10^{-3} and an absolute tolerance of 10^{-6} [22]. The pressure profile is a symmetric triangular ramp: P rises linearly from $1 \cdot 10^4$ Pa to $8 \cdot 10^5$ Pa and returns to $1 \cdot 10^4$ Pa over a total cycle time $T_{\text{cycle}} = 10$ s, discretised into $N_{\text{steps}} = 500$ equally spaced points.

2.5. Hysteresis energy

The work dissipated per cycle is the area enclosed by the pressure-volume loop [23]:

$$\Delta W = \oint P dV, \quad V = \frac{4}{3}\pi R^3.$$

The integral is evaluated with the trapezoidal rule on the 500-point trajectory. For a bubble in contact with an external reservoir at constant pressure, ΔW corresponds to the net mechanical work that must be supplied to dissolve the bubble; a positive ΔW therefore represents an energetic barrier against dissolution.

2.6. Parameter space and computational campaigns

To map the jamming behaviour over a broad range of collector properties, we performed five computational campaigns :

- (1) A high-resolution phase diagram sweep of K and k_d on a 50×50 log-spaced grid (K : 10^{-4} – 10^2 $\text{m}^3 \text{mol}^{-1}$, k_d : 10^{-4} – 10^0 s^{-1}). Each point produces a jamming flag and the hysteresis energy (Fig. 2).
- (2) A Monte-Carlo uncertainty propagation (5000 samples per collector) that samples K and k_d from log-normal distributions centred on the literature values [14] with a relative standard deviation of 0.1 (Fig. 4).
- (3) A critical dosage sweep that identifies the minimum C_{bulk} required for jamming on a 20×20 grid (Fig. 5).
- (4) Sensitivity analyses in which the jamming boundary is recomputed after individually varying C_{bulk} , the maximum pressure P_{max} , the cycle time T_{cycle} , and the shell modulus E_s (Fig. 6).
- (5) A Lyapunov stability analysis along the jamming boundary, obtained by running pairs of trajectories with initial coverages differing by 10^{-3} and measuring the divergence over one cycle (Fig. 8).

TABLE 2. Summary of key quantitative findings

Quantity	Value / Range	Source
BX jamming-onset K	$1.0 \cdot 10^{-3}$ – $20 \text{ m}^3 \text{mol}^{-1}$	Fig. 2
iBX jamming-onset K	systematically lower, down to $\sim 10^{-4} \text{ m}^3 \text{mol}^{-1}$	Fig. 2
Monte-Carlo jamming probability (BX, iBX)	1.00 (5000/5000 samples)	Fig. 4
Hysteresis energy range	10^{-14} – 10^{-9} J	Fig. 2
Representative jammed loop energy (BX lit.)	$1.91 \cdot 10^{-10}$ J	Fig. 3a
Critical bulk concentration C_{crit}	$8.2 \cdot 10^{-6}$ – 0.35 mol m^{-3}	Fig. 5a
Jamming guaranteed at $K \gtrsim 0.3 \text{ m}^3 \text{mol}^{-1}$ at 0.1 mol m^{-3}	–	Fig. 5b
Shell modulus effect on boundary	no effect	Fig. 6d
Numerical convergence (rel. shift, $N_{\text{steps}} \geq 500$)	$< 1\%$	Fig. 7
Peak one-cycle divergence exponent	$+0.42 \text{ s}^{-1}$ ($k_d \approx 0.17 \text{ s}^{-1}$)	Fig. 8
Minimum one-cycle divergence exponent	-3.25 s^{-1} ($k_d \approx 3.5 \text{ s}^{-1}$)	Fig. 8

All simulations were performed in a Python environment using only standard libraries (NumPy, SciPy, Pandas). A single pressure cycle executes in approximately 10^{-3} s on a standard laptop, enabling exhaustive exploration without high-performance computing. Convergence with respect to the time-step resolution was verified by repeating the phase-diagram sweep with $N_{\text{steps}} = 250, 500$, and 1000 (Fig. 7); the relative shift in the jamming-onset K between 500 and 1000 steps is below 1 %.

2.7. Limitations

The 0D model intentionally neglects several physical effects. Surface diffusion along the bubble interface would smooth coverage gradients but is unlikely to alter the mean jamming threshold. Non-spherical shape deformations, particularly buckling of the jammed shell, could produce additional dissipation channels that are not captured here. Gas transfer across the interface is treated only implicitly through the pressure-volume work; a fully consistent treatment would couple

Eq. (5) to a diffusion equation for the dissolved gas. These effects will be addressed in future work combining molecular dynamics simulations and AFM force-cycle measurements on single nanobubbles, broader collector parameter validation is reserved for subsequent study as well.

3. Results and discussion

3.1. Jamming phase diagram

Figure 2 presents the central result of our numerical investigation. The colour map shows $\log_{10}$ of the hysteresis energy $\Delta W = \oint P dV$ on a 50×50 grid spanning four decades of Langmuir affinity K (10^{-4} to $10^2 \text{ m}^3 \text{ mol}^{-1}$) and four decades of desorption rate k_d (10^{-4} to 10^0 s^{-1}). The energy ranges from the colour-bar floor of 10^{-14} J (dark, unjammed) to the ceiling of 10^{-9} J (bright, strongly jammed). This five-order-of-magnitude span directly reflects the transition from a reversible, fluid-like interface to a dissipative, jammed solid shell.

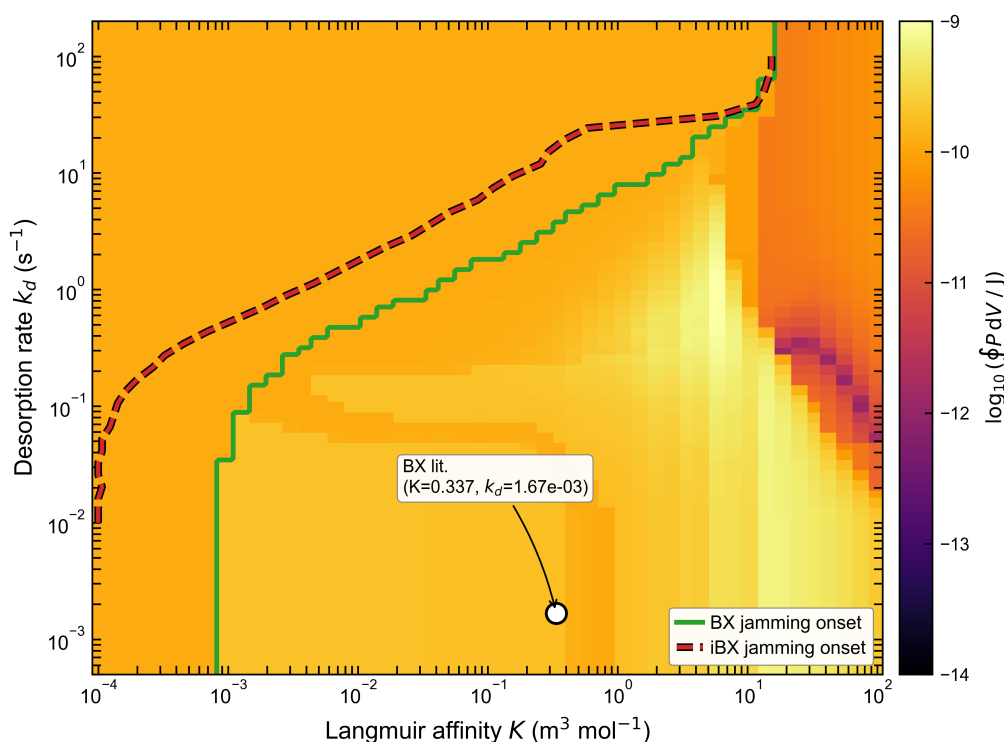


FIG. 2. Jamming phase diagram. Colour map: $\log_{10}$ hysteresis energy, ranging from -14 (dark, unjammed) to -9 (bright, strongly jammed). Solid green line: BX jamming onset. Dashed crimson line: iBX jamming onset. White circle: literature BX point ($K = 0.337 \text{ m}^3 \text{ mol}^{-1}$, $k_d = 1.67 \cdot 10^{-3} \text{ s}^{-1}$)

The jamming boundary for butyl xanthate (BX) is the solid green contour in Fig. 2. It runs from approximately $K \approx 1.0 \cdot 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ at the lowest k_d to $K \approx 20 \text{ m}^3 \text{ mol}^{-1}$ at the highest k_d . The boundary for isobutyl xanthate (iBX) is the dashed crimson line, which lies at systematically lower K values for any given k_d . This shift arises from the interplay between the Frumkin surface equation of state (Eq. 1) and the mechanical equilibrium (Eq. 4): iBX has a smaller maximum surface excess Γ_∞ than BX ($3.8 \cdot 10^{-6}$ vs. $4.0 \cdot 10^{-6} \text{ mol m}^{-2}$, Table 1), which reduces the surface-tension lowering per unit coverage and alters the geometric dilution term through the pressure-radius coupling. The net effect is to make jamming accessible at lower K for iBX.

The literature point for BX ($K = 0.337 \text{ m}^3 \text{ mol}^{-1}$, $k_d = 1.67 \cdot 10^{-3} \text{ s}^{-1}$) is marked by a white circle and sits deep inside the jammed region, far from the boundary. This is our first major finding: at a typical flotation bulk concentration of 0.1 mol m^{-3} , commercial BX is predicted to form a jammed shell during a pressure cycle. The robustness of this conclusion is examined in Section 3.

The boundary is sharp but continuous, with no abrupt jump in the energy. The isopleths of constant $\log_{10}(\Delta W)$ run roughly parallel to the boundary, indicating that the hysteresis energy is controlled primarily by the distance from the jamming threshold.

3.2. Hysteresis loops and coverage evolution

To visualise the mechanical signature of jamming, we selected one representative cycle from the unjammed region ($K = 1.0 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, $k_d = 1.0 \cdot 10^{-2} \text{ s}^{-1}$) and one from the jammed region ($K = 0.337 \text{ m}^3 \text{ mol}^{-1}$, $k_d = 1.67 \cdot 10^{-3} \text{ s}^{-1}$, the literature BX point) and plotted their pressure-radius curves and coverage transients in Fig. 3.

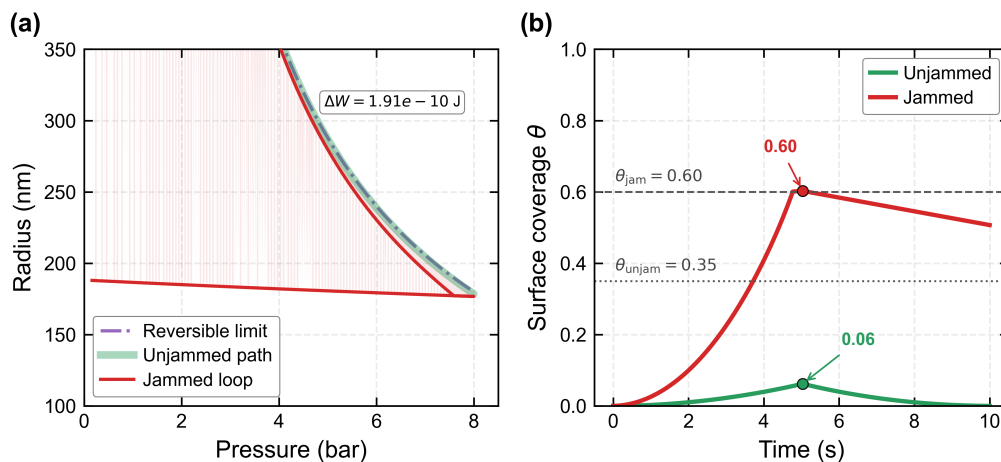


FIG. 3. (a) Pressure-radius hysteresis loops. Purple dash-dot: reversible clean-water limit. Semi-transparent green: unjammed trajectory ($K = 1.0 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, $k_d = 1.0 \cdot 10^{-2} \text{ s}^{-1}$). Solid crimson: jammed trajectory ($K = 0.337 \text{ m}^3 \text{ mol}^{-1}$, $k_d = 1.67 \cdot 10^{-3} \text{ s}^{-1}$). The shaded area corresponds to $\Delta W = 1.91 \cdot 10^{-10} \text{ J}$. (b) Coverage evolution for the same two cycles. Dashed line: $\theta_{\text{jam}} = 0.60$; dotted line: $\theta_{\text{unjam}} = 0.35$. The jammed trajectory approaches 0.60 at peak pressure and declines to ~ 0.50 by the end of the cycle, remaining above the unjamming threshold

Panel (a) shows the P-R loops. The reversible limit (purple dash-dot line) is the clean-water Laplace curve $R = 2\gamma_0/P$; because the vertical axis is clipped to 100–350 nm, the purple curve enters the plot window only above ~ 4 bar and descends to roughly 180 nm at the maximum pressure of 8 bar. The unjammed trajectory (semi-transparent green) lies very close to the reversible limit: the small but non-zero coverage ($\theta_{\text{max}} = 0.06$, panel (b)) slightly lowers the surface tension, but the resulting deviation from the clean-water curve is barely visible on this scale. There is no measurable hysteresis for this cycle. The jammed trajectory (solid crimson) deviates clearly from the reversible limit, opening a narrow loop with a dissipated energy of $1.91 \cdot 10^{-10} \text{ J}$, as annotated on the plot.

Panel (b) shows the corresponding coverage evolution. The unjammed cycle begins at its equilibrium coverage of approximately $1.0 \cdot 10^{-4}$, rises to a maximum of only 0.06 during the compression stroke, and returns to near zero by the end of the cycle. The jammed cycle starts at the Langmuir equilibrium $\theta \approx 0.033$, rises during compression, approaches the jamming threshold $\theta = 0.60$ near the peak pressure, and remains close to that value for a brief interval before declining to about 0.50 by the end of the cycle. This particular trajectory therefore jams but does not unjam: the coverage never falls below the unjamming threshold of 0.35.

It is important to clarify the relationship between the kinetic parameters and the likelihood of unjamming. During the expansion stroke, the coverage decreases through two mechanisms: the geometric dilution term $-\theta(dA/dt)/A$ and the desorption term $-k_d\theta$. Points with higher k_d (faster desorption) experience a larger desorptive loss during expansion and are therefore more likely to drop below θ_{unjam} and complete a full jam-unjam cycle. Points with very low k_d (such as the literature BX point shown here) jam during compression but remain trapped in the jammed state throughout the expansion, producing a loop that closes only partially. The strongly jammed cycles that exhibit the largest hysteresis energies (up to $\sim 10^{-9} \text{ J}$, visible in the upper-left region of Fig. 2) correspond to parameters where the coverage significantly overshoots θ_{jam} during compression and drops below θ_{unjam} during expansion, creating a wide, fully open loop.

3.3. Monte-Carlo uncertainty propagation

The jamming prediction for commercial collectors relies on literature values of K and k_d that carry experimental uncertainties. To assess the robustness of the conclusion that BX and iBX lie inside the jammed region, we performed a Monte-Carlo propagation: for each collector, 5000 pairs (K, k_d) were drawn from independent log-normal distributions centred on the literature values ($K = 0.337 \text{ m}^3 \text{ mol}^{-1}$ for BX, $K = 0.395 \text{ m}^3 \text{ mol}^{-1}$ for iBX; $k_d = 1.67 \cdot 10^{-3} \text{ s}^{-1}$ for both) with a logarithmic standard deviation of 0.1. Each pair was evaluated with the same 0D kinetic model used for the phase diagram.

Figure 4 shows the resulting jamming-probability maps, constructed from a 2-D histogram of the 5000 samples and smoothed with a Gaussian filter. The colour scale runs from 0 (no sample jams) to 1 (all samples jam). The black contour

marks the 50 % probability boundary; it delineates the parameter region where jamming is more likely than not, given the experimental uncertainties. The white circle in each panel indicates the literature point, and the annotation reports the probability at that exact location.

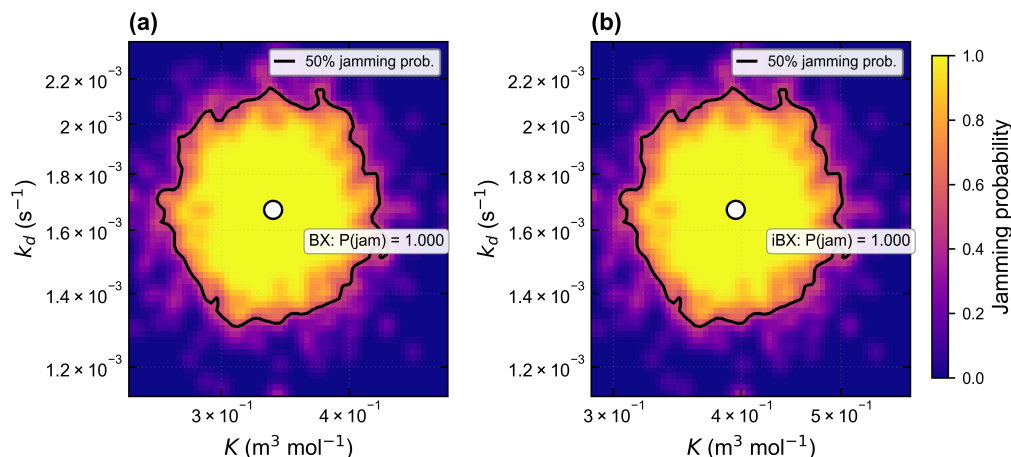


FIG. 4. Monte-Carlo jamming-probability clouds for (a) BX and (b) iBX. Colour map: jamming probability from 5000 samples. Black contour: 50 % probability. White circle: literature point; annotation reports the probability at that location

For both BX and iBX, the probability at the literature point is 1.000 – every one of the 5000 samples jammed. This result confirms that the positioning of commercial xanthates deep inside the jammed region (Fig. 2) is not an artefact of the nominal parameter values; it is robust against plausible experimental uncertainties. The practical implication is that at typical flotation concentrations ($C_{\text{bulk}} = 0.1 \text{ mol m}^{-3}$), the formation of a jammed shell is essentially guaranteed for both collectors.

3.4. Critical collector dosage

A practical question for flotation operators is: “What is the minimum bulk concentration of collector required to guarantee a jammed shell during a compression cycle?” To answer this, we performed a critical-dosage sweep on a 20×20 grid of K and k_d . For each (K, k_d) pair, we used bisection to determine the smallest C_{bulk} – denoted C_{crit} – for which the bubble jams during the standard 10 s pressure cycle.

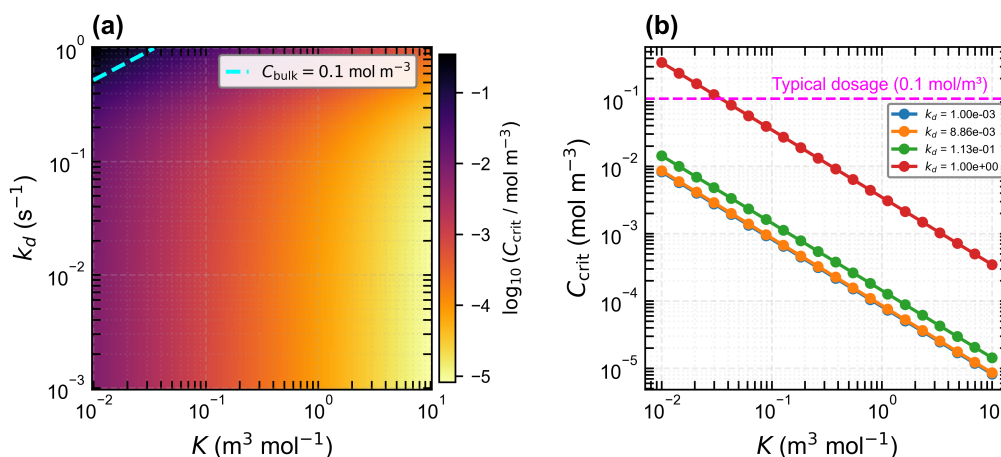


FIG. 5. (a) Critical bulk concentration C_{crit} required for jamming. Colour map: $\log_{10}(C_{\text{crit}}/\text{mol m}^{-3})$; cyan dashed contour marks the typical flotation dosage of 0.1 mol m^{-3} . The colour scale saturates at both ends of the true C_{crit} range. (b) Cross-sections at four representative desorption rates k_d . Magenta dashed line: typical dosage. All curves show that stronger adsorption (larger K) reduces the critical dosage

Figure 5a maps $\log_{10}(C_{\text{crit}})$ over the (K, k_d) plane. A cyan dashed contour marks the typical industrial flotation concentration of 0.1 mol m^{-3} . Points with C_{crit} below this contour require less collector than the standard dosage to

achieve jamming; points above require higher concentrations or more active collectors. The colour scale in panel (a) saturates at both ends of the C_{crit} range: the true values extend from approximately $8 \cdot 10^{-6} \text{ mol m}^{-3}$ (below the colour-bar floor) to about 0.35 mol m^{-3} (above the colour-bar ceiling). The underlying physical trend – that higher affinity and slower desorption reduce the critical dosage – is more clearly seen in the cross-sections shown in panel (b).

Figure 5b plots C_{crit} as a function of K for four representative desorption rates. All curves decrease monotonically with K , confirming that strong adsorption (large K) lowers the dosage threshold. At low K ($10^{-2} \text{ m}^3 \text{ mol}^{-1}$), the fastest-desorbing collector ($k_d = 1.0 \text{ s}^{-1}$, red curve) requires the highest dosage ($\sim 0.2\text{--}0.3 \text{ mol m}^{-3}$), while the three slower-desorbing collectors cluster near $10^{-2} \text{ mol m}^{-3}$. At high K ($10^1 \text{ m}^3 \text{ mol}^{-1}$), all four curves converge to approximately $10^{-5} \text{ mol m}^{-3}$ – roughly four orders of magnitude below the typical flotation concentration. The magenta dashed line at 0.1 mol m^{-3} provides a direct visual reference: for $K \gtrsim 0.3 \text{ m}^3 \text{ mol}^{-1}$, even the fastest-desorbing collector jams at or below the standard dosage.

These results translate into a straightforward design guideline for flotation: choose a collector with the largest possible K (strongest adsorption) and the smallest possible k_d (slowest desorption) to minimise the concentration required for jamming. For the commercial xanthates studied here, the literature values ($K_{\text{BX}} = 0.337 \text{ m}^3 \text{ mol}^{-1}$, $K_{\text{IBX}} = 0.395 \text{ m}^3 \text{ mol}^{-1}$) both lie comfortably in the region where the critical dosage is well below 0.1 mol m^{-3} , consistent with the Monte-Carlo finding that jamming is essentially guaranteed at that concentration.

3.5. Sensitivity to process parameters

To assess how robust the jamming boundary is to changes in operating conditions, we recomputed the boundary while individually varying the bulk concentration C_{bulk} , the maximum pressure P_{max} , the cycle time T_{cycle} , and the shell modulus E_s . The results are shown in Fig. 6.

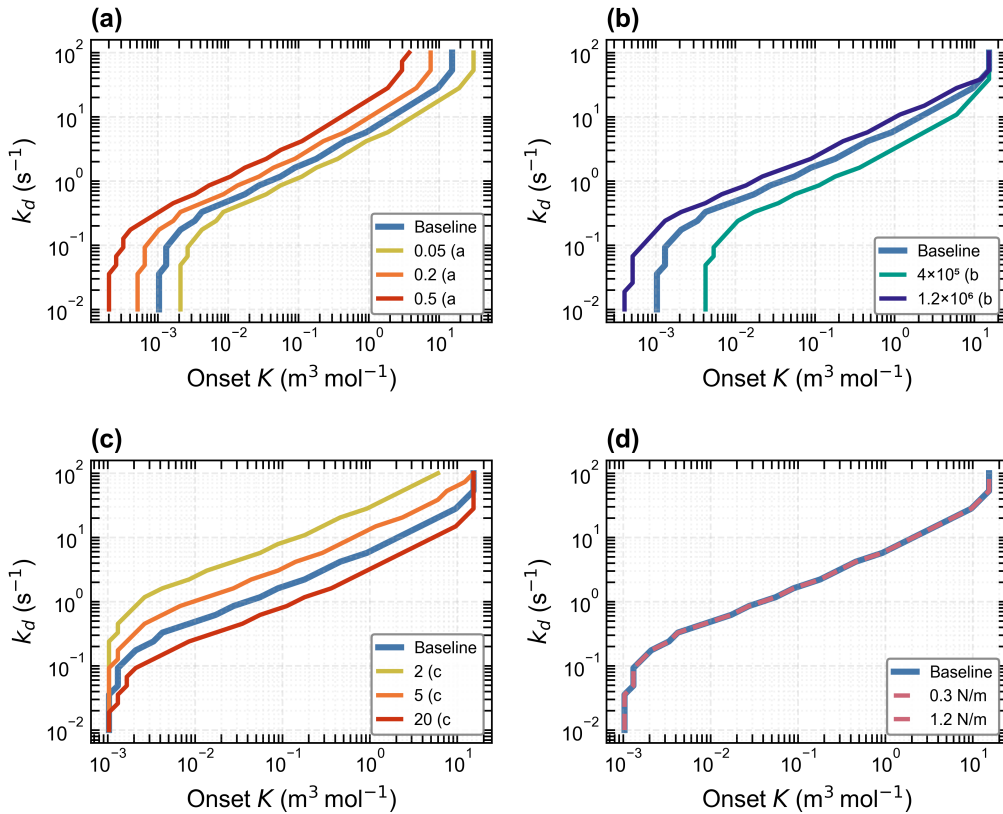


FIG. 6. Sensitivity of the jamming boundary to variations in (a) bulk concentration C_{bulk} , (b) maximum pressure P_{max} , (c) cycle time T_{cycle} , and (d) shell modulus E_s . In all panels, the blue solid line is the baseline boundary. Legend entries: (a) $C_{\text{bulk}} = 0.05, 0.2, 0.5 \text{ mol m}^{-3}$; (b) $P_{\text{max}} = 4 \cdot 10^5 \text{ Pa}, 1.2 \cdot 10^6 \text{ Pa}$; (c) $T_{\text{cycle}} = 2, 5, 20 \text{ s}$; (d) $E_s = 0.3, 1.2 \text{ N m}^{-1}$ (dashed). The shell modulus does not affect the onset of jamming

Increasing C_{bulk} (Fig. 6a) shifts the boundary toward lower K : at a fixed desorption rate, a higher bulk concentration provides a larger adsorptive flux, allowing the surface to reach the jamming threshold at a weaker affinity. The effect is strongest at low K and diminishes as K increases, consistent with the saturation of the Langmuir isotherm.

Decreasing $P_{\max}$ (Fig. 6b, teal curve) shifts the boundary to higher K : a weaker compression produces a smaller geometric concentration effect, requiring a stronger affinity to achieve jamming. Increasing $P_{\max}$ (purple curve) has the opposite effect, moving the boundary to lower K .

Shortening the cycle time (Fig. 6c, yellow curve) also shifts the boundary to higher K , because the adsorption has less time to raise the coverage above the jamming threshold. Lengthening the cycle (red curve) allows more adsorption and moves the boundary to lower K .

The shell modulus E_s (Fig. 6d) has essentially no effect on the jamming boundary: the curves for $E_s = 0.3 \text{ N m}^{-1}$ and $E_s = 1.2 \text{ N m}^{-1}$ lie exactly on top of the baseline. This result confirms that the jamming transition is governed by the adsorption kinetics and the geometric concentration – not by the mechanical properties of the shell. The shell modulus influences the shape of the hysteresis loop after jamming occurs, but it does not control whether jamming occurs in the first place.

These sensitivity tests demonstrate that the jamming boundary is physically well-behaved: the shifts are monotonic, consistent with the underlying kinetic equations, and can be rationalised by simple physical arguments. This strengthens the credibility of the phase diagram as a predictive tool for selecting collectors and process conditions.

3.6. Numerical convergence

To confirm that the jamming boundary is independent of the time-step resolution, we repeated the phase-diagram sweep (Sect. 2.6) with $N_{\text{steps}} = 250, 500$, and 1000 time points per cycle, keeping all other parameters at their baseline values. The resulting jamming-onset boundaries are overlaid in Fig. 7.

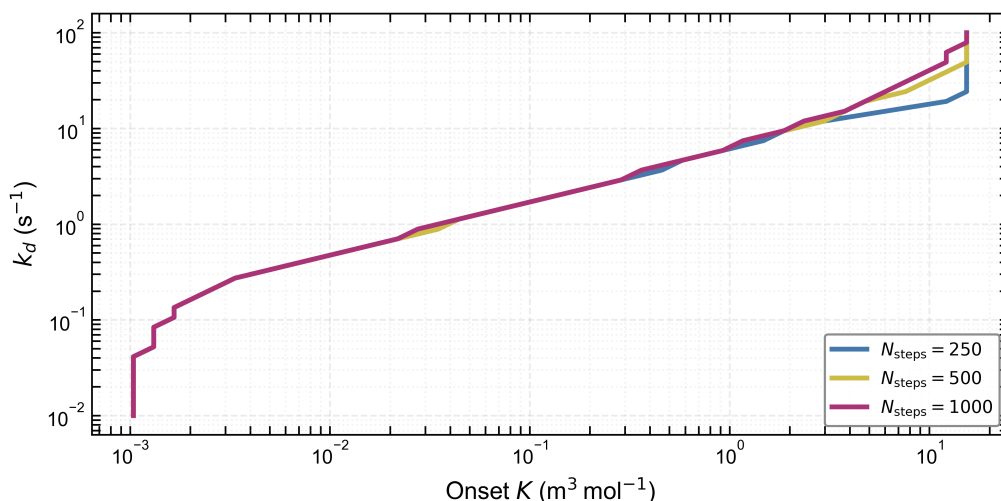


FIG. 7. Convergence of the jamming boundary with time-step refinement. Boundaries computed with $N_{\text{steps}} = 250$ (soft blue), 500 (ochre), and 1000 (magenta) are virtually indistinguishable across the entire parameter range, confirming grid-independence

The three curves are virtually indistinguishable across the entire (K, k_d) plane. A tiny divergence becomes visible only at the extreme upper-right corner of the simulated range – where $K \gtrsim 10 \text{ m}^3 \text{ mol}^{-1}$ and k_d approaches 1 s^{-1} – with the $N = 1000$ curve lying fractionally above the $N = 250$ curve. Everywhere else the lines overlap to within the pixel resolution. The maximum relative shift in onset K between $N = 500$ and $N = 1000$ is below 1 %.

This result confirms that $N_{\text{steps}} = 500$ is sufficient to resolve the jamming boundary across the entire parameter space explored in this work, and that all phase-diagram and sensitivity results reported here are numerically converged.

3.7. Dynamical sensitivity along the jamming boundary

To quantify the sensitivity of the jamming transition, we measured the one-cycle divergence of nearby trajectories along the jamming boundary (Fig. 8). For each k_d on a 30-point log-spaced grid spanning 10^{-2} to 10^2 s^{-1} , we located the onset affinity K_{onset} and ran two pressure-cycle simulations with initial coverages differing by $\Delta\theta_{\text{initial}} = 10^{-3}$. The one-cycle divergence exponent was computed as

$$\Lambda = \frac{1}{T_{\text{cycle}}} \ln \left(\frac{\Delta\theta_{\text{final}}}{\Delta\theta_{\text{initial}}} \right),$$

where $\Delta\theta_{\text{final}}$ is the absolute difference in coverage at the end of the 10 s cycle. This quantity measures the average exponential growth rate of perturbations over a single cycle; it reduces to the largest Lyapunov exponent in the limit of many cycles, but here we report it as a practical, finite-time indicator of critical sensitivity.

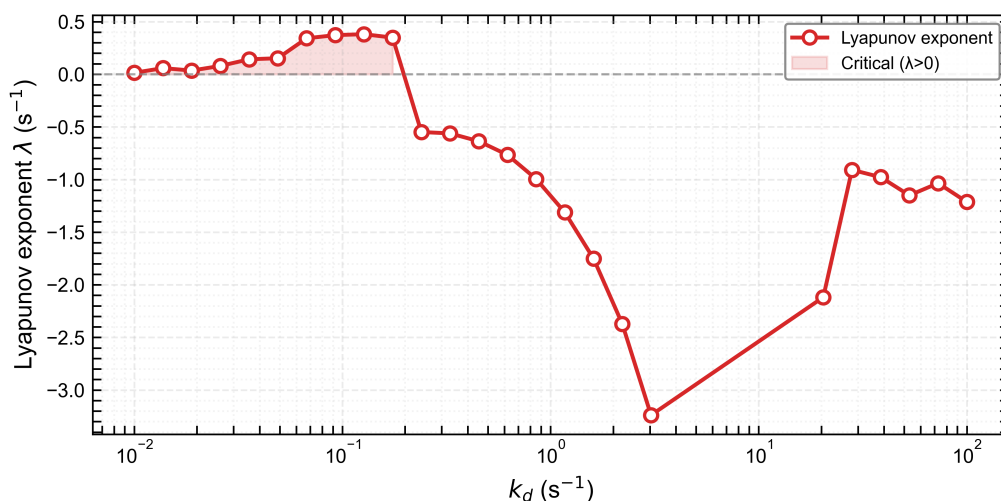


FIG. 8. One-cycle divergence analysis along the jamming boundary. Crimson line with white circles: one-cycle divergence exponent Λ . Light crimson shading: region of positive Λ (critical sensitivity). Grey dashed line: $\Lambda = 0$. The exponent peaks at $+0.42 \text{ s}^{-1}$ near $k_d \approx 0.17 \text{ s}^{-1}$, drops sharply to negative values, and displays a secondary recovery bump at high k_d

The resulting curve displays three distinct regimes. At low desorption rates ($k_d \lesssim 0.05 \text{ s}^{-1}$), Λ is near zero, rising gradually to a plateau peak of $+0.42 \text{ s}^{-1}$ at $k_d \approx 0.17 \text{ s}^{-1}$. This positive region (shaded in Fig. 8) indicates that the system is critically sensitive: a tiny change in initial coverage can determine whether the bubble jams. At $k_d \approx 0.25 \text{ s}^{-1}$, Λ drops sharply, becoming negative, and continues to decrease to a minimum of -3.25 s^{-1} at $k_d \approx 3.5 \text{ s}^{-1}$. This large negative exponent signals a strongly stable, non-jamming response.

Beyond $k_d \approx 3.5 \text{ s}^{-1}$, the curve exhibits a pronounced recovery bump: Λ rises from -3.25 to -0.95 at $k_d \approx 25 \text{ s}^{-1}$, then gradually declines to about -1.15 at the rightmost point ($k_d \approx 80 \text{ s}^{-1}$). This non-monotonic feature reflects the competition between very fast desorption kinetics and the geometric dilution term at the extreme upper end of the parameter space.

The positive peak in Λ provides a clear, testable prediction for interfacial rheology or AFM force-cycle experiments: the variance of the measured mechanical response should be maximal at the collector parameters corresponding to this peak.

4. Conclusion

A sharp jamming boundary exists in the (K, k_d) plane (BX onset $K \approx 10^{-3}$ – $20 \text{ m}^3 \text{ mol}^{-1}$; iBX boundary at systematically lower K). Commercial butyl ($K = 0.337 \text{ m}^3 \text{ mol}^{-1}$) and isobutyl xanthate ($K = 0.395 \text{ m}^3 \text{ mol}^{-1}$) lie deep inside the jammed region, with a Monte-Carlo jamming probability of 1.00 at the typical flotation dosage of 0.1 mol m^{-3} . The hysteresis energy spans 10^{-14} to 10^{-9} J , and the critical bulk concentration C_{crit} ranges from $8.2 \cdot 10^{-6}$ to $(0.35 \text{ mol m}^{-3})$. The boundary shifts predictably with the operating parameters C_{bulk} , P_{max} , and T_{cycle} , but is insensitive to the shell modulus E_s . Numerical convergence is confirmed (relative shift below 1 %), and a one-cycle divergence exponent peaks at $+0.42 \text{ s}^{-1}$ near the transition, indicating critical sensitivity. The minimal OD model provides a predictive tool for surfactant-stabilised nanobubbles across flotation, catalysis, and biomedical nanosystems; the acknowledged simplifications will be addressed in future molecular dynamics and single-bubble experiments while a multi-source parameter library for collectors will also be established in future work.

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Submitted 10 June 2026; revised 15 June 2026; accepted 16 June 2026

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Conflict of interest: the authors declare no conflict of interest.

Calculation of characteristics of subnanometer delta-doped layers in diamond in the quasi-classical approach

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PACS 03.65.Sq, 61.72.U-, 71.30.+h, 73.20.Jc, 73.21.-b, 81.05.ug, 81.15.Gh, 81.70.Jb, 85.35.-p

ABSTRACT It is shown that subnanometer boron delta-doped layers characteristics in chemically vapor deposited diamond films can be calculated in the quasi-classical approximation both in equilibrium and in an external electromagnetic field ionizing doping boron atoms. The corresponding solutions are found, in the first case – analytically, in the second – numerically. The use of the quasi-classical approximation allows one to simplify significantly the mathematical modeling of diamond structures with subnanometer delta-doped layers, necessary for their application in nanoelectronics, for example in high-speed field-effect transistors.

KEYWORDS chemically vapor deposited diamond, delta-doped layers, quasi-classical approximation

ACKNOWLEDGEMENTS The work is fulfilled in the frame of the state assignment of Federal Research Center A.V. Gaponov-Grekhov Institute of Applied Physics of the Russian Academy of Sciences, project FFUF-2024-0032.

FOR CITATION Kukushkin V.A., Kukushkin Y.V. Calculation of characteristics of subnanometer delta-doped layers in diamond in the quasi-classical approach. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 291–296.

1. Introduction

Due to its unique characteristics (high thermal conductivity and electrical strength, chemical and radiation resistance, low coefficient of thermal expansion, etc.), diamond is a promising material for the creation of electronic and optoelectronic devices with record parameters. Being an insulator in its pure state, it requires doping to ensure electrical conductivity. However, at a high degree of doping, necessary to ensure high electrical conductivity, due to scattering on ionized atoms of the doping impurity, the mobility of charge carriers and, as a consequence, the speed of electronic devices based on diamond decreases.

One of the possible solutions to this problem is well known in physics of conventional semiconductors. It reduces to the creation of so-called delta-doped layers [1]. They are thin layers (with a thickness of the order of several lattice constants) of highly doped material enclosed in a lightly (unintentionally) doped (ideally pure) surroundings. In such layers, charge carriers partially penetrate from the potential well formed by ionized impurity atoms of the delta-doped layer into the lightly doped surroundings due to the quantum-mechanical effect. As a result, when moving in the plane of the layer in an external electric field, their scattering on these atoms decreases, and the mobility, therefore, increases compared to the value that it would have in a uniformly doped material with the same concentration of doping impurity as in the delta-doped layer. By forming a sequence of such layers, it is possible to obtain a structure with sufficiently high conductivity and mobility simultaneously.

Calculation of the characteristics of delta-doped layers usually requires a joint solution of the Schrödinger equation for the quantized energy levels and corresponding wave functions of charge carriers in the potential well of such a layer and the Poisson equation for the distribution of the electrostatic potential. Therefore, it is a complex mathematical problem that can only be solved by numerical methods.

In diamond, delta-doped (as a rule, by boron) layers were obtained in chemically vapor deposited films by many researchers [2–11]. It was used in diamond electronics devices, for example in field-effect transistors. Therefore, the problem of calculating their characteristics in dependence on the control parameters, i.e. the layer thickness, the concentration of the doping impurity in its center and in the surrounding material, temperature, etc., is relevant for practice.

In this paper, it is shown that for diamond, this calculation can be performed in the quasi-classical approximation. This significantly simplifies the corresponding numerical procedure allowing one to avoid the calculation of the quantized energy levels and corresponding wave functions of charge carriers in the potential well of such a layer. Moreover, for the thinnest (i.e. of a monolayer thickness) delta-doped layer, this approximation allows one to obtain analytical (in the case

of equilibrium situation) results. The interest to this extremely thin layer is related to its promise of the hole mobility increase (needed for diamond high-speed field-effect transistors), because even in 1 nm thick layers, such an increase was not obtained [10].

In the next section, this calculation is performed for equilibrium monolayer-thick delta-doped layers at room temperature. In Section 3 – for such layers in an external electromagnetic field ionizing the doping impurity. The Discussion and conclusion section analyzes and summarizes the main results of the work.

2. Equilibrium delta-doped layers

Let us consider an ideal case when the delta-doped layer consists of only one heavily boron-doped monolayer (with a thickness of order 0.1 nm) located in a lightly (unintentionally) boron-doped diamond. Since the minimum thickness of a delta-doped layer achieved to date is of the order of 1 nm [2–11] and the maximal doping profile abruptness is 1 decade/nm [12, 13], modern technologies are close to creating such a structure. Let the two-dimensional concentration of boron atoms in such a delta-doped layer be $N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$. In the lightly (unintentionally) doped diamond surrounding the delta-doped layer, let the concentration of boron atoms be equal to $N_{bv} = 10^{15} \text{ cm}^{-3}$, which is determined by the residual boron content in the growth reactor.

Let all the energies be counted from the level of the chemical potential μ so that in what follows the latter is equal to zero. Let us denote the energy of the upper edge of the valence band as $E_v = E_{v0} - e\phi$, where E_{v0} is the energy of the upper edge of the valence band away from the delta-doped layer, e is the elementary charge ($e > 0$), ϕ is the electrostatic potential. The latter satisfies the two-dimensional Poisson equation

$$\frac{d^2\phi}{dx^2} = -\frac{4\pi e}{\varepsilon} \left[N_h - \frac{N_{bv} \exp\left(-\frac{E_{v0}-e\phi}{k_B T}\right)}{4 \exp\left(\frac{E_0}{k_B T}\right) + 2 \exp\left(\frac{E_0-E_{so}}{k_B T}\right)} \right], \quad (1)$$

where x is the Cartesian coordinate in the direction, orthogonal to the delta-doped layer plane $x = 0$, $N_h = N_v \exp\left(\frac{E_{v0}-e\phi}{k_B T}\right)$, $N_v = 0.25 [2k_B T / (\pi \hbar^2)]^{3/2} \{m_{hh}^{3/2} + m_{lh}^{3/2} + m_{so}^{3/2} \exp[-E_{so}/(k_B T)]\}$ [14], k_B is the Boltzmann constant, T is the temperature, which will henceforth be set equal to room temperature ($T = 300 \text{ K}$), $\hbar$ is the Plank constant, $m_{hh} = 0.427m$, $m_{lh} = 0.366m$, $m_{so} = 0.394m$ are the characteristic effective masses of heavy, light and spin split-off holes, respectively [15], m is the free electron mass, $E_{so} = 6 \text{ meV}$ is the energy of spin-orbital splitting [16], $E_0 = 370 \text{ meV}$ is the activation energy of a single boron atom [16], $\varepsilon \approx 5.7$ is the static permittivity of diamond [16]. The first term in the square brackets in (1) is the three-dimensional concentration of non-degenerate hole gas under the condition $-(E_{v0} - e\phi)/(k_B T) > 1$ (the validity of which is confirmed by the final result, see below), the second term is the three-dimensional concentration of negatively charged boron atoms in the lightly (unintentionally) doped diamond surrounding the delta-doped layer under the condition $(E_{v0} - e\phi + E_0 - E_{so})/(k_B T) > 1$ (the validity of which is also confirmed by the final result, see below) [17, 18].

The solution of equation (1) must be symmetrical with respect to the plane $x = 0$ and tend to zero away from the delta-doped layer. In this case, the energy of the upper edge of the valence band away from the delta-doped layer E_{v0} is found from the condition of electrical neutrality, i.e. from the condition of equality to zero of the square bracket in (1) when $\phi = 0$. This gives one that $E_{v0} = -\frac{k_B T}{2} \ln \left\{ \frac{N_v}{N_{bv}} \left[4 \exp\left(\frac{E_0}{k_B T}\right) + 2 \exp\left(\frac{E_0 - E_{so}}{k_B T}\right) \right] \right\}$. A solution of (1) with the indicated properties can be found analytically and is given by the following formula

$$\phi = \frac{4k_B T}{e} \text{Arcth} \left\{ \text{th} \left[\frac{e\phi(0)}{4k_B T} \right] \exp \left(-\frac{\sqrt{2}|x|}{r_D} \right) \right\}, \quad (2)$$

where $\phi(0)$ is the value of the electrostatic potential at $x = 0$, $r_D = \frac{\sqrt{\varepsilon k_B T}}{2e \sqrt{\pi N_v \exp[E_{v0}/(k_B T)]}}$ is the Debye radius in a non-degenerate hole gas with concentration $N_v \exp[E_{v0}/(k_B T)]$.

The value of $\phi(0)$ is related to the two-dimensional concentration N_{b-} of negatively charged boron atoms in the delta-doped layer by means of the boundary condition on the jump of electric field at plane $x = 0$: $-\phi'(+0) + \phi'(-0) = -4\pi e N_{b-}/\varepsilon$. Using (2), this leads to the equation

$$\frac{8\sqrt{2} k_B T}{e r_D} \frac{\text{th}[e\phi(0)/(4k_B T)]}{1 - \text{th}^2[e\phi(0)/(4k_B T)]} = -4\pi e N_{b-}/\varepsilon. \quad (3)$$

On the other hand, the magnitude of N_{b-} can be found using the standard formula [17, 18]

$$N_{b-} = \frac{N_b}{1 + 4 \exp\left[\frac{E_0 + E_v(0)}{k_B T}\right] + 2 \exp\left[\frac{E_0 - E_{so} + E_v(0)}{k_B T}\right]}, \quad (4)$$

where $E_v(0) = E_{v0} - e\phi(0)$. Then, equation (3) becomes an equation for $\phi(0)$, from which the latter can be found numerically.

Figure 1a shows the spatial dependence of $E_v = E_{v0} - e\phi$ found in this way for $N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$. Fig. 1b shows the spatial dependence of the three-dimensional concentration of non-degenerate hole gas N_h for the same parameters.

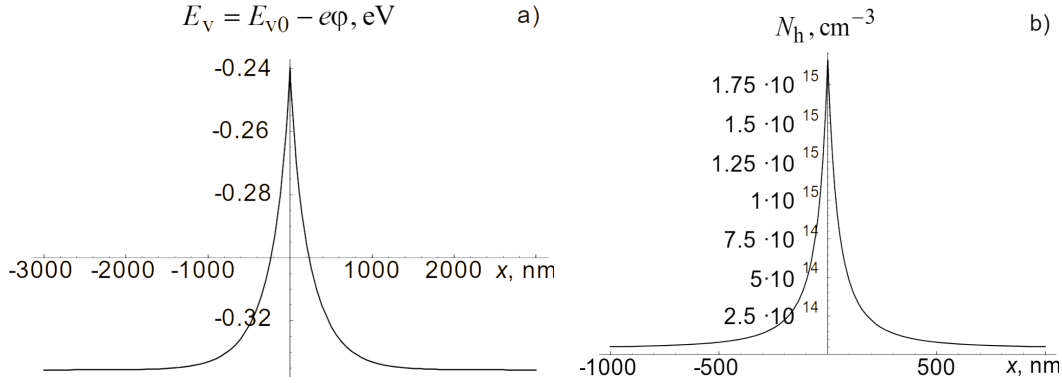


FIG. 1. (a) Energy top edge of the valence zone $E_v = E_{v0} - e\phi$ counted from chemical potential level as a function of Cartesian coordinate x along direction, orthogonal to the delta-doped layer plane $x = 0$ for $N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$. (b) The spatial dependence of the three-dimensional concentration of non-degenerate hole gas N_h for the same parameters

Let us now check the fulfillment of the above assumptions. Firstly, the condition $-(E_{v0} - e\phi)/(k_B T) > 1$ is most difficult to fulfill when $x = 0$, where the value $-(E_{v0} - e\phi)$ is minimal (see Fig. 1a), so it is necessary to demand $-(E_{v0} - e\phi(0))/(k_B T) > 1$. For $N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$, we have $-(E_{v0} - e\phi(0))/(k_B T) \approx 8.9 > 1$. Thus, the condition $-(E_{v0} - e\phi)/(k_B T) > 1$ is satisfied for all x .

Secondly, the condition $(E_{v0} - e\phi + E_0 - E_{s0})/(k_B T) > 1$ is most difficult to fulfill when $|x| \rightarrow \infty$, where the value $E_{v0} - e\phi + E_0 - E_{s0}$ is minimal and equals $E_{v0} + E_0 - E_{s0}$ regardless of the value of N_b . It is easy to check that $(E_{v0} + E_0 - E_{s0})/(k_B T) \approx 5.2 > 1$. Thus, the condition $(E_{v0} - e\phi + E_0 - E_{s0})/(k_B T) > 1$ is satisfied for all x .

Thirdly, we will check the fulfillment of the condition of applicability of the quasi-classical approximation. It is known [19] that this condition means that the thermal de Broglie wavelength of a hole $\lambda \approx \frac{2\pi\hbar}{\sqrt{2m(E + E_v)}}$, where $E + E_v \approx k_B T$ (the hole energy E is measured from the chemical potential level in the direction opposite to the direction of counting the electron energy, so that the hole potential energy is $-E_v$) for any x satisfies the inequality

$$\frac{1}{2\pi} \left| \frac{d\lambda}{dx} \right| \equiv \left| \frac{d\lambda}{dx} \right| \approx \frac{\hbar m e}{(2m k_B T)^{3/2}} \left| \frac{d\phi}{dx} \right| < 1.$$

It is clear from Fig. 1 that $|d\phi/dx|$ is maximal for $x = 0$, therefore if this condition is satisfied for $x = 0$, then it is also satisfied for all other x . To calculate the derivative $|d\phi/dx|$ for $x = 0$, we can use the above boundary condition in the plane of the delta-doped layer, as a result of which the quasi-classical condition is rewritten as $\frac{2\pi\hbar m e^2 N_{b-}}{(2m k_B T)^{3/2} \epsilon} < 1$. For

$N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$, a calculation gives one $\frac{2\pi\hbar m e^2 N_{b-}}{(2m k_B T)^{3/2} \epsilon} \approx 0.02 < 1$, and the quasi-classical condition is indeed satisfied with a large margin. According to [19], the relative error of the above-obtained quasi-classical results is of the same order, i.e. less than 2 %.

The reason for this is that at $N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$, the two-dimensional concentration of negatively charged boron atoms in a delta-doped layer is as follows: $N_{b-} \approx 3.5 \cdot 10^{10} \text{ cm}^{-2}$, i.e. it is small (about 0.1 % of N_b). Accordingly, the three-dimensional concentration of free holes is also small, and therefore the electrostatic potential is a smooth function of x (Fig. 1a).

3. Delta-doped layers in an external electromagnetic field ionizing boron atoms

According to the previous section, in equilibrium even for a large two-dimensional boron atom concentration $N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$, only a small part of them is ionized. In consequence, the concentration of free holes around the doped delta-layer is also small, which leads to a small conductivity of the system. Therefore, let us consider a non-equilibrium situation when boron atoms in the delta-doped layer are fully ionized by an external electromagnetic field whereas the free hole distributions in energy and space are similar to equilibrium ones with ambient temperature. The practical implementation of such a situation is considered at the end of this section.

In this situation, all the boron atoms in the delta-doped layer are negatively charged, i.e. $N_{b-} = N_b$. Poisson's equation has the same form (1), as in the previous section, but with N_h given now by the formula (taking into account that at the considered large concentrations of free holes they will mainly be degenerate)

$$N_h = \int_{-\infty}^{+\infty} (f_{hh} + f_{lh} + f_{so}) d^3p,$$

$$f_{hh} = \frac{2}{(2\pi\hbar)^3} \frac{1}{1 + \exp \{[-E_{v0} + e\phi + p^2/(2m_{hh})]/(k_B T)\}},$$

$$f_{lh} = \frac{2}{(2\pi\hbar)^3} \frac{1}{1 + \exp \{[-E_{v0} + e\phi + p^2/(2m_{lh})]/(k_B T)\}},$$

$$f_{so} = \frac{2}{(2\pi\hbar)^3} \frac{1}{1 + \exp \{[-E_{v0} + E_{so} + e\phi + p^2/(2m_{so})]/(k_B T)\}}$$

are the quasi-classical functions of the Fermi–Dirac distributions of heavy, light and spin-orbit split off holes, respectively, the validity of the condition $(E_{v0} - e\phi + E_0 - E_{so})/(k_B T) > 1$, which allows one to write the three-dimensional concentration of negatively charged boron atoms in the lightly (unintentionally) doped diamond surrounding the delta-doped layer as in (1) [17, 18], is proved in exactly the same way as in the case of the equilibrium delta-doped layer, see the previous section.

The solution of Poisson's equation, as in the case of the equilibrium delta-doped layer above, must be symmetrical relative to the plane $x = 0$, tend to zero away from the delta-doped layer and at $x = 0$ satisfy the boundary condition $-\phi'(+0) + \phi'(-0) = -4\pi e N_b / \varepsilon$. The energy of the upper edge of the valence band away from the delta-doped layer E_{v0} is found from the condition of electrical neutrality, i.e. from the condition of equality to zero of the square bracket in (1) at $\phi = 0$. In this case, quasi-classical functions of the Fermi–Dirac hole distribution are transformed into the Maxwell functions. The result of this is that N_h takes the same form as in the case of the equilibrium delta-doped layer, i.e. $N_h = N_v \exp \left(\frac{E_{v0}}{k_B T} \right)$. Therefore, E_{v0} has the same value as in the previous section. However, due to the complex dependence of N_h on ϕ near the delta-doped layer, it is not possible to find the solution of (1) analytically.

Figure 2a shows a numerical solution of (1) for $N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$, and Fig. 2b – the spatial dependence of N_h for the same parameters.

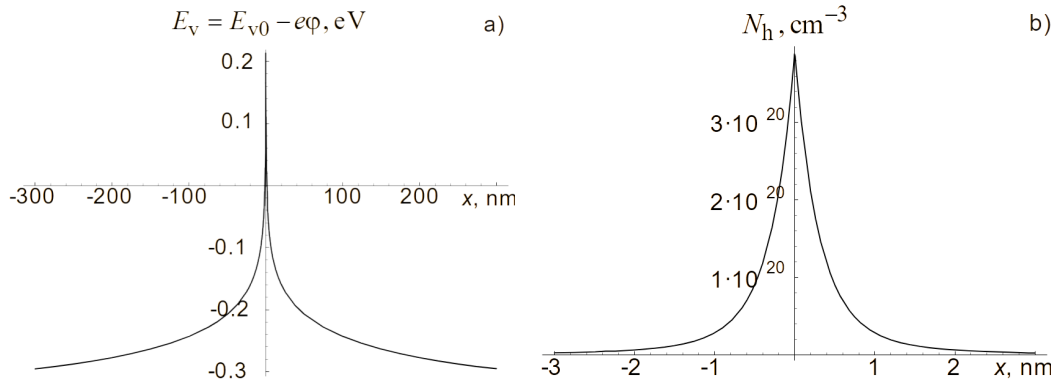


FIG. 2. (a) Energy top edge of the valence band $E_v = E_{v0} - e\phi$ counted from the level of chemical potential as a function of the Cartesian coordinate x along direction, orthogonal to the delta-doped layer plane $x = 0$ for $N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$. (b) The spatial dependence of the three-dimensional concentration of the hole gas N_h for the same parameters

At the point $x = 0$, one has $[E_{v0} - e\phi(0)]/(k_B T) \approx 8.3 \gg 1$, i.e. near the delta-doped layer, the hole gas is degenerate. At the same time, far from this layer, one has $\phi = 0$, and E_{v0} , as was said above, has the same value as in the case of the equilibrium delta-doped layer above, so that the hole gas there is non-degenerate. The transition from degenerate to non-degenerate hole gas with increasing distance from the delta-doped layer causes the complex form of the dependence of N_h on ϕ , which does not allow finding an analytical solution to (1).

Let us now check the fulfillment of the condition of applicability of the quasi-classical approximation. Now, in the formula for the characteristic de Broglie wavelength of a hole $\lambda \approx \frac{2\pi\hbar}{\sqrt{2m(E + E_v)}}$, the characteristic hole energy E is a value of the order of chemical potential, i.e. 0 (due to the above choice of the starting point for counting energies) at $E_v > k_B T$, where the hole gas is degenerate, and of order $-E_v + k_B T$ at $E_v < k_B T$, where the hole gas is non-degenerate. Using the results of the numerical solution to (1), it is easy to show that for $N_b = 3 \cdot 10^{13} \text{ cm}^{-2}$, we have

$\frac{1}{2\pi} \left| \frac{d\lambda}{dx} \right| \equiv \left| \frac{d\lambda}{dx} \right| < 0.6 < 1$ in the region near the delta-doped layer, where the bulk of the holes created by this layer resides. Thus, the condition of the validity of the quasi-classical approximation in order of magnitude is satisfied (although without a reserve). Therefore, according to [19], the relative error of the above-obtained quasi-classical results for the delta-doped layer in an ionizing external electromagnetic field is less than 60 %. So, these results can be used as estimates of the characteristics of such a layer only.

The reason for this is that although in this case the potential energy of a hole is a sharp function of the coordinate near the delta-doped layer (see Fig. 2a), but in this region, due to their high concentration, the kinetic energy of degenerate holes is also high, and therefore their characteristic de Broglie wavelength is small.

Now, let us consider the practical realization of the situation when boron atoms in the delta-doped layer are fully ionized by an external electromagnetic field. First, the photon energy $\hbar\omega$ of this field should be larger than the difference between the chemical potential $\mu = 0$ and the initial energy of a hole, localized on a boron atom, $-E_{v0} + e\phi(0) - E_0 = -584$ meV (see Fig. 2a), to ensure that the final free hole state is at least half-empty. It means that its wavelength should be shorter than $2.1 \mu\text{m}$. Second, the ionization rate of a neutral boron atom should be larger than the recombination rate of free holes with a negatively charged boron ion. The former is estimated as the product of the photon flow $\frac{I}{\hbar\omega}$ (I is the electromagnetic field intensity) by the ionization cross-section, which is, according to [20], is of order 10^{-16} cm^2 . To estimate the latter, let us take a value $1.77 \cdot 10^{-13} \text{ cm}^2$ for the recombination cross-section [21] and multiply it by the free hole Fermi velocity $\sim \sqrt{\frac{E_{v0} - e\phi(0)}{m}} \approx 2 \cdot 10^7 \text{ cm/s}$ and concentration $N_h(0) \approx 3.9 \cdot 10^{20} \text{ cm}^{-3}$ near the delta-doped layer (see Fig. 2) to obtain $1.4 \cdot 10^{15} \text{ s}^{-1}$. For $\hbar\omega = 584$ meV, the equality of these two rates means that I should be larger than $1.3 \cdot 10^{12} \text{ W/cm}^2$. For a focal spot with a diameter of several microns, such intensity can be supplied by a fiber laser. To avoid the diamond damage, the laser should work in a pulsed mode.

Certainly, electromagnetic field with such a large intensity will cause the hole heating. To estimate its rate, let us take a value smaller than 3 fs for the relaxation time of the hole quasimomentum and energy as it follows from the results of [22] for the hole energies more than by 2 times exceeding 165 meV – the energy of diamond optical phonon [16]. A simple estimate by Drude's formula for the hole conductivity [14] gives one that for such energies, a hole energy increase rate is smaller than 90 erg/s. On the other hand, for such energies, a hole energy decrease rate due to optical phonon emission is larger than $165 \text{ meV}/3 \text{ fs} = 90 \text{ erg/s}$, i.e. just the same as the increase rate. So, the hole kinetic energy cannot exceed 2 optical photon energies. As this value is of order $E_{v0} - e\phi(0) = 214$ meV (the maximal kinetic energy of degenerate holes according to the results of the above calculations, see Fig. 2a), then the hole gas will be in a state with energy and space distributions qualitatively similar to those found in this section.

4. Discussion and conclusion

The paper shows that the characteristics of delta-doped layers in lightly (unintentionally) doped diamond can be calculated in the quasi-classical approximation for both equilibrium and non-equilibrium situations. In the first case, the electrostatic potential is a smooth function of the coordinates, which ensures the applicability of the quasi-classical approximation. In the second case, the electrostatic potential is a sharp function of the coordinates, but, due to their degeneracy, the characteristic kinetic energy of holes is also large, which leads to the smallness of their de Broglie wavelengths and, as a consequence, the validity of the quasi-classical approximation. In ordinary semiconductors, such a situation does not occur, since the activation energies of impurities in them are significantly smaller than in diamond.

This result allows one to significantly simplify the calculation of the characteristics of the delta-doped layer in a lightly (unintentionally) doped diamond allowing to avoid the Schrödinger equation solution and finding the quantized energy levels and the corresponding wave functions of holes in a potential well formed by this layer. As a result, analytical formulas were found for the distribution of the electrostatic potential and the three-dimensional concentration of holes in the vicinity of such a layer in a lightly (unintentionally) doped diamond in the equilibrium case. Also, using a simple scheme, a numerical solution was constructed in the non-equilibrium when doping boron atoms in this layer are ionized by an external electromagnetic field.

Because the above quasi-classical solutions are found for a extremely thin (of thickness of 1 monolayer) delta-doped layer which is not created yet, they (e.g. the hole concentration distribution, please see Fig. 1b and Fig. 2b) cannot be compared with existing experimental data (e.g. capacitance-voltage measurements of hole concentration profile [9]). But as the modern technology approaches to the creation of such layers, this comparison is hoped to become possible soon.

The obtained results can be used to calculate the characteristics of diamond nanoelectronic devices with subnanometer delta-doped layers.

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Submitted 14 November 2026; revised 17 April 2026; accepted 19 April 2026

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Conflict of interest: the authors declare no conflict of interest.

Conditions for the occurrence of Josephson-type current-voltage characteristics in carbon materials at room temperature and normal pressure

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PACS 74.10.+v, 74.20.Mn, 81.05.ue

ABSTRACT It is shown in the paper that the interaction of highly oriented graphite flakes and graphene films with alkanes is a necessary but insufficient condition for observing the Josephson current-voltage characteristics in them, which is known to be inherent in all superconducting materials. Another key factor is the creation of a deformation field in the graphene material.

KEYWORDS highly oriented pyrolytic graphite, graphene, alkanes, mechanical stresses, superconductivity

ACKNOWLEDGEMENTS We are grateful to Dr. M. S. Dunaevskiy for assistance in studying the surface of HOPG samples.

FOR CITATION Ionov A.N., Bugrov A.N. Conditions for the occurrence of Josephson-type current-voltage characteristics in carbon materials at room temperature and normal pressure. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 297–303.

1. Introduction

The development of materials with room temperature (RT) superconductivity under normal external pressure is a priority area of solid-state physics. RT superconductors have prospect for practical applications in such fields as power engineering, spintronics, medical diagnostics, transportation, etc. [1]. In this regard, the results of Y. Kawashima, published in [2], are of great interest. He observed a reproducible effect of RT superconductivity in flakes of highly oriented pyrolytic graphite (HOPG), exposed to *n*-octane. In the experiment, graphite flakes with an average thickness of ~ 0.01 mm and an average diameter of ~ 1 mm were gently pressed into a Teflon tube with an internal diameter of 1.6 mm and placed in *n*-octane for one day. To obtain proof that graphite flakes treated in this way conduct current without resistance, the Teflon tube was rolled into a continuous ring. After that, a current was created in the ring using electromagnetic induction, which was recorded by a magnetic field sensor for 50 days without noticeable attenuation at room temperature. This fact indicates the absence of electrical resistance in carbon flakes wetted with *n*-octane. RT superconductivity was observed in HOPG flakes only after prolonged soaking in *n*-octane and disappeared when the alkane was removed from them. For this reason, it was proposed to keep the HOPG flakes together with the alkanes in a closed container or using an external pump, maintain the required density of alkane vapors at the location of the carbon material. Y. Kawashima suggested that when alkanes come into contact with graphite flakes, as well as with graphene [3], protons freely moving along the surface of carbon layers without activation energy are generated, which leads to the appearance of the superconductivity effect [4]. Unfortunately, the RT superconductivity effect presented in [2, 4] was not noticed by the scientific community, i.e., it was neither confirmed nor refuted, which significantly slowed down further development of this scientific direction.

In this study, we observed a Josephson-type current-voltage characteristic (CVCs) in carbon materials under normal external pressure and room temperature after their interaction with alkanes, but with the significant addition that a fluctuating strain field must be present within carbon materials. As is known, the Josephson CVCs are one of the main indication of materials with superconducting properties. The Josephson CVCs can be easily distinguished from the ohmic ones which were observed in carbon materials before contact with alkanes.

2. Experimental

The objects of the study were HOPG flakes and graphene films. HOPG (ZYH_DS types) from “TipsNano” (Estonia) was mechanically exfoliated and then ground under ultrasound treatment to linear dimensions close to those used in [2]. Graphene films from “Rusgraphene” (Russia) with a thickness of less than 1 nm and a grain size of over 20 μm were applied to substrates made of copper foil with a thickness of 25 μm and a purity of 99.8 % from “Thermo Scientific” (India), as well as to quartz and silicon with very smooth surfaces.

Graphene films were obtained by chemical vapor deposition (CVD) from a mixture of methane, hydrogen and argon gases on the surface of copper foil. At high temperatures (800 – 1000 °C), methane decomposed into carbon and hydrogen atoms, with copper acting as a catalyst and carbon deposited on the metal surface. Carbon atoms did not diffuse into the copper volume, since the solubility of carbon in copper is very low. It is also important to note that the formation of a second layer of graphene on copper did not occur, since the catalytic activity of copper decreases sharply as it is covered with graphene [5]. Then, some of the graphene films were transferred from copper substrates to smooth silicon with a surface roughness of 0.2 – 0.37 nm and surface frame size of $2 \times 2 \mu\text{m}^2$ and quartz glass surfaces, where the root-mean-square roughness was in the range of 0.6 – 1.3 nm. Due to its high adhesion, graphene readily conforms to the surface of silicon and quartz substrates. It should be noted that several graphene samples after the CVD process remained on the copper after cooling and were not transferred to a new copper substrate, as was the case with quartz and silicon ones. Thus, three types of samples with graphene films were prepared on different substrates: (I) copper, (II) silicon, and (III) quartz.

As is known, an atomic force microscope is the most commonly used tool for studying the graphene surface at the nanoscale [6]. However, our studies showed that the surface roughness height of graphene less than 30 nm does not change the CVCs after contacting graphene with alkanes. This allowed us to use a simpler tool to inspect the surface of graphene, the microinterferometer MII-9 (OJSC “LOMO”, Russia), which made it possible to monitor surface irregularities with a resolution of 28 nm. The graphene surfaces deposited on silicon and quartz glass substrates were characterized by a smooth surface with the accuracy indicated above. However, on the copper substrate, after cooling (from 800 – 1000 °C), the graphene surface had irregularities with heights much larger than 28 nm (up to 80 – 100 nm) due to the significant difference in the thermal expansion coefficients of carbon and copper, which may lead to strain field fluctuations in graphene.

HOPG flakes had linear dimensions up to 1 mm and a thickness of about 0.01 mm, measured with a Mitutoyo 2109A-10 dial indicator (Japan) in steps of 0.001 mm. Their curved surface was visually observed in an MBS-10 type stereo microscope (OJSC “LOMO”, Russia), indicating the presence of irregularities causing deformation field fluctuations in the samples (Fig. 1).

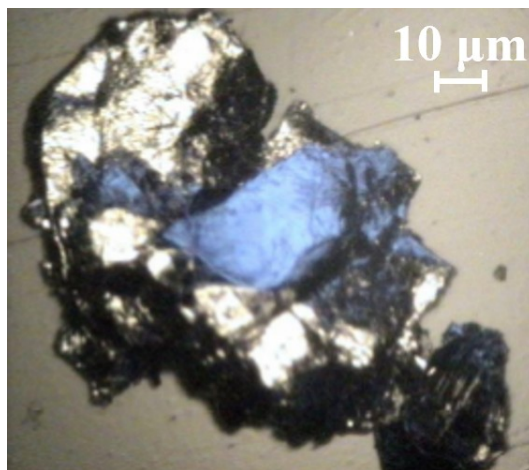


FIG. 1. The image of a single HOPG particle

Measurements of the CVCs of the above samples were carried out in two versions: (a) $I - V$ characteristics of the original sample; (b) $I - V$ characteristics after exposure to alkanes, such as *n*-heptane and *n*-octane. Direct current electrical measurements of the samples were carried out using the four-point probe method in accordance with the standard procedure for materials with metallic conductivity [6]. Current and probe contacts made of silver wires were bonded to the graphene surface using Keller silver-based conductive adhesive. The sample was shielded from extraneous signals. The voltage drop on the probes was measured manually using a digital voltmeter V2-36 (Russia) with an accuracy of $0.01 \mu\text{V}$. In this case, to increase the accuracy of the measurements, with each change in the current, the new voltage value was measured repeatedly relative to the zero current value [6]. The same voltmeter and ammeter were used in different series of experiments, the measurement accuracy of which made it possible to see the difference in the CVCs of different graphene samples before and after contact with alkanes. Our practical experience shows that the presence of noise reduces the voltmeter's sensitivity threshold to 5 nV. In this case, using significantly more accurate instruments is pointless.

3. Results and discussion

The main attention in our work was directed to studying the CVCs type of carbon samples with different surface roughness both before and after their contacts with alkanes. As mentioned above in Y. Kawashima's experiments, due to the high desorption of alkanes from the HOPG flakes, the superconductivity effect disappeared over time, depending on the ambient temperature. In this case, the Josephson CVCs should also gradually transition to ohmic conductivity. For this reason, the CVCs of graphite samples were measured after their direct immersion in alkanes and being kept in it for 24 hours.

Figure 2 shows the CVCs at room temperature and normal pressure for graphene samples on quartz substrate before and after their contacts with *n*-octane. According to the obtained dependences, the treatment of graphene with alkanes did not affect the CVCs in any way, which remained ohmic both before and after the treatment. A similar result was obtained for the Si substrate. These results do not coincide with the statement [3] that after exposure to alkanes, graphene exhibits superconducting properties, which should undoubtedly manifest itself in the appearance of a Josephson CVCs. However, obtained results do not contradict the classical Bardeen–Cooper–Schrieffer theory of superconductivity, according to which the T_c of the transition to the superconducting state should exponentially depend on the density of electron states at the Fermi level.

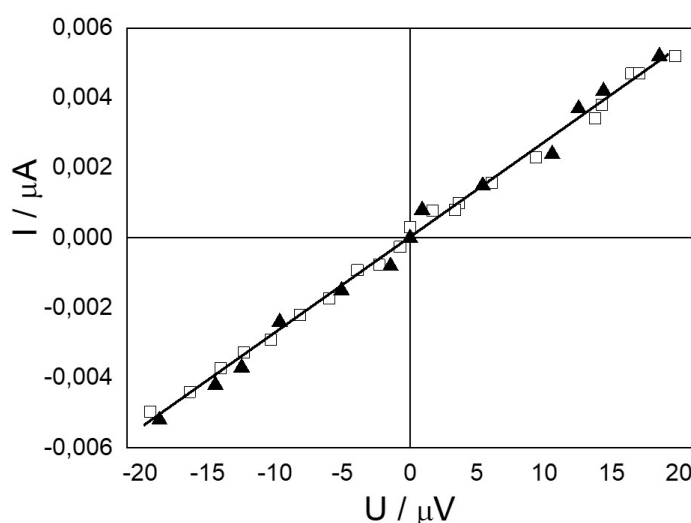


FIG. 2. The CVCs at 300 K and normal pressure for graphene on a quartz substrate without *n*-octan (open square □) and after treatment in *n*-octane (black triangles ▲)

In graphene with smooth surface the energy dependence of the density of states for the conducting and valence zones has the form of cones touching each other with their vertices. Since the valence band is completely filled and the conduction band is empty, it follows that the density of states at the Fermi level is zero. Therefore, within the framework of Y. Kawashima's model, the concentration of protons passing from the homologous series of alkanes to graphene should be negligibly small, which excludes the occurrence of a Josephson CVCs in graphene at room temperature and is consistent with the observation of ohmic ones in our experiments (Fig. 2).

However, the CVCs of HOPG flakes at room temperature, turned out to be not so simple and unambiguous. The experiment showed that the CVCs of less than 0.01 mm thick HOPG flakes which have curvature defects acquired a pronounced Josephson type after contact with *n*-heptane (Fig. 3). In the latter case, at currents below the critical one ($I < \pm I_c$), the voltage drops across the sample was not recorded at normal external pressure and room temperature. This technical zero resistance is in good agreement with the result obtained in [2], where the current was recorded for 50 days in HOPG flakes without noticeable attenuation at room temperature, indicating a superconducting effect. As can be seen from Fig. 2, at a current of 0.001 μA , the voltmeter already records a voltage drop, unlike Figure 3, where a voltage drop is not recorded at a current 100 times greater.

The Josephson CVCs transformed into the ohmic ones in the magnetic field $H = 5.3$ kOe. The effect was reversible i.e. when the magnetic field was switched off, the CVCs of Josephson type were restored again. This behavior of CVCs in a magnetic field is typical for superconducting materials and indicates the complete suppression of superconducting properties ($I_c = 0$) at a certain critical value of H_c , which in our case is ca. 6 kOe. At $H < H_c$, Josephson CVCs are again observed, but with $I < I_c$. After the removal of alkanes from the interlayer space of HOPG flakes upon heating, the Josephson CVCs were irreversibly transformed into ohmic ones. At room temperature in air, the Josephson CVCs was transformed into an ohmic-type within 24 hours. These results are also consistent with those of Y. Kawashima [2],

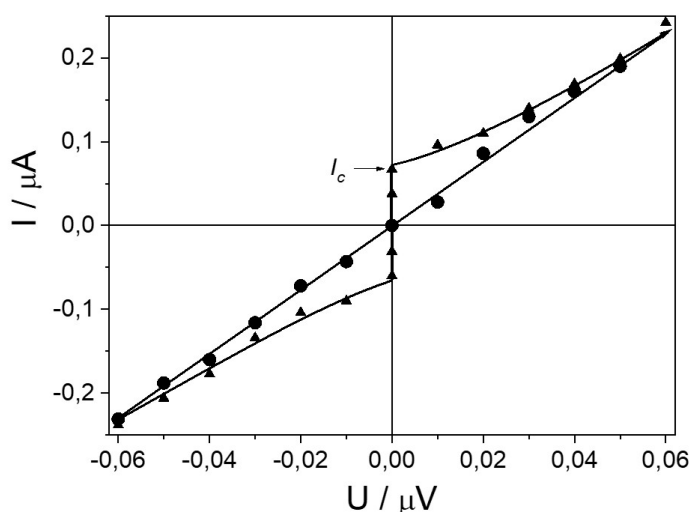


FIG. 3. The CVCs of HOPG flakes after wetting in *n*-heptane at normal pressure and 300 K without magnetic field (black triangles ▲), as well as at $H = 5.3$ kOe (black circles ●)

that superconductivity is observed in HOPG flakes only when in direct contact with *n*-octane. Otherwise, due to the high desorption of *n*-octane from the HOPG flakes, the superconductivity disappeared over a time period dependent on the ambient temperature.

If the strain field in graphene influences the shape of the CVCs, this can be observed in graphene deposited on copper substrates with high surface roughness after wetting them in *n*-octane. The CVCs of a graphene sample on a copper substrate at normal pressure and room temperature after (■) and before (▲) treatment with *n*-octane is presented in Fig. 4. In the first case (Fig. 4, black square ■), graphene does indeed demonstrate a Josephson CVCs with $I_c \approx 24 \mu\text{A}$, while at 10 nV, the conductivity of graphene with $I \approx 25 \mu\text{A}$ is significantly higher than the conductivity ($I \approx 12 \mu\text{A}$) of a copper strip 25 μm thick. Even without taking into account the Josephson CVCs, this result is of great interest for various practical applications. At currents $I < 24 \mu\text{A}$, a technical zero resistance is observed due to a sharp voltage drop across the graphene sheet on the copper substrate, which becomes significantly lower than the voltmeter sensitivity. The Josephson CVCs of graphene sheet on a copper substrate are consistent with the RT superconductivity effect observed in HOPG flakes exposed to *n*-octane [2]. At current $I > 40 \mu\text{A}$ Josephson CVCs in graphene were completely suppressed and the electrical resistance of graphene on copper substrate was shunted by the copper substrate resistance (Fig. 4, black triangles ▲). It should be noted that after heating to 100 °C and cooling to room temperature, the Josephson CVCs of graphene disappear and an ohmic CVCs due to the copper substrate in the experiment is observed (Fig. 4, black triangles ▲).

We suggest that the cause of superconductivity in HOPG flakes, graphene on copper substrate as well as in hybrid particles based on polystyrene and multilayer reduced graphene oxide, may be of the same nature [6, 7]. As mentioned above, the graphene surface on the copper substrate had irregularities significantly greater than 28 nm in height.

The formation of folds during the deposition of graphene layers on substrates leads to the appearance of pseudomagnetic fields, which increase the density of states in graphene [8–10]. In strong pseudomagnetic fields, the density of states of graphene is transformed into flat bands [11–14], which, upon contact with alkanes, are filled with current carriers. According to theoretical calculations, flat bands can radically increase the density of states in localized regions of a carbon material. This leads to the creation of a discrete spectrum of levels within such regions, analogous to Landau levels, and can also facilitate the emergence of superconductivity [9–12], which in our case manifests itself in the Josephson CVCs.

In HOPG, superconductivity can be caused by linear and rhombohedral stacking faults in graphene layers, which arise during their bending, twisting, cleavage, perforation, and other mechanical influences [15]. Fluctuating strain fields lead to the formation of flat bands in the density of graphene sheet states [13, 14]. When in contact with alkanes, HOPG flakes, consisting of mechanically deformed graphene sheets, saturate the interlayer space with charge carriers and, in the presence of flat bands, induce superconductivity.

As our experiment showed, in HOPG flakes pre-crushed to several micrometers (Fig. 5), no Josephson CVC was observed after their contact with alkanes (Fig. 6). Only the ohmic volt-ampere characteristics were observed, which can be explained by the disappearance of the fluctuation field of deformation inside individual graphite flakes as their sizes decreased.

As for bulk HOPG samples with a thickness significantly greater than 0.01 mm, the behaviour here is not unambiguous. On the one hand, in individual HOPG samples at room temperature and normal external pressure, research groups

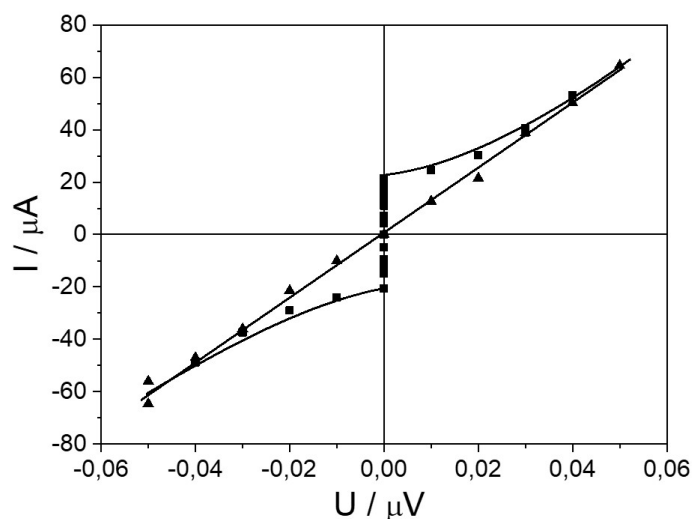


FIG. 4. The CVCs measured for a graphene sheet on a copper substrate 0.8 cm wide and 25×10^{-4} cm thick after (black square ■) and before (black triangles ▲) exposure to *n*-octane. The distance between voltage contacts was ca. 0.8 cm

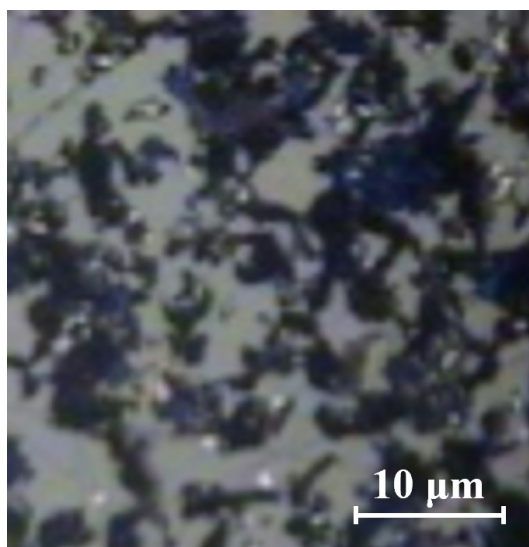


FIG. 5. The image of pre-crushed HOPG flakes

from all over the world observed effects characteristic of type II superconductors [16–21]. On the other hand, many other visually identical HOPG samples did not exhibit RT superconductivity effects. Thus, the observed RT superconductivity in bulk HOPG samples, for unclear reasons, turned out to be technologically uncontrollable, which excluded their practical applications. It should be noted here that curvature defects are impossible in bulk HOPG samples of large thickness. However, if various crystalline phases are present in bulk HOPG samples in a random, uncontrolled manner [18], lattice defects can form. According to the theoretical model proposed in [22], strong fluctuations of the strain gradient can form local drops of Bose condensed superconducting pairs in bulk HOPG samples. If the droplets are small enough, the theoretical model predicts a high critical temperature for superconductivity [22]. Bulk superconductivity can be achieved by tunnelling from one droplet to the neighbouring one. In the proposed model, superconductivity can arise randomly not through external doping with charge carriers, as in the cases discussed above, but through the internal redistribution of charge carriers within a bulk HOPG sample.

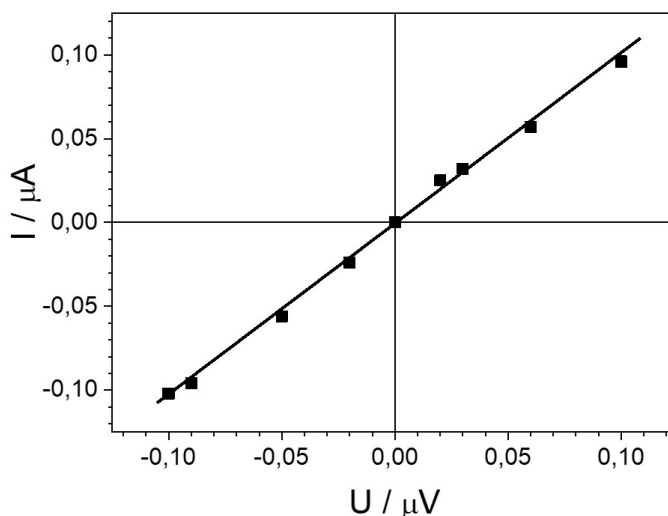


FIG. 6. The CVCs of HOPG flakes pre-crushed to several micrometers after wetting in *n*-heptane at normal pressure and 300 K

4. Conclusions

The correlations shown in this paper between carbon materials with different surface roughness and types of CVCs after their contact with alkanes, clarifies Kawashima's study. Similarly, the deformation of multilayer RGO sheets functionalized with methacrylate groups and copolymerized with styrene after contact with aromatic hydrocarbons (e.g., toluene) in a cross-linked structure, which was examined in our earlier studies, also resulted in the appearance of Josephson CVCs up to room temperature under normal pressure [6, 23, 24]. The Josephson CVCs is consistent with the observed magnetization corresponding to a type II superconductor, whose superconductivity is completely suppressed in a magnetic field ($H > 3$ kOe) [25, 26]. This sample behavior in a magnetic field is consistent with both the literature data [6] and the result of the present work, where it was shown that the Josephson CVCs are completely suppressed by a magnetic field of the same order of strength.

Research in this direction may be important for technological progress in obtaining materials with RT superconductivity and may significantly influence the development of both the theory and practical applications of superconductivity.

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Submitted 16 January 2026; revised 14 May 2026; accepted 17 May 2026

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Conflict of interest: the authors declare no conflict of interest.

Optical absorption and Raman spectroscopy of $\text{HoFe}_3(\text{BO}_3)_4$ ferroborate: experimental study with thermodynamic analysis

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PACS 78.30.-j, 78.20.-e, 63.20.-e

ABSTRACT The vibrational and optical properties of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals have been investigated by Raman spectroscopy and optical absorption measurements. The Raman spectrum, recorded at room temperature, reveals well-defined phonon modes associated with lattice vibrations and internal modes of structural units. Intense bands in the range $1200 - 1450 \text{ cm}^{-1}$ are attributed to internal vibrations of BO_3 groups, while features in the $400 - 700 \text{ cm}^{-1}$ region originate from FeO_6 octahedra. The optical absorption spectrum measured in the range $190 - 1100 \text{ nm}$ exhibits weak narrow bands in the visible and near-infrared regions, corresponding to intra-4f transitions of Ho^{3+} ions, and a pronounced absorption edge in the ultraviolet region associated with $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer transitions. The optical band gap is estimated to be $3.3 - 3.5 \text{ eV}$. A correlation between vibrational and optical properties is established, demonstrating the role of BO_3 groups and FeO_6 octahedra in determining the electronic structure and optical response of the material. The results provide a consistent experimental characterization of $\text{HoFe}_3(\text{BO}_3)_4$ and indicate its potential for optical and magneto-optical applications.

KEYWORDS $\text{HoFe}_3(\text{BO}_3)_4$, rare-earth ferroborates, Raman spectroscopy, optical absorption, optical band gap, charge-transfer transitions, 4f electronic transitions, vibrational properties

FOR CITATION Sharipov M.Z., Nizomova S.K., Fayziyev S.Sh., Dzhuraev D.R. Optical absorption and Raman spectroscopy of $\text{HoFe}_3(\text{BO}_3)_4$ ferroborate: experimental study with thermodynamic analysis. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 304–310.

1. Introduction

Rare-earth iron borates with the general formula $\text{RFe}_3(\text{BO}_3)_4$ (R = rare-earth ion) constitute a class of multifunctional materials characterized by a strong interplay between magnetic, optical, and magneto-optical properties. These effects originate from the coupling between the Fe^{3+} 3d subsystem and localized 4f electronic states of rare-earth ions, resulting in complex magnetic ordering, magnetoelectric coupling, and pronounced optical anisotropy [1, 2].

A key structural feature of ferroborates is their non-centrosymmetric trigonal crystal symmetry, which enables coupling between spin, lattice, and electronic subsystems. Depending on temperature, these compounds may undergo structural phase transitions between the space groups P3_121 and R32 , accompanied by modifications in Fe–O–Fe bond geometry and rare-earth coordination environment [3, 4]. These structural changes directly influence magnetic anisotropy, spin–lattice interaction, and the optical response.

Among this family, $\text{HoFe}_3(\text{BO}_3)_4$ is of particular interest due to the coexistence of interacting Fe^{3+} and Ho^{3+} magnetic sublattices, leading to spin-reorientation transitions, strong magnetoelastic coupling, and pronounced magneto-optical effects [2, 5–7], which are of particular interest for optical and magneto-optical applications in rare-earth-based oxide systems [8–11]. Despite extensive studies of magnetic properties, the relationship between lattice dynamics and optical response remains insufficiently clarified, particularly based on direct experimental data.

Raman spectroscopy provides a sensitive probe of lattice vibrations and local symmetry. In ferroborates, Raman-active modes are primarily associated with internal vibrations of BO_3 groups and FeO_6 octahedra, allowing verification of structural integrity and detection of possible distortions [4, 6]. Optical absorption spectroscopy complements this by probing electronic excitations, including intra-4f transitions of Ho^{3+} ions and $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer processes that determine the fundamental absorption edge [5, 9].

In addition to experimental techniques, thermodynamic stability of complex oxides can be reliably evaluated using first-principles data available in modern materials databases, such as the Materials Project and OQMD [12, 13]. These approaches enable validation of phase stability without performing independent large-scale calculations.

In this work, we present a combined experimental study of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals using Raman spectroscopy and optical absorption measurements, supported by database-driven thermodynamic analysis. The aim is to establish a consistent relationship between lattice dynamics and optical response and to confirm the phase stability of $\text{HoFe}_3(\text{BO}_3)_4$ within the Ho–Fe–B–O system.

2. Materials and experimental-computational methods

2.1. Crystal structure and sample preparation

Holmium ferroborate $\text{HoFe}_3(\text{BO}_3)_4$ belongs to the family of rare-earth iron borates $\text{RFe}_3(\text{BO}_3)_4$ and, in the high-symmetry modification considered in this work, adopts a trigonal crystal structure described by the non-centrosymmetric space group R32 (No. 155). The crystal structure is built from Fe^{3+} ions occupying octahedral FeO_6 coordination sites interconnected by planar BO_3 groups, forming a rigid three-dimensional anionic framework. Ho^{3+} ions reside in trigonal-prismatic oxygen coordination and form cationic sublattices alternating along the crystallographic c axis. Such an arrangement gives rise to pronounced magnetic anisotropy and enables strong spin–lattice and magnetoelastic coupling, which critically influence the optical and magneto-optical properties of the compound.

A schematic representation of the $\text{HoFe}_3(\text{BO}_3)_4$ crystal structure is shown in Fig. 1, illustrating the unit cell and its projection along the c axis. The lattice parameters are $a = b = 9.65 \text{ \AA}$ and $c = 7.63 \text{ \AA}$, corresponding to a unit-cell volume of $615.73 \text{ \AA}^3$ and a calculated density of $4.59 \text{ g}\cdot\text{cm}^{-3}$. These values are consistent with previously reported structural data for R32-type rare-earth ferroborates [3, 4].

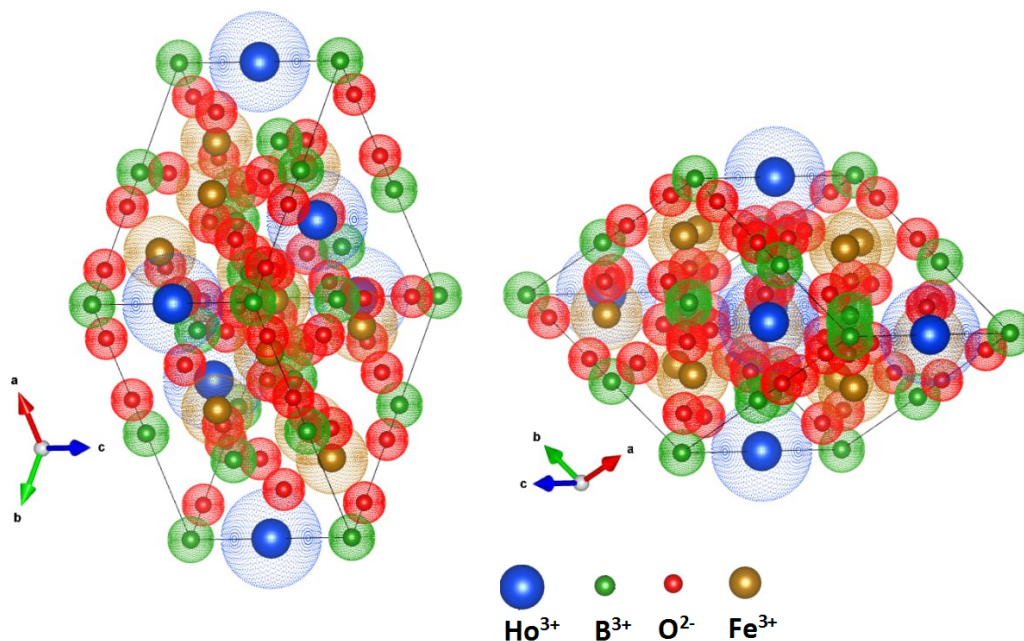


FIG. 1. Crystal structure of $\text{HoFe}_3(\text{BO}_3)_4$

Single crystals of $\text{HoFe}_3(\text{BO}_3)_4$ were grown by the flux method from an oxide melt based on bismuth borate at the Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences. High-purity Ho_2O_3 , Fe_2O_3 , and H_3BO_3 were used as starting materials. The growth process was carried out in platinum crucibles at temperatures of $950 - 1000 \text{ }^\circ\text{C}$, followed by slow cooling to $700 \text{ }^\circ\text{C}$ at a rate of $1 - 2 \text{ }^\circ\text{C}\cdot\text{h}^{-1}$. This procedure yielded homogeneous, optically transparent single crystals with a characteristic dark-pink coloration.

2.2. Raman spectroscopy

Raman spectroscopy was used to investigate lattice dynamics and to verify the structural integrity of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals.

Raman spectra were recorded using a RENISHAW inVia Raman microscope at room temperature in a standard backscattering geometry. Excitation was provided by a solid-state laser with a wavelength of 532 nm . The laser power at the sample surface was kept 50 mW in order to avoid local heating effects and possible modification of phonon line positions or linewidths.

The measurements were performed in the spectral range $100 - 2000 \text{ cm}^{-1}$. The recorded spectra were corrected for background and instrumental response.

The Raman spectra were analyzed with respect to vibrational modes associated with:

- internal vibrations of BO_3 groups,
- stretching and bending modes of FeO_6 octahedra,
- external lattice modes involving Ho^{3+} ions.

Raman spectroscopy provides a sensitive probe of local symmetry and structural order and enables detection of structural distortions or secondary phases that may not be visible in X-ray diffraction data [4, 6].

2.3. Optical and magneto-optical measurements

Optical absorption and magneto-optical measurements were carried out in the wavelength range $190 - 1100 \text{ nm}$ using a double-beam Specord 50 spectrophotometer (Analytik Jena, Germany) operating with polarized light.

Measurements were performed at room temperature and, when required, in the temperature range $80 - 300 \text{ K}$ using a closed-cycle cryostat. Magneto-optical experiments were performed in the Faraday geometry, with magnetic fields up to 10 kOe generated by a Lakeshore EM4 electromagnet. The magnetic field was applied parallel to the optical c axis of the crystal.

For optical studies, thin plate-like samples with thicknesses of $0.2 - 0.5 \text{ mm}$ were prepared. The sample surfaces were carefully polished to optical quality in order to minimize light scattering. The rotation of the polarization plane and magnetic dichroism were measured using modulation techniques with phase-sensitive detection, providing high sensitivity and reproducibility.

All optical spectra were normalized to the optical density of the unmagnetized sample to eliminate surface-related artifacts. Representative as-grown $\text{HoFe}_3(\text{BO}_3)_4$ single crystals are shown in Fig. 2.



FIG. 2. External view of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals grown by the flux method from a bismuth borate-based melt

2.4. Thermodynamic stability analysis

The thermodynamic stability of $\text{HoFe}_3(\text{BO}_3)_4$ was analyzed using formation energies and phase diagram data obtained from open computational materials databases, including the Materials Project and the Open Quantum Materials Database (OQMD) [12, 13].

The stability of the compound was evaluated using the energy above the convex hull (ΔE_{hull}), defined as:

$$\Delta E_{\text{hull}} = E_{\text{compound}} - E_{\text{hull}},$$

where E_{hull} corresponds to the energy of the most stable combination of competing phases at the same overall composition.

According to database data, $\text{HoFe}_3(\text{BO}_3)_4$ is characterized by a small positive value of ΔE_{hull} ($\sim 0.016 \text{ eV/atom}$), which lies within the typical uncertainty of density functional theory calculations and indicates thermodynamic stability or near-stability of the compound.

The phase stability analysis includes competing phases in the Ho–Fe–B–O system as reported in the databases. These data are used for qualitative interpretation of phase equilibria and for consistency analysis with experimentally observed synthesis conditions.

It should be emphasized that no independent first-principles calculations were performed in this work; all thermodynamic data were obtained from validated database sources.

3. Results and discussion

3.1. Raman spectroscopy

The vibrational properties of $\text{HoFe}_3(\text{BO}_3)_4$ were investigated by Raman spectroscopy at room temperature (Fig. 3). The recorded spectrum covers a wide frequency range and reflects both lattice dynamics and internal vibrations of structural units. The observed distribution of Raman modes is consistent with previously reported spectra of rare-earth ferroborates [4, 6].

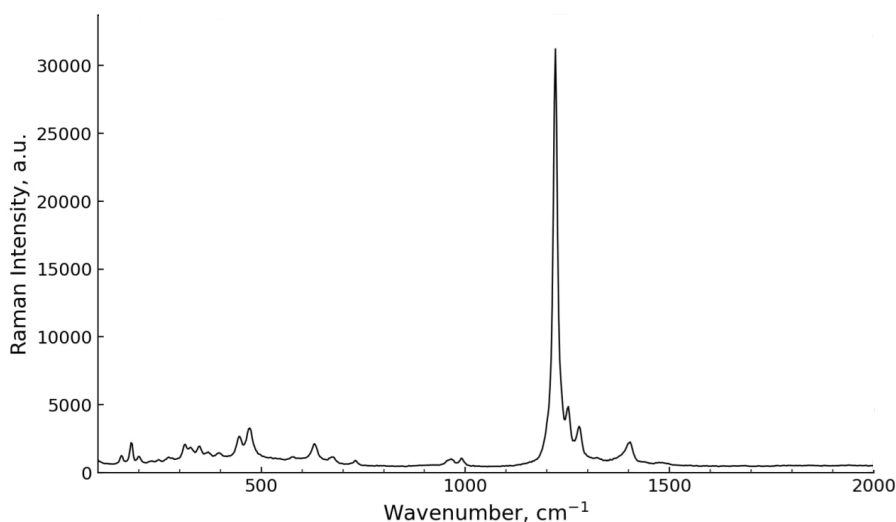


FIG. 3. Raman spectrum of $\text{HoFe}_3(\text{BO}_3)_4$ single crystal measured at room temperature ($\lambda = 532$ nm, backscattering geometry)

In the low-frequency region ($< 300 \text{ cm}^{-1}$), weak bands are observed, which can be attributed to lattice vibrations involving translational motions of heavy Ho^{3+} ions and acoustic modes of the crystal lattice. The intermediate spectral range ($400 - 700 \text{ cm}^{-1}$) is characterized by several bands of moderate intensity associated with vibrations of FeO_6 octahedra. These include both stretching and bending modes of Fe–O bonds and are typical for iron–oxygen coordinated systems.

The most prominent features are located in the high-frequency region between 1200 and 1450 cm^{-1} , where intense peaks are observed. These bands originate from internal vibrations of planar BO_3^{3-} groups. The modes in the range $1200 - 1250 \text{ cm}^{-1}$ are attributed to symmetric B–O stretching vibrations within BO_3 groups, while those in the $1280 - 1400 \text{ cm}^{-1}$ region are associated with asymmetric B–O stretching vibrations. An intense band located around $1410 - 1420 \text{ cm}^{-1}$ is characteristic of BO_3 units and reflects the rigidity of B–O bonds. At frequencies above 1500 cm^{-1} , weak features can be detected, which are attributed to overtone and combination modes. The absence of additional bands associated with impurity phases suggests that the investigated sample is spectroscopically homogeneous.

A more detailed analysis of the spectrum allows the identification of distinct Raman peaks, summarized in Table 1. An intense band at $\sim 1415 \text{ cm}^{-1}$ corresponds to asymmetric B–O stretching vibrations of BO_3 groups. Additional bands in the range $1200 - 1350 \text{ cm}^{-1}$ are also associated with internal vibrations of borate units. Lower-frequency peaks originate from FeO_6 octahedral vibrations and lattice modes involving heavy Ho^{3+} ions. Peak positions were determined from local maxima of the spectra without performing detailed peak deconvolution.

3.2. Optical absorption spectrum

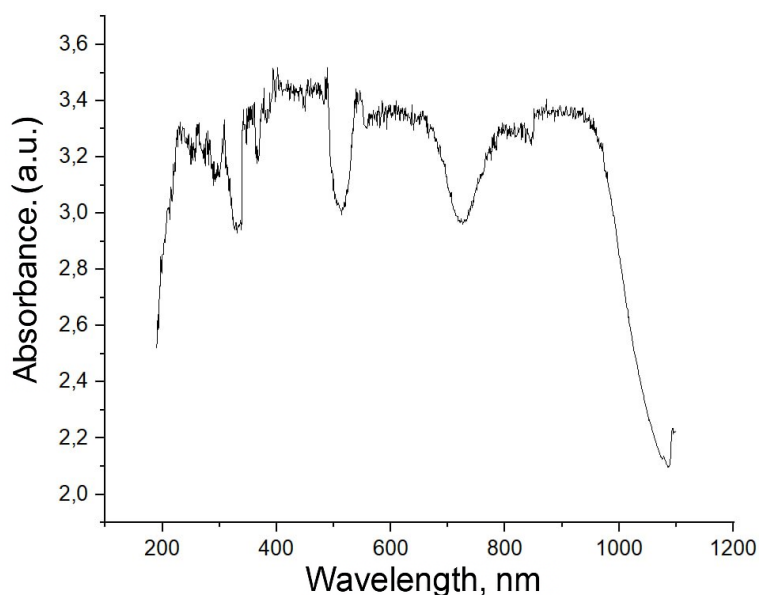
The optical absorption spectrum of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals measured at room temperature in the range $190 - 1100 \text{ nm}$ is shown in Fig. 4. The spectral profile results from the superposition of localized electronic transitions and a broad fundamental absorption edge. These features are consistent with earlier optical studies of $\text{HoFe}_3(\text{BO}_3)_4$ and related compounds [5, 9].

In the visible and near-infrared regions (approximately $350 - 900 \text{ nm}$), the absorption remains relatively low, with several weak and narrow bands superimposed on the background. These features are attributed to intra-4f transitions of Ho^{3+} ions from the ground multiplet 5I_8 to excited states such as 5G_6 , 5F_5 , 5F_4 , 5S_2 , and 5F_3 . Although these transitions are parity-forbidden for free ions, they become weakly allowed in the crystal due to crystal-field-induced mixing.

A pronounced increase in absorption is observed in the ultraviolet region (approximately $250 - 350 \text{ nm}$), which is associated with charge-transfer transitions from O^{2-} ligands to Fe^{3+} ions within FeO_6 octahedra. These transitions define the fundamental absorption edge of the material. The optical band gap was estimated from the onset of strong absorption

TABLE 1. Experimental Raman peaks of $\text{HoFe}_3(\text{BO}_3)_4$

Raman shift (cm^{-1})	Relative intensity	Assignment
~ 1415	medium–strong	asymmetric B–O stretching vibrations
~ 1335	medium	asymmetric B–O stretching vibrations
~ 1255	very strong	symmetric B–O stretching vibrations
~ 1005	medium	mixed B–O vibrations
~ 820	weak–medium	lattice / Fe–O bending
~ 680	medium	FeO_6 vibrations
~ 520	medium	Fe–O stretching
~ 300	weak	lattice modes
$\sim 120 - 200$	weak	external modes (Ho-related)

FIG. 4. Optical absorption spectrum of $\text{HoFe}_3(\text{BO}_3)_4$ single crystal measured at room temperature in the range 190 – 1100 nm ($E \parallel c$)

using linear extrapolation of the absorption edge and is found to be in the range 3.3 – 3.5 eV, corresponding to wavelengths of approximately 354 – 378 nm. The extension of absorption toward shorter wavelengths (down to ~ 250 nm) is attributed to higher-energy charge-transfer states and possible excitonic contributions. At wavelengths above 900 nm, the absorption decreases significantly, indicating high transparency in the near-infrared region.

TABLE 2. Optical absorption features of $\text{HoFe}_3(\text{BO}_3)_4$

Wavelength (nm)	Energy (eV)	Assignment
350 – 900	1.4 – 3.5	Ho^{3+} intra-4f transitions
250 – 350	3.5 – 5.0	$\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge transfer
354 – 378	3.3 – 3.5	optical band gap

3.3. Correlation between vibrational and optical properties

The combined analysis of Raman and optical absorption data provides insight into the relationship between lattice dynamics and electronic structure in $\text{HoFe}_3(\text{BO}_3)_4$. The Raman spectrum is dominated by high-frequency modes associated with internal vibrations of BO_3 groups, particularly in the $1200 - 1450 \text{ cm}^{-1}$ region, indicating the structural rigidity of borate units. At lower frequencies ($400 - 700 \text{ cm}^{-1}$), the observed modes originate from FeO_6 octahedra, reflecting the dynamics of the Fe–O framework. These structural units play an important role in determining the optical properties. The optical absorption edge in the ultraviolet region is governed by $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer transitions within FeO_6 octahedra, while the weak absorption bands in the visible and near-infrared regions arise from localized intra-4f transitions of Ho^{3+} ions. The coexistence of rigid BO_3 groups and FeO_6 octahedra results in a wide band gap ($\sim 3.3 - 3.5 \text{ eV}$) and low absorption in the visible range. This combination of structural stability and optical transparency is characteristic of rare-earth ferroborates and is favorable for magneto-optical applications.

4. Conclusion

In this work, the structural and optical properties of $\text{HoFe}_3(\text{BO}_3)_4$ single crystals have been investigated using Raman spectroscopy and optical absorption measurements, complemented by thermodynamic analysis based on materials databases.

The Raman spectra reveal well-defined phonon modes corresponding to BO_3 groups and FeO_6 octahedra, confirming the structural integrity of the crystal and the absence of secondary phases. The optical absorption spectrum demonstrates a wide transparency window in the visible region and a fundamental absorption edge in the ultraviolet region associated with charge-transfer transitions. The estimated optical band gap ($\sim 3.3 - 3.5 \text{ eV}$) and the presence of localized 4f transitions indicate the coexistence of localized and band-like electronic states. The consistency between vibrational and optical characteristics highlights the dominant role of BO_3 and FeO_6 structural units in determining the physical properties of the compound. Thermodynamic analysis based on database data confirms that $\text{HoFe}_3(\text{BO}_3)_4$ is located near the convex hull, indicating its stability within the Ho–Fe–B–O system.

The obtained results provide an experimentally supported description of the lattice dynamics and optical behavior of $\text{HoFe}_3(\text{BO}_3)_4$ and indicate its potential applicability in optical and magneto-optical devices consistent with previous studies on rare-earth iron oxides and garnets [14–20].

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Submitted 17 January 2026; revised 2 May 2026; accepted 8 May 2026

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Conflict of interest: the authors declare no conflict of interest.

A variational study of electronic thermal conductivity of Anderson lattice model: an application to CMR manganites ($\text{Re}_{1-x}\text{A}_x\text{MnO}_3$)

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PACS 71.10.Fd, 75.47.Gk, 65.40.-b

ABSTRACT Using the variational method, we have investigated the temperature dependence of the electronic thermal conductivity (k_{el}) in rare-earth manganites doped with alkaline-earth ions, which display the well-known CMR behavior. The analysis is based on a two-band ($l-b$) Anderson lattice model Hamiltonian appropriate for the strong electron-lattice Jahn–Teller (JT) coupling regime, consistent with two-fluid descriptions incorporating ($l-b$) hybridization. Key model parameters includes Coulomb repulsion U , strong Hund's coupling J_H between e_g and t_{2g} spins and hybridization V between l -polarons and d -electrons of the same spin. In the ferromagnetic metallic phase, calculations show that the k_{el} increases with increasing temperature and near the transition temperature $T_c \approx 400$ K, it shows a minimum or a dip in k_{el} for a fixed value of V , J_H and x . The results of k_{el} exhibit a typical crystalline character with grain boundary scattering as a main mechanism limiting the heat transfer in these compounds.

KEYWORDS Anderson lattice model hamiltonian, CMR manganites, electronic thermal conductivity, variational method

FOR CITATION Rahul Saini, Sunil Panwar A variational study of electronic thermal conductivity of Anderson lattice model: an application to CMR manganites ($\text{Re}_{1-x}\text{A}_x\text{MnO}_3$). *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 311–316.

1. Introduction

Manganites of perovskite structure, with the general formula $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$ (where $\text{Re} = \text{La, Pr, Nd, etc.}$, and $\text{A} = \text{Ca, Sr, Ba, etc.}$) have gained tremendous significance across condensed matter research due to the strong coupling between their charge, orbital, and spin degrees of freedom [1,2]. These materials drew remarkable scientific attention following the discovery of colossal magnetoresistance (CMR), a striking phenomenon in which the resistivity drastically decreases upon application of a magnetic field [3,4]. The CMR effect, since its discovery, has motivated extensive theoretical and experimental studies owing to its relevance in magnetic sensing, data storage, and spintronic device applications.

Several theoretical frameworks have been proposed to explain the underlying mechanisms responsible for the celebrated CMR effect. The double exchange (DE) mechanism, arising from electron hopping between Mn^{3+} and Mn^{4+} ions, provides a fundamental understanding of ferromagnetism and metallic conduction in these oxides [5]. However, the DE model alone cannot account for all the transport and magnetic properties observed in doped manganites. Additional mechanisms such as the Jahn-Teller (JT) effect [6], polaronic interactions, and phase separation [7,8] have been introduced to explain the wide range of experimental results. The interplay between these effects gives rise to a wide variety of electrical and magnetic behaviours in doped manganites, revealing the profound role of lattice distortions and electron correlations in determining their macroscopic properties.

Among various thermal properties of doped CMR manganites, thermal conductivity (k) stands out as an important probe of the scattering processes of phonons and electrons, providing valuable insights into the complexity of charge-lattice interactions in these compounds. A careful examination of previous studies reveals two major thermal transport behaviours [9,10]. In the paramagnetic insulating phase, k is typically low and displays an amorphous-like temperature dependence ($dk/dT > 0$), suggesting dominant phonon scattering and localized electronic states. Conversely, in the ferromagnetic-metallic phase, k exhibits a crystalline-like behaviour ($dk/dT < 0$), indicative of coherent heat transport and delocalized charge carriers. The crossover between these two regimes occurs near the Curie temperature (T_c), producing a characteristic minimum in $k(T)$. This transition, accompanied by the restructuring of MnO_6 octahedra, reflects the fundamental coupling between structural and electronic degrees of freedom in these materials.

Studies on CMR materials have also employed many advanced many-body theoretical approaches, such as dynamical mean field theory developed by T.V. Ramakrishnan [11] and the current-carrier density collapse (CCDC) model [12].

These approaches have been successful in explaining the transport behaviour over the entire temperature range. In particular, the CCDC model attributes the electrical transport mechanism to a temperature-dependent collapse in carrier density, while the electrical resistivity is governed by changes in the relative volume fractions of the paramagnetic and ferromagnetic phases.

Ramakrishnan et al. [11] proposed a theoretical model describing the coexistence of localized Jahn–Teller (JT) polarons and itinerant band electrons in doped rare-earth manganites of the general form $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$. According to their framework, this coexistence arises naturally under conditions of strong (JT) coupling and orbital degeneracy, offering a unified picture capable of accounting for the simultaneous presence of metallic conductivity and local distortions. Despite this theoretical progress, a quantitative explanation of electronic thermal conductivity (k_{el}) within a microscopic model that includes both hybridization and electron correlation remains lacking.

To address these limitations, Panwar et al. [13–16] introduced a variational approach based on the Anderson lattice model, initially developed to study the ground-state and thermal properties of heavy-fermion systems. This method was subsequently extended to examine magneto-transport phenomena, including thermoelectric power and electrical resistivity, in doped manganites across a wide temperature range and varying magnetic field conditions [17–19]. These studies demonstrated that the variational formalism successfully captures the temperature dependence of electrical resistivity $\rho(T)$ and the interplay between electronic correlations and spin disorder in such complex oxides. However, a detailed and systematic investigation of electronic thermal conductivity using this approach has not yet been undertaken.

In an ideal metallic system, the relationship between electronic and thermal conductivities is governed by the Wiedemann–Franz law [20], which predicts a constant Lorenz number under elastic scattering conditions. Nevertheless, for doped CMR manganites, this law often fails due to strong electron-phonon coupling, polaron formation, and spin fluctuations, which disrupt quasiparticle coherence [21, 22]. Therefore, a unified theoretical description capable of encompassing both electronic correlation and lattice distortion effects is essential for a complete understanding of thermal transport in these systems.

In this work, we present a variational study of electronic thermal conductivity (k_{el}) as a function of temperature for different doping concentrations x , hybridization strengths V , and Hund’s coupling J_H parameters in doped CMR manganites. This study extends the previously developed variational formalism, which had been successfully applied to model the temperature dependence of electrical resistivity $\rho(T)$ [17] and applies it to investigate thermal transport processes. The objective is to establish a microscopic framework that captures how hybridization and electron correlation collectively determine k_{el} and its deviation from conventional metallic behaviour.

2. Basic formulation

2.1. Model

In this study, a theoretical model is developed to quantitatively examine the electronic thermal conductivity (k_{el}) of doped colossal magnetoresistive (CMR) manganites within the strong electron-lattice Jahn–Teller (JT) coupling regime. We employ a Hamiltonian H_{lb} derived from the Anderson lattice formalism as proposed in earlier studies [11, 17], which effectively describes the coexistence of localized JT polarons (l -electrons) and itinerant band (b -electrons).

$$H_{lb} = - \sum_{\langle ij \rangle \sigma} \tilde{t}_{ij} (b_{i\sigma}^\dagger b_{j\sigma}) - \sum_{i\sigma} E_{jt} l_{i\sigma}^\dagger l_{i\sigma} + U \sum_{i\sigma} n_{i\sigma}^l n_{i\sigma}^b - J_H \sum_i \mathbf{s}_i \cdot \mathbf{S}_i - J_F \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_{k\sigma} V_K (l_{k\sigma}^\dagger b_{k\sigma} + h.c.). \quad (1)$$

The details of symbols used are given in our previous work in Ref. [17].

Here, each term carries a specific physical significance. In Eq. (1), the b -electrons, which form a broad conduction band, hop between nearest-neighbor sites with an effective amplitude $\tilde{t}_{ij}$, while the localized l -polarons occupy energy levels at $-E_{JT}$ owing to the strong JT distortion. The term U represents the on-site Coulomb repulsion between l -polarons and b -electrons of identical spin at the same site i , while V_k is the l - b hybridization between l -polarons and b -electrons of the same spin. J_H is the Hund’s coupling that aligns the itinerant e_g spin ($\mathbf{s}_i$) with the localized t_{2g} core spin ($\mathbf{S}_i$), and J_F is the effective ferromagnetic exchange coupling between neighboring t_{2g} core spins ($\mathbf{S}_i, \mathbf{S}_j$). Together, these terms account for the essential competing interactions governing charge, spin, and lattice dynamics in CMR manganites.

In the case of finite U , the ground state of the system can be expressed by a modified variational wave function in k -space [17] as

$$\psi_{lb} = \prod_{k\sigma} [1 + A_{k\sigma} l_{k\sigma}^\dagger b_{k\sigma}] |\Phi_d\rangle, \quad (2)$$

where $|\Phi_d\rangle$ represents the Fermi Sea of delocalized d -electrons, and $A_{k\sigma}$ is the variational parameter characterizing the hybridization strength between localized and itinerant states. Optimization of the system’s energy expectation value with

respect to $A_{k\sigma}$ yields:

$$A_{k\sigma} = \frac{1}{2V_k} \left[\left(\epsilon_k + \frac{U}{2} n_\sigma^l - \epsilon_{d\sigma} \right) + \sqrt{\left(\epsilon_k + \frac{U}{2} n_\sigma^l - \epsilon_{d\sigma} \right)^2 + 4V_k^2} \right], \quad (3)$$

where

$$\epsilon_{d\sigma} = \frac{U}{2} n_\sigma^b + \frac{J_H}{2} n_\sigma^l - E_{JT} - J_F \sigma m - h. \quad (4)$$

Here, J_F involves the number of nearest neighbors and m is the site magnetization per atom given by

$$m = \frac{1}{N} \sum_{k\sigma} \sigma l_{k\sigma}^+ l_{k\sigma} \quad (5)$$

and N is the total number of lattice sites. The average occupation numbers for the itinerant b-electrons and localized l-electrons are defined as

$$n_\sigma^d = \frac{1}{N} \sum_k n_{k\sigma}^d, \quad n_\sigma^b = \frac{1}{N} \sum_k n_{k\sigma}^b = \frac{1}{N} \sum_k \frac{f_{k\sigma}^-}{(1 + A_{k\sigma}^2)} \quad (6)$$

and

$$n_\sigma^l = \frac{1}{N} \sum_k n_{k\sigma}^l = \frac{1}{N} \sum_k \frac{A_{k\sigma}^2 f_{k\sigma}^-}{(1 + A_{k\sigma}^2)}, \quad (7)$$

where $f_{k\sigma}^-$ is the Fermi–Dirac distribution function corresponding to the lower quasiparticle branch $E_{k\sigma}^-$

$$f_{k\sigma}^- = 1 / [\exp(\beta(E_{k\sigma}^- - \mu)) + 1] \quad (8)$$

with μ denoting the chemical potential and $\beta = 1/(k_B T)$. The lower quasiparticle energy branch, representing the hybridized electronic states, is then given by the following formula

$$E_{k\sigma}^- = \frac{1}{2} \left[\left(\epsilon_k + \frac{U}{2} n_\sigma^l + \epsilon_{d\sigma} \right) - \sqrt{\left(\epsilon_k + \frac{U}{2} n_\sigma^l - \epsilon_{d\sigma} \right)^2 + 4V_k^2} \right]. \quad (9)$$

This formulation allows the study of electronic structure renormalization arising from hybridization and correlation effects, offering a direct means of evaluating transport properties in manganites across different temperature and doping regimes.

2.2. Electrical resistivity

The electrical resistivity $\rho(T)$ serves as an essential precursor to determine the electronic component of thermal conductivity. Following the approach used in earlier variational studies [17], the temperature-dependent electrical conductivity $\sigma(T)$ is given by

$$\sigma(T) = \int \left(-\frac{\partial f_{k\sigma}^-}{\partial E_{k\sigma}^-} \right) \sigma'(E_{k\sigma}^-) dE_{k\sigma}^-, \quad (10)$$

where

$$\sigma'(E_{k\sigma}^-) = \sigma_0 [N^C(E_{k\sigma}^-)]^2 \quad (11)$$

and $N^C(E_{k\sigma}^-)$ represents the density of perturbed conduction band (e_g) states. This relation provides the link between the electronic structure and electrical transport, enabling the computation of resistivity as a function of temperature and hybridization parameters within the variational framework.

2.3. Thermal conductivity

In manganites exhibiting relatively high electrical resistivity, the contribution of electrons to the total thermal conductivity cannot be ignored, particularly in the ferromagnetic metallic phase. Here, the Wiedemann–Franz law [20] provides a phenomenological bridge between electrical and thermal transport. Neglecting lattice contributions, the electronic thermal conductivity k_{el} can be expressed as

$$k_{el} = \rho^{-1} L_0 T, \quad (12)$$

where $L_0 = 2.45 \times 10^{-8} \text{ W}\cdot\Omega/\text{K}^2$ is the Lorenz number, and ρ represents the electrical resistivity obtained from the variational calculations. Although deviations from the Wiedemann–Franz law have been observed experimentally in manganites due to strong electron-phonon coupling and localization effects, this relationship remains a reliable approximation in the ferromagnetic metallic region [21, 22]. The k_{el} calculations from resistivity data are plotted in Figs. 1–3.

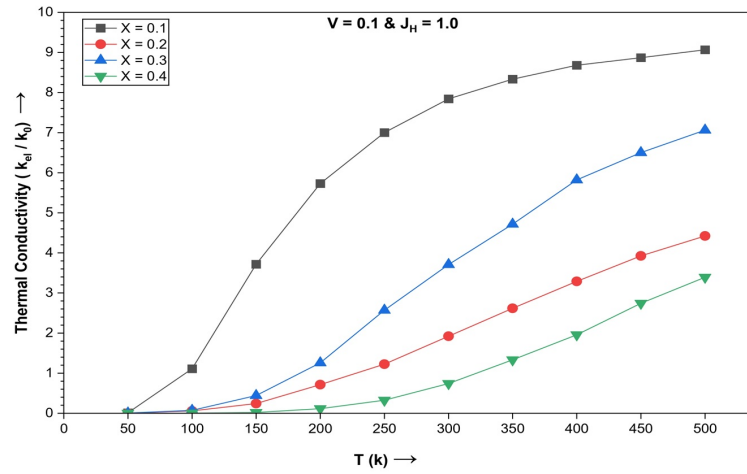


FIG. 1. Variation of electronic thermal conductivity k_{el} with temperature for different values of doping x at $V = 0.1$ and $J_H = 1.0$

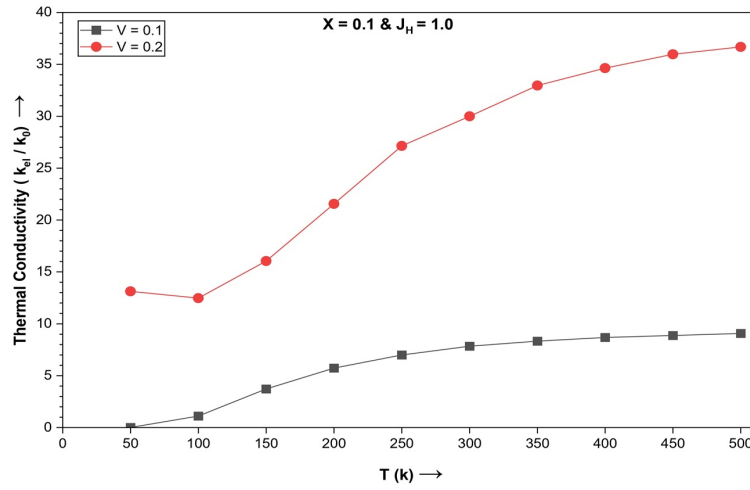


FIG. 2. Variation of electronic thermal conductivity k_{el} with temperature for different values of hybridization V at $x = 0.1$ and $J_H = 1.0$

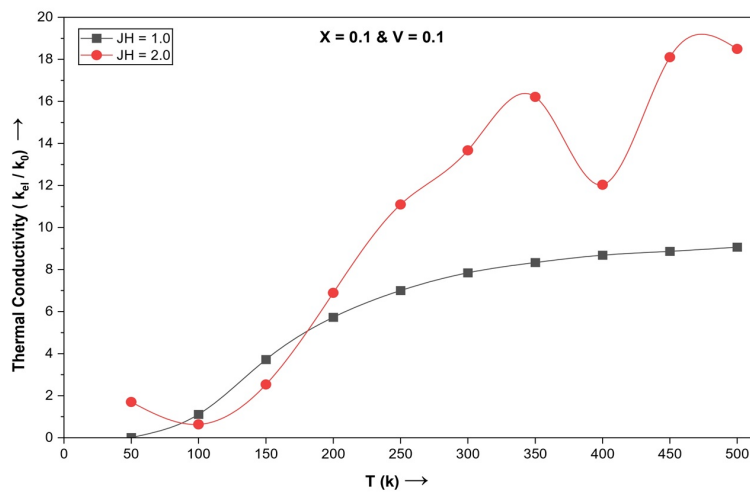


FIG. 3. Variation of electronic thermal conductivity k_{el} with temperature for different values of J_H at $x = 0.1$ and $V = 0.1$. Curve for $J_H = 2.0$ (red color) shows a minimum at transition temperature $T_c = 400$ K

3. Results and discussion

In the present calculations, the unperturbed conduction band of the three-dimensional manganite system is considered using a simple semi-circular density of states $N_{\sigma}^c(\epsilon_k) = (2/\pi)\sqrt{1 - \epsilon_k^2}$, centered around zero energy, which effectively captures the essential electronic structure of a strongly correlated perovskite lattice. The total bandwidth is taken as $W = 2.0$ eV, corresponding to realistic energy scales of e_g band electrons in CMR manganites. The on-site Coulomb interaction $U = 5.0$ eV, Jahn–Teller energy $E_{JT} = 0.5$ eV, hybridization strengths $V = 0.1$ and 0.2 eV and Hund’s coupling constants $J_H = 1.0$ and 2.0 eV. The Fermi energy $\epsilon_F = -0.238$ corresponds to a doping level of $x = 0.3$, while the doping concentration x itself is varied from 0.1 to 0.4 to investigate its effect on thermal transport.

In Figs. 1–3, we illustrate the temperature dependence of electronic thermal conductivity $k_{el}(T)$ for different values of doping (x), hybridization (V), and Hund’s coupling (J_H), respectively. Across all parameter sets, the general behavior of $k_{el}(T)$ exhibits a distinct crossover from low-temperature metallic characteristics to high-temperature insulating tendencies. In the ferromagnetic metallic region, we find that the $k_{el}(T)$ at low temperature increases with increasing temperature and near transition temperature $T_c \sim 400$ K it shows a minimum or a dip in k_{el} for a fixed value of hybridization V , Hund’s coupling J_H and doping x .

The behavior of k_{el} as a function of doping x is shown in Fig. 1. For a fixed hybridization strength V and Hund’s coupling (J_H), an increase in the doping concentration from $x = 0.1$ to 0.4 leads to a gradual decrease in $k_{el}(T)$ throughout the temperature range. Below $T = 150$ K, the thermal conductivity values for all doping levels are nearly identical, indicating that low-temperature transport is dominated by itinerant electron contributions with minimal influence from lattice distortions. However, at higher temperatures, the reduction in k_{el} becomes more pronounced for higher doping levels. This trend can be attributed to the increasing formation of Jahn–Teller polarons, which act as effective scattering centers for both charge carriers and phonons, thereby reducing the overall electronic contribution to thermal transport [9, 21]. The decrease in magnitude of k_{el} with increasing x , thus, signifies enhanced lattice disorder and polaronic scattering, consistent with experimental observations [4].

Figures 2 and 3 further illustrate the dependence of k_{el} on the hybridization parameter (V) and Hund’s coupling (J_H), respectively. A systematic increase in both parameters leads to a noticeable enhancement in k_{el} , accompanied again by a pronounced dip at $T_c \approx 400$ K. The increase in k_{el} with higher V indicates that greater hybridization strengthens the coupling between localized and itinerant states, thereby facilitating more coherent electronic transport and reducing localization effects. Similarly, a higher Hund’s coupling (J_H) enhances the alignment of the e_g electron spins with the localized t_{2g} core spins, promoting spin-polarized conduction and thus improving thermal transport efficiency in the ferromagnetic metallic phase [5].

For $J_H = 2.0$ eV, $V = 0.1$ eV and $x = 0.1$, a well-defined minimum in $k_{el}(T)$ is observed at $T_c = 400$ K beyond which thermal conductivity increases sharply with temperature (Fig. 3). This minimum corresponds to the transition region where spin disorder scattering and polaron formation reach their maximum influence. Above T_c , the increasing thermal agitation and breakdown of magnetic ordering lead to carrier localization, thereby reducing the electronic contribution to thermal conduction. Such behavior aligns with experimental trends reported for doped manganite samples such as $\text{Pr}_{0.6}\text{Sr}_{0.35}\text{Ag}_{0.05}\text{MnO}_3$ [22].

The overall results obtained from this variational formulation qualitatively reproduce the experimentally observed features of $k_{el}(T)$ in CMR manganites. The suppression of k_{el} with increasing doping and its enhancement with higher hybridization or Hund’s coupling emphasize the critical role of electron-lattice and spin-charge interactions in governing heat transport. The theoretical framework captures the essential interplay among these parameters, providing a unified interpretation of thermal transport anomalies in CMR manganites.

4. Conclusion

In this paper, a variational method has been used for the investigation of the electronic thermal conductivity k_{el} at different temperatures for various values of the model parameters like doping x , hybridisation V and J_H parameters. By increasing temperature, we obtain the ferromagnetic transition at $T_c \sim 400$ K in the metallic state. A dip or minimum in thermal conductivity is observed at the ferromagnetic transition temperature ($T_c \sim 400$ K) (Fig. 3). This minimum arises from the complex interplay of lattice dynamics and electron transport during the phase transition. The thermal conductivity k_{el} of colossal magnetoresistance (CMR) manganites shows strong and anomalous temperature dependence with distinct behaviours in the paramagnetic (insulating) and ferromagnetic (metallic) phases. In the low-T metallic phase, it decreases as temperature falls ($dk_{el}/dT < 0$), similar to the typical crystalline behaviour. k_{el} shows an appreciable enhancement as electrons gain mobility and contribute to the thermal transport in the metallic state.

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Submitted 27 January 2026; revised 3 February 2026; accepted 30 May 2026

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Conflict of interest: the authors declare no conflict of interest.

Molecular modeling viscosity of hybrid nanofluids with carbon nanotubes and copper nanoparticles

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PACS 61.20.Ja, 61.48.De, 66.20.Cy

ABSTRACT Molecular dynamics method was used to study the viscosity coefficients of benzene-based hybrid nanofluids with single wall carbon nanotubes and copper nanoparticles. The dependence of the viscosity of these nanofluids on the concentration of carbon nanotubes and nanoparticles, as well as on their morphology was studied. It was shown that viscosity of all the studied nanofluids is significantly higher than that of the base fluid and conventional coarse-dispersed fluids. The viscosity coefficient of nanofluid with carbon nanotubes at a given concentration increases with increasing their length (aspect ratio). At equal concentrations, the viscosity of hybrid nanofluids significantly exceeds the viscosity of nanofluid with nanoparticles or carbon nanotubes and increases with decreasing in nanoparticle size. One of the principal factors responsible for the observed increase in the viscosity of nanofluid is the structuring of the base fluid molecules near the nanoparticles or carbon nanotubes.

KEYWORDS carbon nanotube, hybrid nanofluids, molecular dynamics method, nanofluids, nanoparticles, structure of nanofluid, viscosity

FOR CITATION Rudyak V.Ya., Krasnolutskii S.L., Lezhnev E.V., Rafalskaya T.A. Molecular modeling viscosity of hybrid nanofluids with carbon nanotubes and copper nanoparticles. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 317–326.

1. Introduction

Nanofluids (NF), whose active study commenced approximately thirty years ago, have been called dispersed fluids with solid nanoparticles (ranging in size from 1 to 100 nm). Later, after the creation of various production technologies of carbon nanotubes (CNTs), dispersed fluids with CNTs were also called NFs. Initially, interest in nanofluids was driven mainly by their potential use in various applications. Today, NFs are used or are planned to be used in biomedical and cosmetology technologies, in various thermophysical applications, in tribology, in the creation of new materials and coatings, etc. [1–7]. Later it became clear that NFs are an unusual dispersed fluid. Their thermophysical properties are not described by classical theories [7]. One of the main properties of NFs is their viscosity. By now, the viscosity of NFs with conventional spherical nanoparticles (NPs) has been well studied. It has been found that the dependence of the NF viscosity on NP concentration is described by a parabolic function [7–10], however, in addition, it also depends on the size of NPs [7, 10–12] and their material [7, 10, 13]. It is important to emphasize that the viscosity of these NFs is greater the smaller the size of the NPs.

By now, the properties of NFs with CNTs have also been experimentally studied quite well (see [7, 14–18] and the references therein). First of all, it was found that the viscosity and rheology of NFs are determined by the type of CNTs, which can be either single-walled (SWCNTs) or multi-walled (MWCNTs). The viscosity of NFs with SWCNTs is significantly higher than that of NFs with MWCNTs at the same weight concentrations. In addition, it was established that even at sufficiently low concentrations of SWCNTs the corresponding NFs become non-Newtonian and exhibit appeared percolation structure. The presence of percolation also results in the viscoelastic properties appearing in the NFs.

The significant difference in the morphology of NPs and CNTs and the corresponding nanofluids has initiated the creation of another new type of dispersed fluids, called hybrid nanofluids (HNFs). Two distinct classes of HNFs can be identified. The first class comprises NFs wherein two (and sometimes, three) grades of conventional NPs are used. The second class of HNFs is prepared using CNTs and conventional NPs. The great interest in hybrid nanofluids is primarily due to their high thermal conductivity compared to conventional nanofluids. The thermophysical properties of HNFs have been actively studied for approximately a decade. In the preceding five to seven years, approximately two dozen specialized reviews have been appeared, with some of these available in [19–27]. This is due to two factors: the amazing properties of HNFs and their almost infinite diversity (the number of combinations of base fluids, types of NPs and CNTs is very large). Such a great diversity has led to a huge number of experimental facts in the literature indicating the unusual properties of HNFs. Unfortunately, the lack of systematicity in these data does not yet allow answering the

question of what accounts for these unusual properties and whether they can be predicted. For this reason, in order to understand the qualitative impact of concentration, size, and material of CNTs and NPs on the thermal conductivity and viscosity of HNFs, it is essential to employ molecular dynamics (MD) method. This will also facilitate the elucidation of the mechanisms governing transport processes in such NFs.

To date, simulation of HNFs with CNTs and NPs has not been performed employing MD method. In the only paper [28] that we are aware of, the viscosity and thermal conductivity of water-based HNFs with copper and silver particles were studied by the MD method. The volume concentration of NPs in this study ranged from 3 to 9 %; however, this was achieved by increasing the size of the NPs, which varied from 1.21 to 1.75 nm. It was found that the viscosity of HNFs in all cases was higher than that of NF with separately added copper or silver particles. At the same time the viscosity of Ag-containing NF was higher than that of Cu-containing. However, it should be understood that changing the size of nanoparticles we get different nanofluids in all cases. These nanofluids cannot be compared at all.

The objective of the present work is to conduct MD simulations and a systematic study of the viscosity of benzene-based HNFs with SWCNTs and copper NPs. The selection of benzene as the base fluid was predicated on the fact that SWCNTs are hydrophobic, rendering the formation of a water-based nanofluid containing them unfeasible without the use of surfactants. Conversely, SWCNTs exhibit lyophilic behavior towards benzene, as well as a range of other alcohols (isopropanol, ethylene glycol, etc.). Armchair SWCNTs with chirality (8,8) were used as nanotubes with a diameter of 1.1 nm and lengths of 1.1, 3.5, 7.2, and 14.6 nm. The SWCNTs comprised 160, 480, 960, and 1920 carbon atoms, respectively. The diameter of copper nanoparticles was 1.39, 2.5, and 3.2 nm, respectively. In the simulation, the number of SWCNTs ranged from 4 to 48, while the number of nanoparticles ranged from 6 to 24. The number of benzene molecules in the simulation cell ranged from 6,700 to 38,000. The weight concentrations of nanotubes were 3, 9, and 15 %, which was approximately equivalent to a volume concentration of 1, 3, and 5 %. The complexity of objective interpretation of the obtained results required the parallel simulation of the viscosity of NFs containing separately CNTs and copper NPs. The comparison of the MD viscosity data of the NFs with CNTs and Cu NPs was partially done in paper [29]. These data and some new ones will be used in the present paper.

In all cases, the following questions were required to be addressed: (i) What is the effect of the aspect ratio (nanotube length-to-diameter ratio) of CNTs on the viscosity of HNFs? (ii) How does the viscosity of HNFs depend on the concentration of CNTs and NPs? (iii) How does the viscosity of HNFs depend on the length of CNTs? (iv) What is the correlation between the viscosities of HNF and NFs with CNTs and spherical NPs?

2. Simulation technique

The viscosity of a fluid is determined by the momentum dissipation occurring within the system. The shear viscosity coefficient is determined by the fluctuation-dissipation theorem, which is also known as the Green–Kubo formula [30–32]:

$$\eta = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}(0) : \mathbf{J}(t) \rangle dt = \frac{V}{k_B T} \int_0^{\tau_p} \chi_\eta(t) dt, \quad (1)$$

where the microscopic momentum flux tensor of the considered mixture has the form

$$\mathbf{J} = \frac{1}{V} \left(\sum_{\alpha=1}^3 \sum_{i=1}^{N_\alpha} m_\alpha \mathbf{v}_i \mathbf{v}_i + \frac{1}{2} \sum_{\alpha,\beta=1}^3 \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \mathbf{F}_{ij} \mathbf{r}_{ij} \right). \quad (2)$$

Here indices $\alpha, \beta = 1$ refer to the molecules of the carrier fluid, index 2 refers to the nanotube atoms, while index 3 refers to the nanoparticles, m_i is the mass of the corresponding particle (molecule of the carrier fluid, nanotube atom, or nanoparticle), V is the volume of the system, T is the temperature of the medium. $\mathbf{F}_{ij}$ is the force acting on the particle (molecule or nanoparticle), $\mathbf{v}_i$ is the velocity of molecule i , $\mathbf{r}_{ij}$ is the radius-vector between the centers of interacting particles, k_B is the Boltzmann constant, N_α and N_β are the numbers of the carrier fluid molecules, nanotube atoms, or nanoparticles, respectively. The angle brackets in (1) denote ensemble averaging.

According to (1), the viscosity coefficient is a function of time. Its actual (measurable) value is achieved only when the function $\eta(t)$ reaches a plateau value, the duration of which is determined by the time τ_p [32]. During this period, the autocorrelation function of the viscosity $\chi_\eta(t)$ decays. The calculation of this correlation function requires the determination of the microscopic momentum flux tensor $\mathbf{J}(t)$ at successive time moments. This requires knowing the positions $\mathbf{r}_i(t)$ and velocities $\mathbf{v}_i(t)$ of all particles in the system. In the MD method, these phase variables are determined as a result of solving the corresponding Newton equations.

The dynamics of the phase variables of the systems under consideration are determined by the interaction of the constituent particles. Each CNT was simulated as a set of carbon atoms interacting with one another via the AIREBO potential [33]. The interaction between benzene molecules and carbon or copper atoms was determined by the Lennard–Jones potential

$$\Phi_{LJ}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right], \quad (3)$$

where σ_{ij} is the effective diameter of molecules (atoms), ε_{ij} is the depth of the potential well, $r = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the centers of molecules i and j .

The following potential parameters (3) were used for benzene molecules: $\sigma_1 = 5.034 \text{ \AA}$, $\frac{\varepsilon_1}{k_B} = 544.3 \text{ K}$ [29]. The potential parameters for carbon atoms belonging to different CNTs were sourced from [34]: $\sigma_2 = 3.4157 \text{ \AA}$, $\frac{\varepsilon_2}{k_B} = 27.7 \text{ K}$. Finally, the parameters of the interaction potential of copper atoms were selected based on the viscosity of fluid copper at a temperature of 1356 K and pressure of 1 atm [35] and were equal to: $\sigma_3 = 2.2268 \text{ \AA}$, $\frac{\varepsilon_3}{k_B} = 2255.3 \text{ K}$.

The parameters of the interaction potential (3) of the carrier fluid molecule with a carbon atom of CNT or a nanoparticle atom were calculated using combinatorial relations [36]: $\sigma_{12} = \sqrt{\sigma_1 \sigma_2}$, $\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}$. Since the potential (3) has an infinite radius of action, it was truncated in the course of simulation process, the truncation radius was equal to $2.5 \sigma_i$ ($i = 1, 2$).

One of the most challenging aspects of simulating NFs with NPs and NPs with each other is the construction of the corresponding interaction potentials. These potentials are known as the Rudyak–Krasnolutsii (RK) [37] potential and the Rudyak–Krasnolutsii–Ivanov one (RKI) [38]. They were derived on the assumption that the NPs are solid and spherical. These potentials are discussed in details in [29, 32].

The NF was simulated using the conventional MD method [39], with the LAMMPS software [40] employed for this purpose. The simulation was conducted in cubic cells with periodic boundary conditions. At the initial moment, benzene molecules were uniformly distributed within the cubic simulation cell, with the exception of the volume occupied by CNTs and NPs. The initial velocities of the carrier fluid molecules, CNT and NP atoms were set in accordance with the Maxwell distribution at a given temperature. The calculation commenced following an initial relaxation period of 1 – 2 ns, during which the simulated system attained equilibrium at a given temperature and pressure. Typical screenshot for HNF with NPs diameter 1.6 nm and CNT with length 14.6 nm are presented in Fig. 1. Here the volume concentrations of the NPs and CNTs are equal to 2 and 1 %, correspondingly.

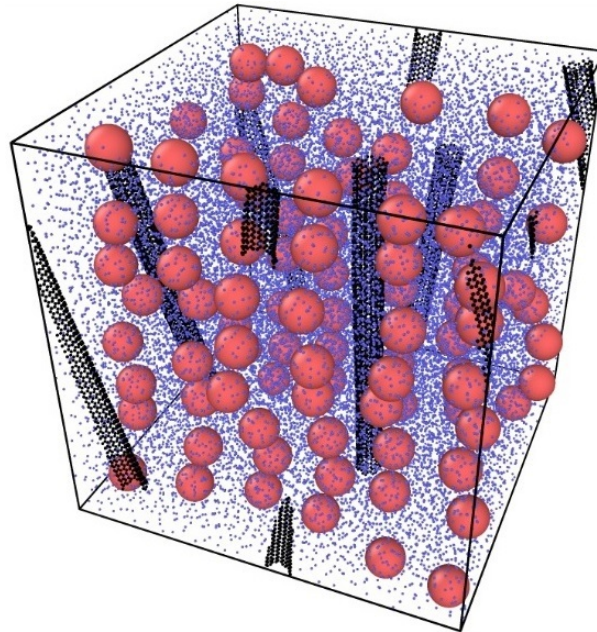


FIG. 1. Screenshot of a hybrid nanofluid simulation cell

The Verlet scheme was employed for the integration of Newton's equations. The NPT Nosé–Hoover thermostat [41, 42] was used, maintaining the given average values of pressure $p = 1 \text{ atm}$ and temperature $T = 25 \text{ }^\circ\text{C}$. It is important to note that the simulation of the nanofluid evolution imposes more stringent constraints on the simulation cell size in comparison to a homogeneous medium. Since the nanotube should not interact with itself, it is necessary that the side length of the cubic cell should be significantly larger than the length of the nanotube. The mean cell size for CNTs with lengths of 1.1 and 3.5 was a minimum of 10.1 nm, while for CNTs with lengths of 7.2 and 14.6 nm it was at least 11.2 and 17.5 nm, respectively. As a consequence of the local instability and mixing observed during the computation of the phase trajectories of the system [43, 44] the obtained data should be averaged over the ensemble of independently constructed phase trajectories. In the present study, the data were averaged over a minimum of 1,000 phase trajectories. The computation time per phase trajectory was 50 ns.

3. Viscosity of nanofluid with carbon nanotubes

In this paper, the viscosity of benzene-based HNFs with CNTs and copper NPs was studied. The analysis of the obtained data requires their comparison with the viscosity of NFs separately with CNTs and copper NPs. Such data were partially obtained earlier in paper [29]. These data are used in the present paper; in addition, some new data necessary for further analysis are presented.

The accuracy of MD modeling was determined in our paper [29]. For this purpose, the viscosity coefficient of pure benzene was simulated at atmospheric pressure and a temperature of 25 °C. It was found that the obtained value (0.6 mPa·s) agrees with high accuracy with the experimental value (0.604 mPa·s [45]). Further, in [29], the dependence of the viscosity of nanofluids with spherical nanoparticles on their concentration and diameter was systematically studied. It has been shown that this viscosity significantly exceeds the corresponding values for coarse-dispersed fluids and increases with decreasing particle size. This is consistent with the existing experimental data [7, 10–12]. The second conclusion obtained in this paper is related to nanofluids with CNTs. The dependence of the viscosity coefficient on the CNT concentration was also studied, showing that it increases with increasing CNT length. However, the nature of this dependence was not explored. The analysis of the last obtained data allows drawing several conclusions. The first conclusion is that the viscosity coefficient of all NFs increases monotonically with rising CNT concentration. This growth is significantly greater than that observed in coarse-dispersed fluids, for which the viscosity is described by Batchelor's theory [46]. Secondly, as the length of the CNTs increases, the viscosity of the corresponding NFs increases rapidly and exceeds the viscosity of NF with copper particles at all concentrations. Figure 2 shows the correlation between the relative viscosity coefficient $\eta_r = \eta / \eta_b$ (η_b is the viscosity coefficient of the based fluid) of NF and the length of CNTs at varying CNT concentrations. The observed increase in the viscosity of the NF with increasing CNT length is well described by the following logarithmic function

$$\eta_r(L) = a(\varphi) \ln(L) + b(\varphi). \quad (4)$$

The parameters $a(\varphi)$ and $b(\varphi)$ in equation (4) are given in Table 1, here φ is the volume concentration of CNTs. These correlations are illustrated in Fig. 2 by means of various lines.

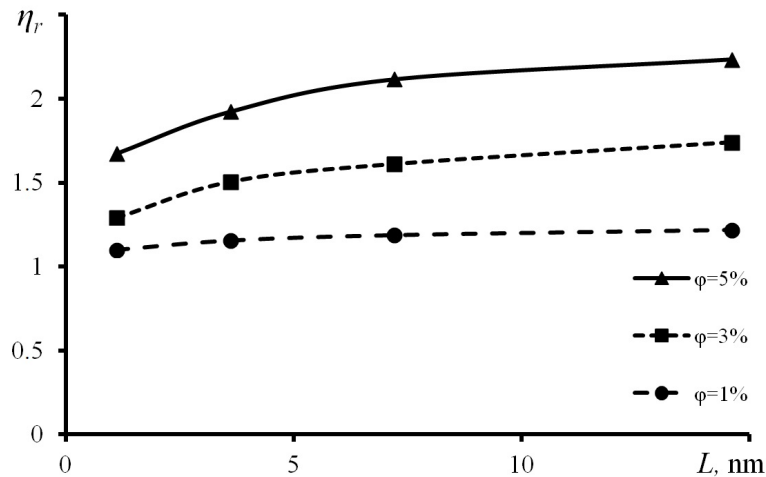


FIG. 2. Dependence of the relative viscosity coefficient of the nanofluid on the CNT length at different volume concentrations φ

Thus, it is shown that the viscosity of NFs with CNTs is significantly higher than the viscosity of NFs with spherical particles. It's not surprising. For suspensions with solid ellipsoidal particles, the viscosity coefficient was obtained by J.B. Jeffrey [47]. The viscosity coefficient of a dispersed medium increased as the shape of the particles deviated from a spherical configuration. This is expected due to the shorter Brownian rotation time in comparison with the considered hydrodynamic time period. Consequently, the rotation of the particles results in an increase in the effective volume they occupy. The elongated ellipsoid is an effective model for the solid CNT. Later, it was shown in [48] that suspensions comprising ellipsoidal particles should manifest viscoelastic properties. For NFs with SWCNTs, this was revealed experimentally in [17, 18].

NF is a complex dispersed system. Its viscosity is determined by the processes of momentum dissipation in the system. In turn, this dissipation process is determined by various contributions in the viscosity coefficient (see (1) and (2)). Therefore, to understand the mechanisms of momentum dissipation in NFs, it is necessary to analyze the various contributions to the viscosity coefficient (1), (2). Previously, such an analysis was performed for NFs with spherical NPs [49, 50]. Several important facts were revealed. Firstly, it was shown that the contribution of kinetic processes to momentum transport (viscosity) in NFs is insignificant and lower than in the base fluid. This reduction is due to the decrease in the number density of molecules in the NFs compared to the base fluid. The main increase in the viscosity

TABLE 1. Parameter values in formula (4)

$\varphi, \%$	$a(\varphi)$	$b(\varphi)$
1	0.2224	1.6508
3	0.1729	1.2758
5	0.0465	1.0937

coefficient is attributed to nanoparticle–molecule interactions as well as correlations between molecule–molecule and nanoparticle–molecule interactions. Below such an analysis is made for a nanofluid with CNTs.

The microscopic momentum flux tensor (2) for a binary system has the following form

$$\mathbf{J} = \mathbf{J}_k + \mathbf{J}_p, \quad (5)$$

where the kinetic contribution is

$$\mathbf{J}_k = \frac{1}{V} \sum_{\alpha=1}^2 \sum_{i=1}^{N_{\alpha}} m_{\alpha} \mathbf{v}_i \mathbf{v}_i.$$

In turn, the potential contribution consists of two parts

$$\mathbf{J}_p = \mathbf{J}_{p1} + \mathbf{J}_{p2},$$

related to the carrier fluid

$$\mathbf{J}_{p1} = \frac{1}{2V} \sum_{i=1}^{N_1} \sum_{j=1}^{N_1} \mathbf{F}_{ij} \mathbf{r}_{ij} + \frac{1}{2V} \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \mathbf{F}_{ij} \mathbf{r}_{ij}$$

and to the CNTs

$$\mathbf{J}_{p2} = \frac{1}{2V} \sum_{i=1}^{N_2} \sum_{j=1}^{N_2} \mathbf{F}_{ij} \mathbf{r}_{ij} + \frac{1}{2V} \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \mathbf{F}_{ij} \mathbf{r}_{ij}.$$

Accordingly, it is also convenient to divide the viscosity coefficient (1) into several summands

$$\eta = \eta_k + \eta_p + \eta_{kp}, \quad (6)$$

which determine the kinetic contribution

$$\eta_k = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_k(0) : \mathbf{J}_k(t) \rangle dt, \quad (6a)$$

potential contribution

$$\eta_p = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_p(0) : \mathbf{J}_p(t) \rangle dt \quad (6b)$$

and cross kinetic-potential contribution

$$\eta_{kp} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_k(0) : \mathbf{J}_p(t) + \mathbf{J}_p(0) : \mathbf{J}_k(t) \rangle dt. \quad (6c)$$

Further, the potential contribution to the viscosity coefficient can be represented as follows

$$\eta_p = \eta_{p1} + \eta_{p2} + (\eta_{p1p2} + \eta_{p2p1}), \quad (7)$$

where

$$\eta_{p1} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_{p1}(0) : \mathbf{J}_{p1}(t) \rangle dt, \quad \eta_{p2} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_{p2}(0) : \mathbf{J}_{p2}(t) \rangle dt, \quad (7a)$$

$$\eta_{p1p2} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_{p1}(0) : \mathbf{J}_{p2}(t) \rangle dt, \quad \eta_{p2p1} = \frac{V}{3k_B T} \int_0^{\tau_p} \langle \mathbf{J}_{p2}(0) : \mathbf{J}_{p1}(t) \rangle dt. \quad (7b)$$

The contributions to the viscosity coefficient of pure benzene and NF with CNTs are presented in Table 2. Here, the length of the CNTs is 7.2 nm and their weight concentration is 3 %. The viscosity of NF is 12.9 % greater than that of benzene. This increase is mainly due to the potential contribution, which in turn has increased by 7.7 % due to the rise in the viscosity of the carrier fluid (η_{p1}), and by 5.2 % due to the viscosity of the nanotubes (η_{p2}). The latter term determines

not only the interaction of the nanotubes themselves, but also the cross-interaction of CNTs with the base fluid molecules (see (7a) and (7b)).

The viscosity of fluid is determined by the local destruction of the short-range order within the fluid and the formation of a new order. The contributions of η_{p1} and η_{p2} to the viscosity coefficient (1) encompass direct interactions between the base fluid molecules and CNTs as well as cross-interactions between CNTs and the base fluid molecules. The increase in viscosity should therefore be attributed to a change in the structure of the base fluid in the NF, and the possible formation of a short-range order of the CNT pseudo-fluid. The radial distribution function (RDF) serves as an indicator of the fluid short-range order. The structuring of base fluid molecules around spherical NPs by MD method has been established previously [51, 52]. This structuring is determined by the surface area of NPs at given interaction potential parameters.

Similarly, the structuring of the base fluid molecules near the CNTs also occurs in the NF. Fig. 3 presents a comparison of the RDFs (g_2) of benzene fluid molecules (solid line) and benzene molecules of the NF with 1.1-nm diameter CNTs and 1.45, 3.56, 7.25, and 14.61 nm long. In all cases, the volume concentration of CNTs is 2 %. As the length of the nanotubes increases, the RDF maxima of benzene molecules in the NF and the short-range order extent also increase. At the maximum length of the CNTs, the first maximum of the RDF exceeds the corresponding value for pure benzene more than twice. The second, third, and subsequent maxima increase even more. In addition, the extension of the short-range order in NF with CNTs nearly doubles in comparison with that in pure benzene. The viscosity of the fluid also increases with the growth of the magnitude of the RDF maxima and their number. Structuring of the base fluid molecules around CNTs is exactly one of the main factors influencing the growth of the viscosity of NF. As previously mentioned, the structuring of the molecules depends on the surface area of NPs or CNTs. In paper [29], it was shown that the surface area of CNT is almost always larger or even much larger than the surface area of a spherical NP (at the same CNTs concentration, of course). As a result, the structuring of the base fluid molecules near CNT is significantly greater than near a spherical NP. Therefore the viscosity of the NF with CNTs will be greater than that of the NF with spherical NPs.

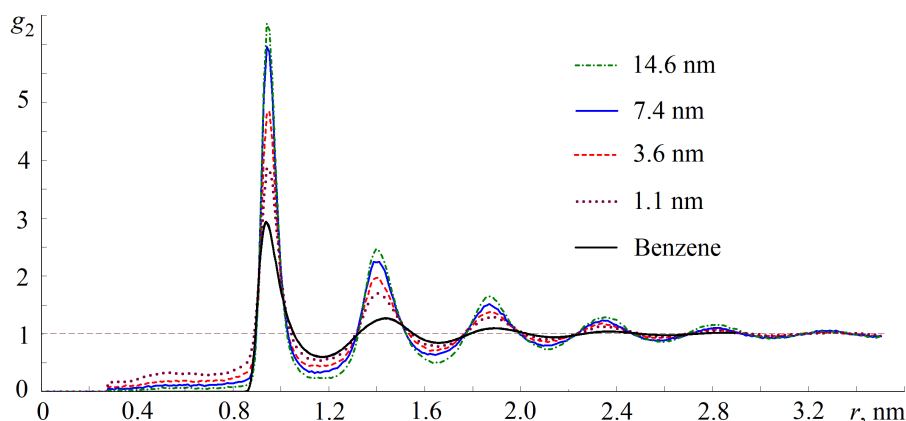


FIG. 3. Radial distribution functions of benzene molecules in benzene and benzene-based nanofluid containing different size CNTs

The analysis of data in Table 2 shows that the contribution made by the term η_{p2} to the viscosity coefficient is rather significant. This, in particular, may indicate the structuring processes of CNT pseudogas. Such structuring can also be studied by analyzing the corresponding RDFs, which are shown in Fig. 4. Here, in all cases, the volume concentration of CNTs is equal to 2 %. The behavior of the RDF strongly depends on the CNT length. At the maximum CNT length, a short-range order from CNTs starts to form in the NF.

In experiments examining the viscosity and rheology of NF with SWCNTs, it was demonstrated that starting from CNT weight concentrations of 0.05 %, the NF exhibits non-Newtonian behavior [7, 17, 18]. This rheological behavior is largely related to the percolation of CNTs within the NF. The formation of a percolation structure of CNTs in the NF is a threshold phenomenon that is dependent on the concentration of CNTs. The corresponding critical concentration is determined by the average distance between CNTs. Once the distance between the CNTs reaches the order of the radius acting of van der Waals forces, percolation begins to form. In the above presented MD computation data percolation was not observed. This is due to two circumstances. Firstly, the concentration of CNTs was insufficient for this purpose, since CNT length is relatively small. The second reason is that the interaction of CNT atoms is determined by the potential (3), whereas in real CNTs, the van der Waals forces acting between them are significantly larger [53, 54].

4. Viscosity of hybrid nanofluids

Analysis of the data from the above MD computations allows concluding in general terms what result should be expected when simulating the viscosity of HNFs. The viscosity of NFs comprising both NPs and CNTs is predominantly

TABLE 2. Contributions to the viscosity coefficient (mPa·s) of benzene and benzene-based nanofluid with CNTs, $w = 0.03$, $\varphi \approx 0.01$

	Benzene	Benzene–CNT
η	0.604	0.6819
η_k	0.0051	0.0056
η_p	0.5942	0.6732
η_{kp}	0.0047	0.0031
η_{p1}	0.5942	0.6412
$\eta_{p2} + \eta_{p1p2} + \eta_{p2p1}$		0.0320

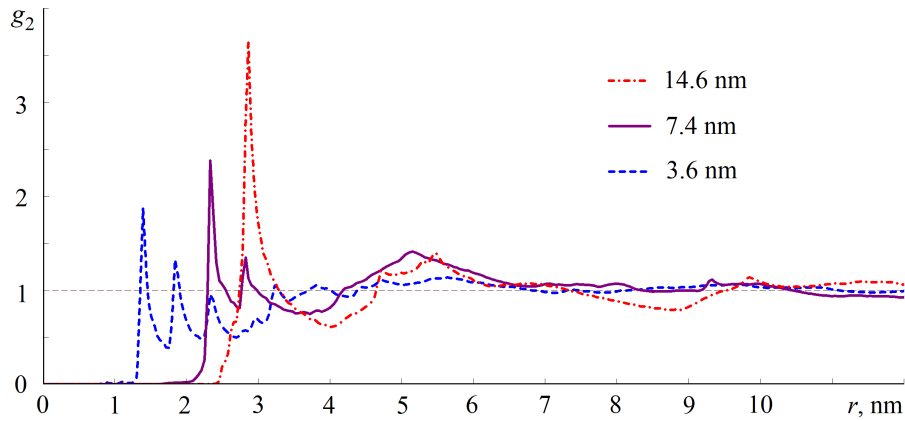


FIG. 4. Radial distribution functions of CNTs of different sizes in benzene-based nanofluid

influenced by the structuring of the base fluid molecules. In HNFs, the molecules of the base fluid are structured around both the NPs and the CNTs. For this reason, at a given volume concentration of NPs and CNTs, the molecules of the base fluid are significantly more structured compared to those in NF with NPs or NF with CNTs at the same volume concentration. Therefore, it is to be expected that the viscosity of the HNFs will be greater than that of the NF with NPs or NF with CNTs. However, this conclusion requires further verification.

The MD simulation data on the viscosity of HNFs with CNTs of length 14.6 nm and copper NPs of diameters equal to 1.4 and 3.2 nm in benzene at temperature $T = 25^\circ\text{C}$ and atmospheric pressure are presented in Fig. 5. The volume concentrations of CNTs φ_{CNT} were 0.5 or 1 %, and the concentration of Cu NPs φ_p ranged from 1 to 5 %. Thus, the simulations provided information on the effects of both CNT and Cu NP concentrations on the viscosity of HNF. Fig. 5 presents the MD simulation data on the dependence of the relative viscosity coefficient of the specified benzene-based HNF on the NP volume concentration at fixed CNTs volume concentration (0.5 or 1 %). The HNF with CNTs at a concentration of 1 % as well as 1.4 nm copper NPs are represented by circle symbols, whereas those with a size of 3.2 nm are depicted by rhombus symbols. Triangle symbols correspond to the CNTs and 1.4 nm copper NPs at a volume concentration of 0.5 %. The presented data indicate that the viscosity of HNF is significantly higher than the viscosity of NF with CNTs (see Fig. 2) and the viscosity of NFs with NPs (see data in [29]). Furthermore, it should be noted that the viscosity of HNF increases with increasing CNT concentration. Finally, the viscosity of HNF depends on the size of the NPs; it is greater the smaller the size of the NPs.

The dependences shown in Fig. 5 are well approximated by the following quadratic function of the effective volume concentration φ_{eff}

$$\eta_r = 1 + c_1\varphi_{\text{eff}} + c_2\varphi_{\text{eff}}^2, \quad (8)$$

where the effective volume concentration is determined by the following relation

$$\varphi_{\text{eff}} = \varphi_p + \varphi_{\text{CNT}}. \quad (9)$$

The constants c_1 and c_2 in formula (8) for the HNFs, presented in Fig. 5, are summarized in Table 3 (here d_p is the NP diameter in nm). The lines in Fig. 5 correspond to the correlation (8).

For a fixed CNT length and concentration, the viscosity of the corresponding HNF is determined by the NP concentration and size. The viscosity of HNF normalized to that of base fluid (benzene) is then be described by the following

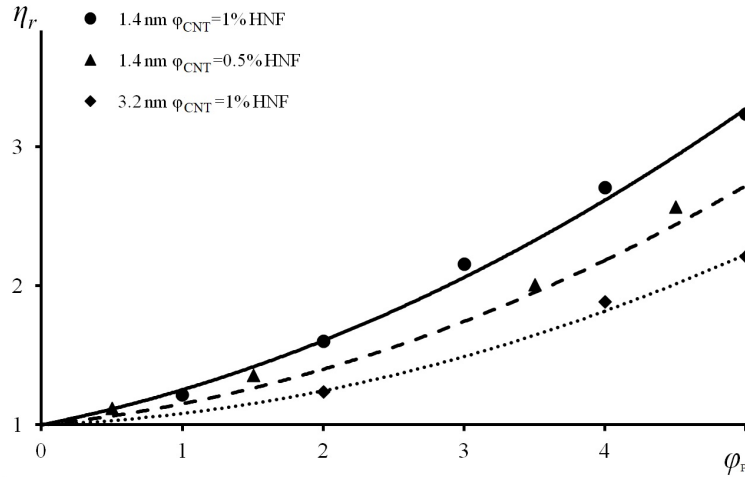


FIG. 5. Dependence of the relative viscosity coefficient of benzene-based hybrid nanofluids on the effective volume concentration of CNTs and nanoparticles

TABLE 3. Parameters of formula (8) for hybrid nanofluids

φ_{CNT}	d_p	c_1	c_2
1 %	1.4	16.169	555.84
1 %	3.2	4.098	408.88
0.5 %	1.4	37.695	104.4

correlation

$$\eta_r = \tilde{a}_0 + \tilde{a}_1 \varphi_p + \tilde{a}_2 \varphi_p^2, \quad (10)$$

For the studied nanofluids, the parameters $\tilde{a}_0$, $\tilde{a}_1$, and $\tilde{a}_2$ are summarized in Table 4.

TABLE 4. Parameters of correlation (11) for benzene-based hybrid nanofluids with CNTs and copper nanoparticles

$\varphi_{\text{CNT}}, \%$	d_p	$\tilde{a}_0$	$\tilde{a}_1$	$\tilde{a}_2$
1	1.4	1.22	28.85	526.82
1	3.2	1.22	7.02	418.20
0.5	1.4	1.12	40.48	70.96

5. Conclusions

In this paper, the MD method was used to simulate the viscosity coefficients of benzene-based NFs with CNTs and HNF with CNTs and copper NPs. In all cases, the dependence of the viscosity of these NFs and HNFs on the concentration of CNTs and NPs, as well as on the morphology of dispersed particles, was studied. The data obtained are systematically analyzed. The findings allow drawing the following conclusions.

- The viscosity of all the studied NFs is significantly higher than that of the base fluid and conventional coarse-dispersed fluids [7, 46].
- The viscosity coefficient of NF with CNTs at a given volume concentration increases with increasing their length (aspect ratio).
- The viscosity coefficient of NF with CNTs at fixed volume concentrations is higher than those for NF with spherical nanoparticles.
- One of the principal factors responsible for the observed increase in the viscosity of NF in comparison with the corresponding value for the base fluid is the structuring of the base fluid molecules near the NPs or CNTs. This structuring is determined by the parameters of the interaction potential between the base fluid molecules and the atoms of the NPs or CNTs, as well as their surface area.

- At equal concentrations, the viscosity of HNF significantly exceeds the viscosity of NF with NPs or CNTs and increases with decreasing in nanoparticle size. The obtained MD data fundamentally allow us to qualitatively predict the viscosity of HNFs with CNTs and NPs.
- The influence of the NPs and CNTs concentrations on the HNF viscosity can be described by the effective volume concentration (9). In this case the dependence of the HNFs on the effective concentration has the ordinary quadratic form (8).

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Submitted 2 May 2026; accepted 16 May 2026

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Conflict of interest: the authors declare no conflict of interest.

Skyrmion collapse and nucleation in synthetic antiferromagnet islands with pinned boundaries

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PACS 75.70.Kw, 75.70.Cn, 75.60.Jk, 75.75.+a

ABSTRACT Magnetic skyrmions in synthetic antiferromagnets are promising nanoscale bits, but their usefulness depends on how reliably a written pair survives and can be created. Using a reduced lattice model, we compute minimum energy paths for collapse of an antiferromagnetically bound skyrmion pair and for reverse nucleation from a pinned antiferromagnetic reference state. With antiferromagnetically pinned boundaries, the main saddle energy changes only weakly with pinned-island size, whereas the skyrmion-pair minimum carries a strong size-dependent boundary penalty. For large pinned islands, collapse is layer-sequential and can pass through a single-layer skyrmion intermediate whenever this state satisfies the relaxation criterion. The much larger reverse barrier for nucleation shows a strong asymmetry with collapse in the same pinned-boundary model and is consistent with assisted layer-sequential writing.

KEYWORDS synthetic antiferromagnets; magnetic skyrmions; minimum energy path; collapse barrier; nucleation barrier; racetrack memory.

ACKNOWLEDGEMENTS The study was supported by the Russian Science Foundation grant No. 24-72-00089, <https://rscf.ru/en/project/24-72-00089/>.

FOR CITATION Potkina M.N. Skyrmion collapse and nucleation in synthetic antiferromagnet islands with pinned boundaries. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 327–338.

1. Introduction

Magnetic skyrmions are localized chiral spin textures that can be moved by spin-polarized currents and are therefore considered as information carriers for racetrack-type memory and logic devices [1–3]. For memory applications, however, miniaturization creates a direct tension between bit density and thermal stability. Nanometer-scale skyrmions in ultrathin ferromagnetic films can have low activation barriers against collapse, whereas larger skyrmions stabilized by dipole–dipole interactions are less attractive for dense memory because stray fields increase their size and mediate unwanted long-range interactions between neighboring bits [4].

Antiferromagnetic and compensated ferrimagnetic systems offer a natural way to reduce these drawbacks. In compensated materials the net magnetization and dipolar fields are small, and the cancellation of the gyrotropic response suppresses the skyrmion Hall effect. Fast current-driven motion of domain walls and small skyrmions has been demonstrated in compensated ferrimagnets [5]. Transition-state-theory calculations for ideal antiferromagnetic films have shown that, in the absence of magnetostatic effects, the activation barriers and entropic factors for skyrmion collapse are closely related to those in corresponding ferromagnetic films, while the dynamics can modify the prefactor of the rate [6].

A practical difficulty in intrinsic antiferromagnets is detecting and controllably manipulating individual topological textures. This has motivated the use of synthetic antiferromagnets (SAFs), where two ferromagnetic layers are separated by a nonmagnetic spacer that mediates antiferromagnetic Ruderman–Kittel–Kasuya–Yosida (RKKY) coupling [7]. The ferromagnetic layers can be optimized separately, the interlayer coupling can be tuned by the spacer, and the two components of a coupled skyrmion pair remain accessible to layer-sensitive probes. Early theoretical work proposed multilayer SAF racetracks as thermally robust skyrmion conduits with suppressed transverse motion [8]. Bilayer theory further showed that interlayer coupling can bind skyrmions in the two films and modify their collective response compared with isolated ferromagnetic skyrmions [9]. Artificial SAF multilayers also provide a tunable platform in which the effective coupling and field balance can be adjusted by the multilayer design [10]. Subsequent experiments demonstrated room-temperature formation and current-induced motion of synthetic antiferromagnetic skyrmion bubbles with negligible skyrmion Hall deflection [11], room-temperature stabilization of antiferromagnetically coupled skyrmions of about ten nanometers in Pt/Co/Ru-based SAFs [12], and zero-field skyrmions in uncompensated SAF multilayers [13]. Material-specific modeling of Co/Pt-based multilayers has clarified how DMI, anisotropy, layer thickness, and interlayer exchange select FM- or AFM-coupled skyrmion states [14]. More recent experiments have shown local nucleation by current injection and ultrafast laser pulses [15] and current-induced motion in compensated SAFs with velocities up to

hundreds of meters per second [16]. These results establish SAF skyrmions as a realistic platform for memory and logic devices.

The writing problem is more challenging than controlling motion. Several assisted writing protocols have already been proposed or demonstrated. Local current injection and ultrafast laser excitation can nucleate SAF skyrmions [15]. Voltage-controlled magnetic anisotropy has been proposed for writing a skyrmion at a chosen position in an SAF race-track [17]. Thermal assistance has been used to control skyrmion generation in SAFs [18]. In single-layer skyrmion tracks, nonmagnetic impurities and engineered defects can also affect skyrmion memory operation [19]. MEP calculations have shown, in particular, that notches and linear vacancy defects can lower nucleation barriers [20, 21]. Hybrid ferromagnet/SAF geometries have also been proposed, where a skyrmion created in a ferromagnetic section enters the SAF section and generates a corresponding skyrmion in the second layer through interlayer exchange coupling [22]. Together, these works make assisted or sequential writing technologically plausible. The question here is whether a layer-by-layer route is only a convenient dynamical protocol, or also a feature of the energy landscape of a pinned SAF island.

The thermal stability of skyrmions is determined by rare transitions between local minima of the magnetic energy. Minimum energy path (MEP) calculations and harmonic transition state theory (HTST) provide a microscopic way to find the relevant saddle points and activation barriers [23, 24]. A complete thermal-stability estimate would additionally require the dynamical prefactor, Hessian determinants, and conversion of the reduced energy scale to the physical multilayer. For single-layer skyrmions, related MEP studies have shown that size, texture shape, and field-dependent shifts of metastable and saddle-point energies all enter the activation barrier [25, 26]. For SAFs, previous calculations have shown that interlayer exchange can change both the collapse barrier and the collapse mechanism [27, 28]. These studies established that interlayer coupling can produce non-simultaneous, layer-resolved collapse. The new elements addressed here are the behavior of this mechanism in pinned islands, the lateral-size dependence of the interior-collapse barrier separated into saddle and pair-minimum contributions, the connection between collapse and the reverse layer-sequential nucleation path on the same MEP, and the stability map of the independently relaxed upper-layer single-skyrmion intermediate. However, for a skyrmion used as a memory bit, two distinct questions must be separated. The first is barrier-limited retention: what collapse barrier protects an already written skyrmion pair against thermally activated decay? The second is writability: if the pinned collinear antiferromagnetic state is the unwritten reference state, what route can create the skyrmion pair without relying on exponentially rare spontaneous nucleation?

Here we calculate MEPs for collapse and nucleation of bound skyrmion pairs in pinned SAF islands using a reduced lattice model parameterized, for the retained interaction terms, from the length and energy scales of the Legrand-type SAF stack [12]. The experimental stack used for this parameterization consists of two magnetic layers separated by a nonmagnetic metal layer. The effective exchange interaction between magnetic layers, described by the Ruderman–Kittel–Kasuya–Yosida (RKKY) mechanism, has a strength and sign that depend on the thickness of the nonmagnetic spacer. This thickness is chosen so that the interlayer interaction is antiferromagnetic. The magnetic layers are Co films interfaced with the heavy metal Pt, which induces Dzyaloshinskii–Moriya antisymmetric exchange in the magnetic subsystem. To obtain spatially localized bound skyrmion pairs in the SAF, additional $[\text{Pt}(0.45 \text{ nm})/\text{Co}(0.6 \text{ nm})]_4$ magnetic layers with strong perpendicular uniaxial anisotropy were introduced into the system. These layers induce a fixed effective bias field $\mathbf{B}_b$ via the Pt spacer in the nearest magnetic layer of the SAF.

The model retains intralayer exchange, interfacial DMI, antiferromagnetic RKKY coupling, and Zeeman terms for the applied field and the fixed effective bias field, which are the interactions most directly involved in the collapse path studied below. It is a reduced energy-landscape model rather than a full micromagnetic description of the experimental multilayer: perpendicular anisotropy, magnetostatic/dipolar fields, and dynamical prefactors are not included explicitly. Antiferromagnetic compensation in SAFs is expected to reduce the net moment and the long-range stray field, which is one reason such structures are attractive for dense skyrmion devices [7, 8]. Residual demagnetizing fields from unequal layer textures, finite layer separation, and edges can still matter, especially in asymmetric multilayers [29]. The calculations therefore identify mechanisms and trends within the retained interactions; quantitative skyrmion radii, stability windows, activation barriers, and lifetimes for a specific Legrand- or Juge-type stack require the omitted terms and prefactors.

Here the pinned island has a limited role: it lets us estimate the saddle point for an interior collapse event in an infinite or sufficiently large collinear SAF region, provided the saddle is localized away from the artificial boundary. For such a localized saddle, increasing the island size gives a direct convergence check, and the saddle energy is the quantity the method is designed to estimate accurately. The boundary correction to the energy of the skyrmion-pair minimum is treated only approximately. Since fixed boundary spins impose an additional constraint on the relaxed texture, the calculated pair energy should be regarded as an upper-bound estimate for the corresponding skyrmion-pair branch when boundary relaxation is allowed. The reported barriers combine a localized interior-saddle estimate with a boundary-dependent estimate of the skyrmion-pair minimum. This distinction explains the size trend: changes in the pinned-boundary barrier can originate from the boundary penalty to the skyrmion-pair energy rather than from a comparable shift of the interior saddle. Accordingly, “barrier” below means the calculated pinned-boundary MEP-channel barrier unless explicitly stated otherwise.

Within this reduced model, the MEPs lead to three main conclusions. First, for the antiferromagnetically pinned boundary used here, the calculated interior saddle energy varies only weakly with pinned-island size, while the energy

of the skyrmion-pair minimum changes strongly. For the parameters studied below, the pinned-boundary collapse barrier of this channel is almost zero in the smallest pinned island, reaches several exchange energies for intermediate sizes, and becomes largest for the largest islands considered because it is measured as $\Delta E_{\text{coll}} = E_{\text{sp}} - E_{\text{pair}}$. The applied field produces only a secondary change over the explored range. Second, the collapse is generally not simultaneous in the two SAF layers. For the field orientation used here, the lower-layer skyrmion collapses first and the path can pass through a single-skyrmion state in the upper layer. This upper-layer state satisfies the relaxation-based local-minimum criterion only in part of the size-field diagram; when it is absent, the collapse becomes effectively single-stage. Third, the reverse nucleation barrier from the pinned collinear antiferromagnetic reference state is much larger than the collapse barrier of an already written pair. Within the same reduced barrier picture, this makes spontaneous formation along the calculated path unlikely but also makes direct thermal nucleation an inefficient writing route. This points to layer-sequential writing: if the upper-layer skyrmion is created or injected first, interlayer exchange can complete the bound SAF pair through a lower second-step barrier.

2. Model and method

We use a lattice spin model representing two ferromagnetic layers of an SAF separated by a nonmagnetic spacer. Each lattice site carries a unit vector $\mathbf{S}_i^{(l)}$, where $l = 1, 2$ labels the two magnetic layers. The intralayer interactions include ferromagnetic exchange and Dzyaloshinskii–Moriya interaction (DMI). The two layers are coupled antiferromagnetically through an RKKY-type interlayer exchange. Following the experimental geometry of Ref. [12], a third, uniformly magnetized bias layer is not treated dynamically; its effect is included as a fixed effective bias field acting on the lower SAF layer.

The reduced Hamiltonian is written as [28]

$$\begin{aligned} \mathcal{E} = & - \sum_{l=1}^2 \sum_{\langle i,j \rangle} \left[J \mathbf{S}_i^{(l)} \cdot \mathbf{S}_j^{(l)} + \mathbf{D}_{ij} \cdot (\mathbf{S}_i^{(l)} \times \mathbf{S}_j^{(l)}) \right] \\ & - J_{12} \sum_i \mathbf{S}_i^{(1)} \cdot \mathbf{S}_i^{(2)} - \mu \sum_i \left[(\mathbf{B}_b + \mathbf{B}) \cdot \mathbf{S}_i^{(1)} + \mathbf{B} \cdot \mathbf{S}_i^{(2)} \right]. \end{aligned} \quad (1)$$

Here $J > 0$ is the intralayer exchange constant. For a nearest-neighbor bond directed from site i to site j , $\mathbf{e}_{ij} = (\mathbf{r}_j - \mathbf{r}_i)/a$, the interfacial DMI vector is

$$\mathbf{D}_{ij} = D (\mathbf{e}_{ij} \times \mathbf{e}_z), \quad D > 0. \quad (2)$$

With this convention, bonds along $+\mathbf{e}_x$ and $+\mathbf{e}_y$ have $\mathbf{D}_{ij} = (0, -D, 0)$ and $(D, 0, 0)$, respectively, as in the numerical model. The interlayer coupling is antiferromagnetic, $J_{12} < 0$. The vector $\mathbf{B} = B\mathbf{e}_z$ is the applied field, identical for both SAF layers. The vector $\mathbf{B}_b = B_b\mathbf{e}_z$ is the fixed effective bias field from the additional layer, acting only on the lower layer ($l = 1$). Thus the net field entering the Zeeman term is $\mathbf{B}_b + \mathbf{B}$ in layer 1 and $\mathbf{B}$ in layer 2. Equation (1) is a reduced Hamiltonian. It keeps the local exchange, interfacial DMI, interlayer RKKY coupling, applied-field Zeeman term, and fixed effective bias field that enter directly into the collapse pathway considered below. The omitted terms include a separate perpendicular anisotropy, $-K \sum_i (S_{i,z}^{(l)})^2$, and the long-range dipole-dipole interaction. The stabilizing

influence of anisotropy and magnetostatics is therefore not resolved explicitly; instead, the calculation assumes that the skyrmion-pair and single-layer-skyrmion states can be relaxed for the chosen effective parameters. Consequently, the absolute stability windows, skyrmion radii, collapse paths, activation barriers, and lifetimes are model-level quantities rather than one-to-one predictions for the full multilayer.

The mapping from discrete parameters to micromagnetic ones is controlled by dimensionless ratios. For a square discretization with lattice constant a and magnetic layer thickness d , the intralayer exchange scale can be written as

$$J = 2d\mathcal{A}, \quad (3)$$

where $\mathcal{A}$ is the micromagnetic exchange stiffness. The DMI ratio is

$$\frac{|D_{ij}|}{J} = \frac{a\mathcal{D}}{2\mathcal{A}}, \quad (4)$$

where $\mathcal{D}$ is the interfacial DMI density. The interlayer RKKY coupling gives

$$\frac{|J_{12}|}{J} = \frac{a^2 \mathcal{J}_{\text{RKKY}}}{2d\mathcal{A}}, \quad J_{12} < 0, \quad (5)$$

where $\mathcal{J}_{\text{RKKY}}$ is the interfacial RKKY energy density. For the fixed-bias Zeeman term, the corresponding dimensionless parameter is

$$\frac{\mu B_b}{J} = \frac{a^2 M_s B_b}{2\mathcal{A}}, \quad (6)$$

where M_s is the saturation magnetization. Because the RKKY coupling is interfacial, its ratio to J scales as $1/d$. This distinction is important for device interpretation: changing the magnetic thickness can change both the absolute energy scale and the effective coupling ratios, whereas changing the lateral size S at fixed parameters mainly probes finite-size confinement. In this sense, parameterization from the Legrand-type SAF stack means that the length scale and the coefficients of the retained interaction terms are chosen from the corresponding micromagnetic and experimental scales. The complete Legrand multilayer also contains perpendicular anisotropy, magnetostatic fields, thickness-dependent material parameters, and the detailed bias-layer structure, all of which contribute to skyrmion stabilization.

The parameters of the retained terms were taken from the continuous-model scales and experimental data of Ref. [12]: $a = 0.2505$ nm, $d = 1.47$ nm, $\mathcal{A} = 10 \cdot 10^{-12}$ J/m, $\mathcal{D} = 0.5 \cdot 10^{-3}$ J/m², $\mathcal{J}_{\text{RKKY}} = 0.23 \cdot 10^{-3}$ J m⁻², $M_s = 1.2 \cdot 10^6$ A/m, $B_b = 50$ mT, which gives the following set of discrete-model parameters: $J = 183.5$ meV, $D/J = 6.3 \cdot 10^{-3}$, $|J_{12}|/J = 5 \cdot 10^{-4}$, $\mu = 12\mu_B$. The pinned islands are represented as square regions on square lattices, with linear size S in lattice units. The MEP barrier calculations use $S = 100, 300$, and 500 , with applied fields $B = -25, 0, 10, 20, 30$ mT. With $a = 0.2505$ nm, these three sizes correspond to lateral lengths of approximately 25, 75, and 125 nm, respectively. The stability diagram of the upper-layer intermediate in Fig. 4(b) is obtained from an additional grid of independent relaxations with $S = 100, 200, 300, 400, 500$ and $B = -20, -10, 0, 10, 20, 30$ mT. The boundary spins are pinned in the antiferromagnetic state and kept fixed throughout the calculation. The pinned sites form the outermost lattice contour of the island; all interior spins are free to relax. Such a boundary condition is best viewed as a pinned island embedded in an extended collinear antiferromagnetic background, or as an island coupled to a rigid antiferromagnetic surrounding. It fixes the far-field background and focuses the calculated MEP on interior collapse; open-edge deformation, skyrmion escape, and edge-assisted annihilation paths are outside this boundary-value problem. The fixed edge also suppresses DMI-induced twisting of the homogeneous reference state. Thus E_{AFM} below is the energy of the pinned collinear reference state. Pinning changes the absolute energies of finite-size skyrmion states because the texture cannot relax freely at the boundary. This effect is expected to be strongest for the smallest pinned island, where the skyrmion-pair texture occupies a large fraction of the island. Since pinning restricts the variational space, the relaxed skyrmion-pair energy obtained in this way is an upper-bound estimate for the corresponding pair state when boundary relaxation is allowed. To the extent that the main saddle is more localized in the interior than the relaxed pair, its energy relative to the pinned collinear background is less sensitive to the missing edge relaxation. This is the intended interpretation of E_{sp} : an estimate of the interior-collapse saddle in a fixed extended antiferromagnetic background, not a free-edge saddle of an isolated island. Because E_{pair} is raised by the boundary constraint, $\Delta E_{\text{coll}} = E_{\text{sp}} - E_{\text{pair}}$ tends to underestimate the interior-channel barrier. Competing open-edge routes may have smaller barriers and are separate problems. The size dependence reported below is therefore the lateral-confinement trend of this pinned-boundary interior-collapse channel. For each MEP parameter set we separately relax the homogeneous antiferromagnetic state, the bound skyrmion pair, and an initial state with a skyrmion only in the upper layer ($l = 2$). These single-configuration relaxations are performed by nonlinear conjugate gradient minimization on the fixed-length spin manifold until the maximum tangent-space energy gradient is below 10^{-9} in units of the exchange energy J . Under this relaxation, the homogeneous antiferromagnetic state remains unchanged within numerical precision and is used as the pinned collinear reference state in the MEP analysis. For the field orientation used here, the optimized collapse paths first lose the lower-layer skyrmion ($l = 1$), so the stationary intermediate, when it exists, is the upper-layer skyrmion. The lower-layer-only configuration is not a separate intermediate on the reported MEPs. The independently relaxed upper-layer state is used to test the local stability of intermediate images by this relaxation criterion. MEPs connecting the skyrmion pair and the homogeneous state are obtained with a constrained MEP algorithm for fixed-length magnetic moments [24, 30, 31]. The path is represented by a sequence of spin configurations, or images, on the product of unit spheres. The end images are the relaxed local minima; they are kept fixed. The initial path is generated by linear interpolation in the embedding spin-vector space, followed by renormalization of each spin to unit length. The number of images is increased with the accumulated Euclidean length of the path, which grows with pinned-island size. The final optimized chains used in the figures contain 20, 23–37, and 27–37 images for $S = 100, 300$, and 500 , respectively, including the two fixed endpoint images.

At each iteration the energy gradient of every free spin is projected onto the local tangent plane of the unit sphere, and the path tangent is estimated from neighboring images using the energy-weighted prescription of the climbing-image NEB method. Moving images are relaxed using the component of this tangent-space gradient perpendicular to the path. Images at energy maxima are treated as climbing images; for these images the tangential component is reversed so that the image converges to the saddle point on the MEP. Images at energy minima along the path are treated as descending images. After every relaxation step all spins are projected back to unit length, and the moving images are redistributed by interpolation at equal intervals of accumulated Euclidean distance. The extrema images are kept fixed during this reparametrization, as in the constrained implementation of Ref. [31].

The distance between two images p_m and p_n is the Euclidean distance in the embedding spin-vector space,

$$\ell(p_m, p_n) = \left[\sum_{l=1}^2 \sum_{i \in \Omega} |\mathbf{s}_{i,m}^{(l)} - \mathbf{s}_{i,n}^{(l)}|^2 \right]^{1/2}, \quad (7)$$

where Ω denotes the spins included in the path; fixed boundary spins make no contribution because they are identical in all images. The horizontal coordinate in the MEP plots is the accumulated distance $s_n = \sum_{m < n} \ell(p_m, p_{m+1})$.

Convergence of the path is monitored by the maximum tangent-space force perpendicular to the path for moving images and by the full tangent-space force at the climbing and descending images. For the stationary configurations used as endpoints, saddle points, and intermediate minima, the maximum tangent-space energy gradient after the final relaxation is below 10^{-9} in units of the exchange energy J . The number of images and relaxation iterations were increased until the saddle energies and the presence or absence of the single-layer minimum no longer changed at the energy resolution used for the path analysis. All reported barriers are evaluated from the optimized discrete images, not from the interpolating curves used only for plotting. Candidate saddle points are the final climbing images at strict local maxima of the discrete energy profile. Their position is checked by an additional reparametrization of the neighboring moving images; the images on the two sides must relax toward the adjacent minima or endpoints. The upper-layer single-skyrmion state is counted as locally stable only when the corresponding path image is a strict discrete minimum, relaxes independently by nonlinear conjugate gradient to a stationary configuration with maximum tangent-space gradient below $10^{-9}J$, and is separated from adjacent saddle configurations on the optimized path. For the accepted intermediate minima in the final data, the smallest energy decrease relative to the neighboring images is $8 \times 10^{-4}J$; shallower features below $5 \times 10^{-4}J$ are treated as numerical path resolution rather than as separate metastable states. No Hessian spectra were evaluated in the present work. Consequently, the stability classification is based on nonlinear relaxation and discrete MEP structure rather than on a positive-definite Hessian test. The saddle terminology refers to the climbing-image stationary points on the optimized MEP, while quantitative HTST prefactors are outside the scope of the calculation.

Two activation barriers are useful. The collapse barrier of an already written skyrmion pair is

$$\Delta E_{\text{coll}} = \max_{\text{path}} E - E_{\text{pair}}, \quad (8)$$

where E_{pair} is the energy of the bound pair. The reverse barrier from the pinned collinear antiferromagnetic reference state is

$$\Delta E_{\text{nuc}} = \max_{\text{path}} E - E_{\text{AFM}}. \quad (9)$$

Throughout this paper, the terms “collapse” and “nucleation” refer to thermally activated transitions on the static energy landscape of Eq. (1), with no nonconservative driving force. Thus ΔE_{nuc} is an equilibrium reverse MEP barrier for spontaneous formation along this path. Current-, voltage-, laser-, or geometry-assisted writing is a nonequilibrium process and need not follow the reverse static MEP; the reverse path calculated here provides a reference energy scale and identifies possible intermediate states for such driven protocols. In the pinned-boundary MEPs below, the relaxed homogeneous state is lower in energy than the calculated pair minima, so $E_{\text{pair}} - E_{\text{AFM}} > 0$ and ΔE_{nuc} is much larger than ΔE_{coll} . These statements are conditioned on the pinned-boundary states and reference energy defined above. The optimized MEPs reported below define one interior collapse/nucleation channel for this boundary-value problem; random, spiral, edge-twisted, and edge-escape routes were not searched for competing lower barriers.

3. Results

3.1. Layer-by-layer collapse mechanism

Figure 1 shows representative configurations along the MEP for $B = 30$ mT and $S = 500$. The initial state is a bound skyrmion pair with opposite core magnetizations in the two layers. Skyrmions in the upper and lower layers have different sizes because the lower layer is subject to a net field of magnitude $B_b + B = 80$ mT, opposite to the direction of magnetization at the skyrmion core, while the upper layer is subject only to the applied field of magnitude $B = 30$ mT, parallel to the magnetization at the center. Increasing the applied field decreases the skyrmion size in the lower layer but increases it in the upper layer. When the applied field is set to $B = -B_b/2$, the skyrmion radius in both layers is the same. The collapse is not simultaneous. First, the skyrmion in the lower layer collapses through the higher saddle point, while the skyrmion in the upper layer remains localized. The path then relaxes to a local minimum corresponding to a single skyrmion in the upper layer. The second, lower saddle point corresponds to the collapse of this remaining skyrmion, after which the system reaches the homogeneous antiferromagnetic state. Equivalently, the layer-resolved topological charge changes sequentially. The initial SAF pair has one skyrmion charge in each layer, with opposite signs for the antiferromagnetically coupled textures. At the first saddle the lower-layer charge changes to zero, while the upper-layer charge remains nonzero. The intermediate therefore carries topological charge only in the upper layer. At the second saddle this remaining charge is also lost, and the final pinned collinear state has zero topological charge in both layers.

The same structure is seen in the full set of MEPs in Fig. 2. The path starts from the skyrmion-pair minimum at positive energy relative to the pinned collinear reference state. It then climbs to the main saddle point, drops to the energy range of the upper-layer skyrmion, crosses a lower saddle point, and finally reaches the homogeneous state. The position along the horizontal axis is the accumulated Euclidean distance in the full spin configuration space; it is therefore larger for larger pinned islands and should not be interpreted as a real-space coordinate.

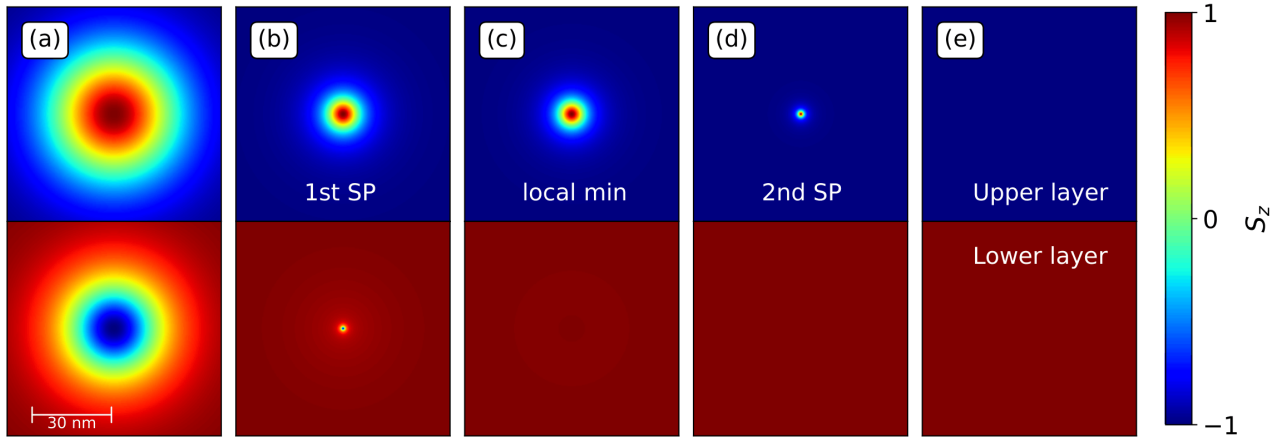


FIG. 1. Configurations along the minimum energy path for skyrmion-pair collapse at $B = 30$ mT and $S = 500$. The color scale shows the spin component S_z . The top row shows the upper layer and the bottom row shows the lower layer. Only the central 300×300 spins of the full system are shown. The path starts from a bound skyrmion pair (a). At the first saddle point the lower-layer skyrmion collapses (b), leaving a local minimum with a single skyrmion in the upper layer (c). The remaining skyrmion collapses through the second saddle point (d), and the path ends in the pinned homogeneous antiferromagnetic reference state (e).

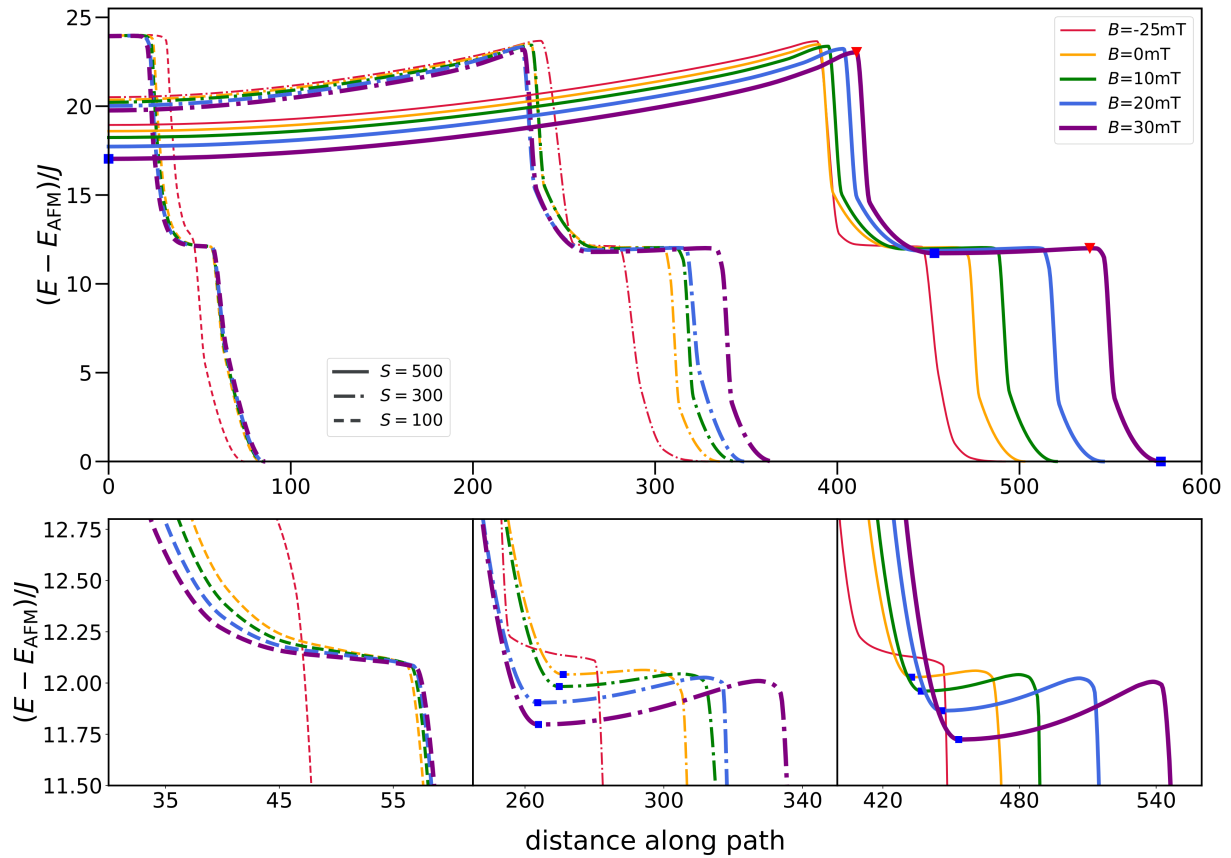


FIG. 2. Minimum energy paths for skyrmion-pair collapse at different applied fields B and pinned-island sizes S . Energies are measured relative to the pinned homogeneous antiferromagnetic reference state. Representative local minima and saddle points are marked by squares and triangles, respectively. The lower insets enlarge the single-layer-skyrmion segment; from left to right, they correspond to $S = 100, 300$, and 500 . In all panels, color and line width code B , while the dash pattern codes S (dashed 100, dash-dotted 300, solid 500). The intermediate minimum is the upper-layer skyrmion.

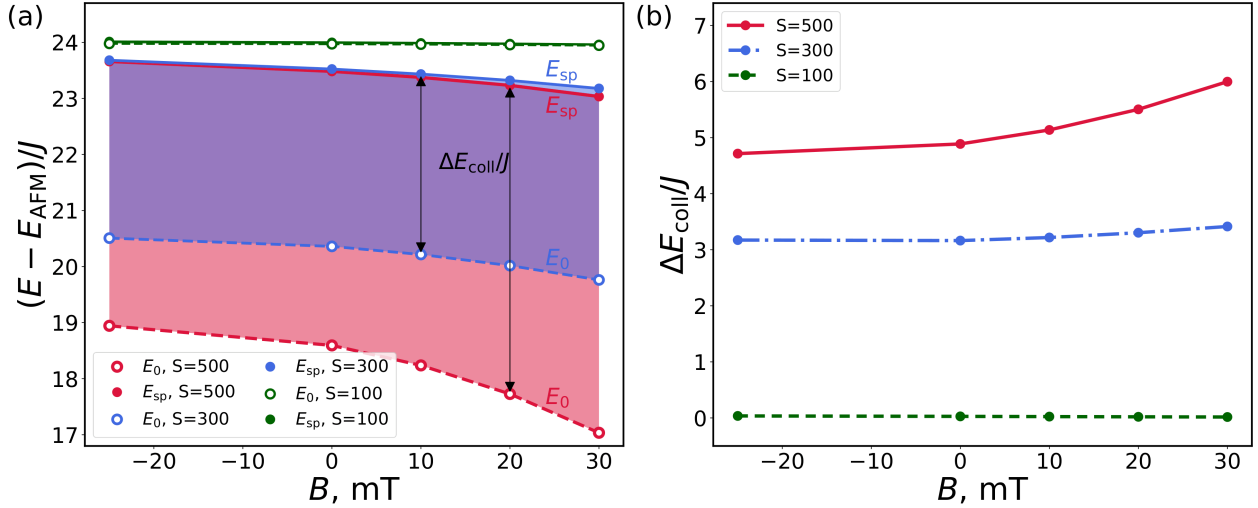


FIG. 3. (a) Energy of the skyrmion-pair minimum E_0 and the main saddle point E_{sp} relative to the pinned collinear antiferromagnetic reference state as a function of the applied field B . (b) Pinned-boundary interior collapse barrier $\Delta E_{\text{coll}} = E_{\text{sp}} - E_0$ for different pinned-island sizes S . In panel (b), line styles encode S as in Fig. 2. In this pinned-boundary calculation, the size dependence of the barrier is dominated by the strong change of the skyrmion-pair minimum E_0 , while the main saddle energy varies much more weakly.

The reverse process follows the same MEP in the opposite direction. Starting from the pinned collinear reference state, the upper-layer skyrmion is nucleated first, and only then is the lower-layer partner nucleated. When this single-layer state is a local minimum, it is a genuine intermediate on the path.

3.2. Interior collapse barrier and role of confinement

Figure 3 shows the energy of the skyrmion-pair minimum E_0 and the energy of the main saddle point E_{sp} , together with the resulting collapse barriers for this MEP channel. The skyrmion pair is a local minimum in all cases shown, although its energy lies above the pinned collinear reference state. The two energy branches have different size dependences. The main saddle energy varies comparatively weakly with S and remains in a narrow interval near 23–24 J . By contrast, the absolute energy of the skyrmion pair depends strongly on pinned-island size and should be read as an upper-bound estimate that includes the boundary penalty imposed by the fixed collinear edge. For $S = 100$, E_0 is close to 24 J and is nearly degenerate with the saddle point, leading to an almost vanishing collapse barrier. For $S = 300$, E_0 lies near 20 J and the barrier is about 3.1–3.4 J . For $S = 500$, E_0 decreases from about 19 J at $B = -25$ mT to about 17 J at $B = 30$ mT, while the saddle energy remains near 23 J . As a result, the barrier of this channel increases from about 4.7 J to about 6.0 J .

The main observation from Fig. 3 is that the pinned-boundary energy barrier for collapse $\Delta E_{\text{coll}} = E_{\text{sp}} - E_0$ is controlled mainly by the skyrmion-pair energy rather than by a variation of saddle energy. Increasing B also raises the barrier by lowering the skyrmion-pair energy, but over the explored interval its effect is moderate compared with the change of lateral size from $S = 100$ to $S = 500$. The smallest pinned island is an important limiting case: the relaxed pair exists as a local configuration, but the saddle point is so close in energy that the pair has essentially no barrier protection against thermal collapse. For an open finite island, the corresponding barrier would have to be recalculated with boundary relaxation and possible edge-assisted paths.

The field-induced increase of the barrier is almost absent for $S = 100$ and becomes noticeable only for $S \gtrsim 300$. Thus, over the explored range, an applied field acts as a secondary tuning parameter compared with lateral confinement.

In the reduced model, this result gives a qualitative estimate for the calculated interior collapse channel. In HTST, the lifetime of a metastable state has the Arrhenius form

$$\tau \simeq \tau_0 \exp \left(\frac{\Delta E_{\text{coll}}}{k_B T} \right), \quad (10)$$

where τ_0 contains the dynamical and entropic prefactors. With the parameter mapping used here, $J = 183.5$ meV. Representative reduced barriers of 3 J , 5 J , and 6 J therefore correspond to approximately 0.55, 0.92, and 1.10 eV, or about 21, 35, and 43 in units of $k_B T$ at $T = 300$ K ($k_B T \simeq 25.9$ meV). These numbers are useful for interpreting the exponential factor of the pinned-boundary reduced Hamiltonian, but an absolute lifetime would also require the Hessian and dynamical prefactors, the omitted anisotropy and magnetostatic contributions, and a check for competing edge-assisted paths. For a

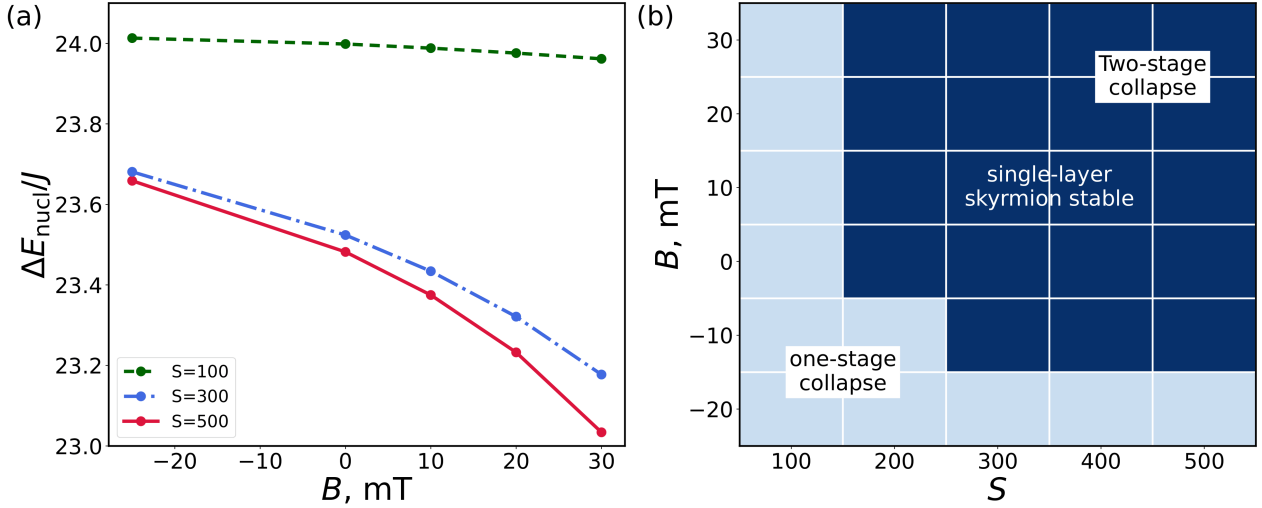


FIG. 4. (a) Reverse barrier ΔE_{nucl} from the pinned collinear antiferromagnetic reference state to the bound skyrmion pair along the same minimum energy path; line styles encode S as in Fig. 2. (b) Stability diagram for the upper-layer ($l = 2$) single-skyrmion intermediate as a function of applied field B and pinned-island size S . The bound skyrmion pair satisfies the relaxation-based local-stability criterion throughout the displayed region. Each colored cell represents one calculated grid point; no interpolation between grid points is used. The darker cells mark parameters where the upper-layer single-skyrmion state also satisfies this criterion: the state remains after independent nonlinear conjugate-gradient relaxation, the optimized MEP contains a strict intermediate minimum, and the minimum is deeper than $5 \times 10^{-4}J$ relative to the neighboring images. In these cells the collapse/nucleation path is genuinely two-stage, but the seed-decay barrier $E_{\text{sp},2} - E_{\text{lsk}}$ remains small, 0.022–0.282 J , compared with barrier for completing the pair $\Delta E_{\text{comp}} \approx 11J$.

given material and operating temperature, this gives the formal Arrhenius scale condition:

$$\Delta E_{\text{coll}}(S, B) \gtrsim k_{\text{B}}T \ln \left(\frac{\tau_{\text{ret}}}{\tau_0} \right), \quad (11)$$

where τ_{ret} is the target retention time. The figures show the dimensionless value $\Delta E_{\text{coll}}/J$; multiplying it by the material exchange scale J gives the energy scale of this pinned-boundary model barrier. Thus the present barrier map gives the Arrhenius exponent of the calculated interior collapse channel. The inequality is used here as a scale comparison for the exponential part of the rate; converting it into a device retention criterion requires the additional ingredients listed above.

3.3. Reverse barrier and assisted writing

The reverse transition has a very different energy scale. Fig. 4 shows the reverse barrier measured relative to the pinned collinear antiferromagnetic reference state. It is approximately 23–24 J over the whole parameter range, much larger than the collapse barrier of an existing skyrmion pair. The barrier decreases slightly with increasing positive applied field for the larger pinned islands, but the change is small compared with the absolute value of the barrier.

The numerical values underlying Figs. 2–4 are listed in Table 1. Here $E_{\text{sp},1}$ is the main, higher saddle point, $E_{\text{sp},2}$ is the lower saddle, and $\Delta E_{\text{comp}} = E_{\text{sp},1} - E_{\text{lsk}}$ is the barrier for completing the pair from intermediate minimum. The competing decay barrier of the intermediate is $E_{\text{sp},2} - E_{\text{lsk}}$.

The single-layer intermediate is a shallow state. Where it is present, its decay barrier $E_{\text{sp},2} - E_{\text{lsk}}$ is only 0.022–0.282 J . With $J = 183.5$ meV, this corresponds to about 0.16–2.0 $k_{\text{B}}T$ at room temperature. By contrast, the barrier for completing the pair from the same intermediate, ΔE_{comp} , is about 11 J . Thus, in an undriven thermal process, the single-layer state would be expected to decay over the lower saddle much more readily than to complete the pair. For writing, it marks a configuration that an external drive could create, maintain, or rapidly convert before it relaxes back to the pinned collinear state.

Within the calculated pinned-boundary MEPs, the barrier for nucleation is much larger than the interior collapse barrier in Fig. 3, implying a strong activation-barrier asymmetry between formation from the pinned reference state and this particular decay channel of an already written skyrmion bit. A large ΔE_{nucl} raises the Arrhenius exponent for spontaneous thermal formation from the pinned collinear state, which is desirable if this state represents the unwritten bit. The same large barrier also means that direct thermal nucleation of a complete SAF pair would be inefficient in this

TABLE 1. Numerical summary of the calculated MEPs. $L = Sa$ is the lateral size in nanometers. Energy columns are in units of J relative to the pinned collinear reference state. A dash means that no accepted upper-layer single-skyrmion minimum is present on the final discrete path.

S	L (nm)	B (mT)	N_{img}	E_0/J	$E_{\text{sp},1}/J$	$\Delta E_{\text{coll}}/J$	E_{1sk}/J	$E_{\text{sp},2}/J$	$\Delta E_{\text{comp}}/J$	$\Delta E_{\text{nucl}}/J$
100	25.1	-25	20	23.977	24.013	0.036	—	—	—	24.013
100	25.1	0	20	23.971	23.998	0.028	—	—	—	23.998
100	25.1	10	20	23.964	23.988	0.024	—	—	—	23.988
100	25.1	20	20	23.956	23.976	0.020	—	—	—	23.976
100	25.1	30	20	23.945	23.962	0.017	—	—	—	23.962
300	75.2	-25	23	20.508	23.681	3.173	—	—	—	23.681
300	75.2	0	32	20.360	23.524	3.164	12.042	12.064	11.482	23.524
300	75.2	10	32	20.215	23.434	3.219	11.983	12.045	11.451	23.434
300	75.2	20	32	20.017	23.321	3.304	11.904	12.027	11.417	23.321
300	75.2	30	37	19.762	23.177	3.415	11.798	12.010	11.380	23.177
500	125.3	-25	37	18.944	23.659	4.715	—	—	—	23.659
500	125.3	0	32	18.594	23.482	4.888	12.028	12.060	11.454	23.482
500	125.3	10	27	18.237	23.375	5.138	11.961	12.041	11.414	23.375
500	125.3	20	34	17.728	23.232	5.505	11.865	12.023	11.368	23.232
500	125.3	30	34	17.035	23.034	5.999	11.724	12.006	11.310	23.034

reduced model. Writing through this path would require an external drive, such as current, voltage, laser heating, or a geometric injector, to bypass or reshape the equilibrium energy barrier.

The two-stage path clarifies what such a drive should accomplish. If the system starts from the pinned collinear reference state and no external drive is maintained, the overall rare-event exponent along this path is still set by the highest saddle point relative to E_{AFM} . The intermediate minimum alone does not reduce the equilibrium reverse-path exponent. However, if the upper-layer skyrmion is deliberately created, or injected into the SAF region from a single-layer part of the device, the relevant second step starts from the upper-layer skyrmion minimum rather than from the pinned collinear reference state. The barrier for completing the pair is then the energy difference between the high saddle point and the single-layer minimum. In the paths shown here this is roughly half of the full static reverse barrier. This lower second-step barrier motivates layer-selective or layer-sequential writing.

3.4. Stability of the upper-layer intermediate

The intermediate upper-layer skyrmion does not always satisfy the relaxation-based stability criterion. Figs. 2 and 4(b) show enlarged parts of the MEPs and the corresponding relaxation-based stability map near the single-layer segment. For $S = 100$ the path contains no accepted local minimum in this region. After the lower-layer skyrmion collapses, the remaining upper-layer skyrmion is unstable, and the path continues directly toward the homogeneous state. In this sense, the collapse is effectively single-stage.

For $S = 300$, the upper-layer single-skyrmion state passes the relaxation criterion for most of the explored fields, although the minimum is shallow and absent or marginal at the most negative field. The depth of the minimum shifts with B , indicating that the applied field controls the stability of the upper-layer seed, even though it has a weaker effect on the total collapse barrier than the lateral size.

For $S = 500$, the local minimum is well developed for nonnegative fields, while the $B = -25$ mT path has no accepted intermediate minimum in the final discrete MEP. Where the minimum is present, the two-stage character of the path is well resolved: the pair first loses one of its two skyrmions, then the upper-layer skyrmion survives as a relaxed local configuration, and only after crossing the lower saddle point does the system become homogeneous.

The resulting relaxation-based stability map is summarized in Fig. 4(b). The bound skyrmion pair satisfies this criterion in the whole parameter range considered. The upper-layer single-skyrmion state satisfies it only in the darker region. Operationally, a darker cell means that the independently relaxed upper-layer state remains stationary with maximum tangent-space gradient below $10^{-9}J$, appears as a strict discrete MEP minimum, and has a depth of at least $5 \times 10^{-4}J$ relative to the neighboring path images. The state is absent in the smallest pinned islands, appears at nonnegative or weakly negative applied fields for intermediate sizes, and passes the relaxation criterion over a wider field range as the pinned-island size increases. However, Fig. 4(b) is an existence map of the local minimum rather than a passive-retention map for the seed. For every dark cell in the present parameter set, the barrier for losing the single-layer skyrmion, $E_{\text{sp},2} - E_{\text{1sk}}$, is only 0.022–0.282 J . This corresponds to 0.16–2.0 $k_{\text{B}}T$ at room temperature and is much smaller than $\Delta E_{\text{comp}} = E_{\text{sp},1} - E_{\text{1sk}} \simeq 11.3$ –11.5 J , the barrier for completing the pair from the same intermediate.

For writing, Fig. 4(b) complements the barrier plot. A layer-by-layer writing protocol requires the first skyrmion to be maintained long enough to seed the second layer. For the field orientation used here, this corresponds to first creating the upper-layer skyrmion and then the lower-layer partner. The dark region of the stability diagram identifies where such a state exists as a relaxed local minimum; the small decay barrier makes it an actively maintained intermediate rather than

a thermally robust seed. In the light region, an upper-layer seed is not metastable; a writing pulse would need to create the second skyrmion before the first one collapses, or maintain the seed dynamically throughout the process.

4. Model implications for SAF skyrmion memory

The calculated energy landscape of the reduced Hamiltonian distinguishes two quantities: the pinned-boundary interior collapse barrier and the reverse barrier for nucleation from the pinned collinear reference state. For fixed reduced-model parameters and this boundary condition, the pinned-island size is the dominant control parameter for the calculated interior-collapse channel. The size dependence enters mainly through the energy of the skyrmion-pair minimum: the interior saddle energy changes comparatively weakly, but the pair minimum is strongly affected by the fixed boundary. The smallest pinned island therefore has an almost zero barrier despite containing a relaxed skyrmion-pair configuration, whereas the larger pinned islands develop channel barriers of several exchange energies. Increasing the applied field raises the barrier in the explored range, but it does not compensate for strong lateral confinement. Thus a stationary relaxed pair in a small pinned island is insufficient to establish useful barrier-limited stability.

Changing the magnetic layer thickness is another parameter that could affect the barrier scale, but its effect is ambiguous. In a simple scaling picture, if the dimensionless texture and all coupling ratios remain fixed, $J \propto d$ and the activation barriers scale approximately linearly with the magnetic thickness. In that limit a thicker layer increases the barrier exponent without changing the shape of the MEP. In a real SAF, however, RKKY coupling is an interfacial effect controlled mainly by the spacer and interfaces. Increasing the magnetic thickness can therefore reduce J_{12}/J and the fixed-bias ratio in the effective lattice model, even while increasing the absolute exchange scale. Thickness changes should consequently be viewed as a trade-off between increasing the energy scale and preserving the effective interlayer coupling needed to bind the two skyrmions. Because thickness, anisotropy, and dipolar interactions are not taken into account explicitly in (1), the calculations provide a map of the retained effective parameters rather than an optimization of a real stack. In particular, no control MEP with an explicit perpendicular anisotropy K or with magnetostatic fields was performed. These terms can change the skyrmion radius, the local-stability region of the single-layer state, the absolute pair and saddle energies, and the numerical lifetime estimate in Pt/Co/Ru-based SAF stacks. The structural trends are the most likely to survive these added terms: once an antiferromagnetically bound pair exists, interlayer exchange and layer asymmetry can make the transition layer-resolved; the reverse static MEP can pass through a one-layer configuration; and this configuration can be useful for actively driven layer-by-layer writing. By contrast, the quantitative values of E_0 , E_{sp} , the decay barrier of the one-layer state, ΔE_{comp} , and the size threshold for useful stability should be recalculated in a model that includes perpendicular anisotropy and demagnetizing fields. Because SAF compensation reduces the long-range stray field but does not remove residual layer-imbalance and edge magnetostatics, such a calculation is also needed to decide whether a competing edge-assisted path becomes the lowest decay route in a real device geometry.

For writing, the relevant process is actively driven. Assisted writing of SAF skyrmions has already been studied by current pulses, laser excitation, voltage control, thermal effects, and hybrid FM/SAF geometries [15, 17, 18, 22]. In the pinned-boundary reduced model, the MEP connects the bound pair and the pinned collinear reference state through an upper-layer single-skyrmion intermediate. Therefore, for the present field orientation, a writing scheme that first creates the upper-layer skyrmion and then uses the interlayer exchange to generate its lower-layer partner is consistent with this reduced-model energy landscape, provided the drive maintains or rapidly converts the single-layer state.

A similar idea appears in hybrid FM/SAF proposals [22]. For example, one can consider an asymmetric island in which one ferromagnetic layer extends beyond the overlap region. A skyrmion is first nucleated in the single-layer or weakly compensated part, where layer-selective manipulation is easier, and then driven into the bilayer SAF region. Once inside the overlap region, the seed skyrmion produces a nonuniform exchange field that acts on the second layer and can assist the formation of the antiferromagnetically coupled partner skyrmion. The MEP calculations add that, in the explored parameter range, the upper-layer skyrmion satisfies the relaxation-based local-minimum criterion only above a size-dependent threshold, and even there its own decay barrier is small. They also show that completing the pair has a much smaller bottleneck when an external drive prepares and supports the upper-layer seed than when the system nucleates the full pair spontaneously from the pinned collinear reference state.

5. Conclusions

Minimum energy paths for pinned SAF islands show that the pinned-boundary activation energy for interior collapse along the calculated MEP channel is strongly affected by lateral confinement. This size trend is dominated by the skyrmion-pair minimum, whose energy carries the boundary penalty, rather than by a comparable shift of the localized saddle energy. In the parameter range studied here, the resulting barrier is nearly zero for $S = 100$, reaches about $3J$ for $S = 300$, and increases to about $5\text{--}6J$ for $S = 500$. Using $J = 183.5$ meV, these representative barriers correspond to roughly 0.55 eV and 0.92–1.10 eV, or about 21 and 35–43 in units of $k_B T$ at room temperature. The applied field also increases the barrier by lowering the skyrmion-pair energy, but its influence is weaker than that of the lateral size. Thus the smallest pinned island contains a relaxed stationary pair with negligible protection along the calculated interior-collapse channel, whereas the larger pinned islands develop channel barriers of several exchange energies.

This boundary condition matters, but the size trend remains clear. The pinned edge represents a fixed homogeneous antiferromagnetic background and suppresses edge twisting and skyrmion escape. It also raises the absolute energy of finite skyrmion-pair textures, so pair energies should be regarded as upper-bound estimates relative to boundary-relaxed calculations. The saddle energies, by contrast, characterize the localized interior collapse mechanism targeted by the MEP. The reported barriers therefore give the Arrhenius exponent for this reduced pinned-boundary channel; full lifetimes and device-level retention estimates require the omitted anisotropy, magnetostatic terms, HTST prefactors, and possible competing edge-assisted paths. Other decay routes, including edge-assisted ones, require separate calculations.

For the field orientation used here, the larger pinned islands show a layer-sequential transition. The lower-layer skyrmion collapses first, leaving an upper-layer skyrmion minimum when that state satisfies the relaxation criterion, and only then does the remaining skyrmion collapse. The reverse nucleation path is therefore also layer-sequential. The stability map shows where this upper-layer intermediate exists as a relaxed local minimum. However, its own decay barrier is small, about $0.02\text{--}0.28J$ in the accepted cases, so it is better viewed as an actively supported intermediate for layer-by-layer writing than as a thermally robust seed.

The reverse barrier for nucleation from the pinned collinear antiferromagnetic reference state is much larger than the collapse barrier of an already written pair, about $23\text{--}24J$ over the explored parameter range. This asymmetry makes spontaneous formation along the calculated path unlikely and points to assisted writing rather than direct thermal nucleation. In particular, if the upper-layer skyrmion is created or injected first, interlayer exchange can complete the bound SAF pair through a much smaller second-step barrier, provided the nonequilibrium drive acts before the single-layer seed decays. Overall, the MEPs separate two roles of the energy landscape: the interior-collapse barrier quantifies the size trend of the calculated decay channel, while the upper-layer intermediate provides a candidate state for actively driven layer-by-layer writing with this field orientation.

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Submitted 20 April 2026; revised 10 May 2026; accepted 12 May 2026

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Conflict of interest: the authors declare no conflict of interest.

Effect of spin-orbit interactions on an off-center D^0 impurity in an asymmetric quantum dot under a magnetic field

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ABSTRACT We evaluate the ground state energy of an off-centre Coulomb impurity in an asymmetric Gaussian GaAs quantum dot under a constant magnetic field. Using a unitary transformation, we take into account the combined effect of the Rashba and Dresselhaus interactions treating the coupling terms up to quadratic order. We next treat the transformed Hamiltonian using a variational approach with a suitable ansatz. The findings reveal that the ground state energy increases with growing impurity distance from the confinement centre and with increasing potential asymmetry. Finally, we examine how the asymmetry in the Gaussian confinement influences the magnetic moment and susceptibility of the impurity.

KEYWORDS Asymmetric GaAs quantum dot, off-centre impurity energy, spin-orbit interactions, magnetic field and susceptibility

FOR CITATION Saini P., Mukhopadhyay S., Popov I.Y., Chatterjee A. Effect of spin-orbit interactions on an off-center D^0 impurity in an asymmetric quantum dot under a magnetic field. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 339–345.

1. Introduction

Quantum dot (QD) systems have attracted significant interest due to their applications in semiconductor technology and their ability to probe quantum phenomena at the nanoscale [1–10]. Their discrete energy spectrum and strong confinement lead to a range of novel physical properties, as demonstrated in numerous studies [11–29].

In realistic systems, the presence of impurities is unavoidable, making their influence on the QD properties particularly important. In this regard, two key aspects are of primary interest: the role of impurities on quantum dot characteristics and the modification of impurity states under quantum confinement. Bastard [30] first considered a Coulomb impurity in a quantum well and employed a variational approach to determine its energy spectrum. Following his work, various authors have investigated impurity-related effects in low-dimensional nanostructures. For example, Shaer *et al.* [31] have examined the influence of a Gaussian impurity on the electrons confined in a lateral QD.

Another important interaction in QD systems is the relativistic spin-dependent interaction or the spin-orbit (SO) interaction (SOI) which forms a fundamental driving factor in the development of spintronic research. The key idea in spintronic devices is to utilize the electron spin, rather than its charge, as the primary carrier of information [32–35]. In solid-state systems, SO coupling generally arises from two primary mechanisms. The first is the Rashba spin-orbit interaction (RSOI) [36], which originates from structural inversion asymmetry, while the second is the Dresselhaus spin-orbit interaction (DSOI) [37], resulting from bulk inversion asymmetry. The degree of coupling of the DSOI is essentially determined by the intrinsic properties of the QD, whereas the RSOI can be tuned by both structural parameters and external fields [38]. This tunability of RSOI has been widely exploited in spintronic applications [39, 40].

In recent years, many authors have analysed how SOIs shape critical material characteristics and key attributes of quantum-confined geometries. Kumar *et al.* [41] have examined the role of RSOI on the energetics and magnetic properties of a many-electron harmonic QD using the Johnson-Payne model potential [42] for the electron-electron interaction. Elsaid and collaborators [43] have examined the thermodynamic and magnetic features of a parabolic GaAs QD under electric and magnetic fields factoring in the impact of impurities and the Rashba coupling. Li *et al.* [44] have investigated the influence of RSOI on the electronic states of a D^0 impurity in a GaAs/GaAlAs quantum well. Khordad [45] has examined the combined effects of electron–electron interaction, Rashba coupling, and an external magnetic field on the magnetic susceptibility of a parabolic QD at finite temperature. Gisi *et al.* [46] have analyzed the role of Rashba interaction and magnetic field on the optical absorption properties of a parabolic quantum wire. Saini *et al.* [47, 48] have reported

the binding energy of the D^0 and D^- impurities in a GaAs QD considering the Gaussian function as the confinement potential under the influence of RSOI and DSOI.

In most of the earlier investigations, the impurity has been assumed to be at the bottom of the confinement potential, and such an impurity is normally referred to as an on-centre impurity. Later, of course, quite a few investigations have also considered off-centre impurities [50–52]. However, a comprehensive analysis of both RSOI and DSOI on an off-center Coulomb impurity within an asymmetric GQD (AGQD) placed in a magnetic field has remained hitherto unexplored. Our work endeavours to explore this aspect. We will consider an off-centre hydrogenic impurity in a GaAs AGQD and calculate its ground state and binding energies, and the magnetic properties.

2. Theoretical model and Mathematical formalism

An off-centre D^0 impurity situated in an AGQD with RSOI and DSOI and placed under a magnetic field can be modelled by the following Hamiltonian:

$$\mathcal{H} = \left(\frac{1}{2m^*} \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 - \frac{e^2}{\varepsilon |\mathbf{r} - \mathbf{D}|} \right) I - IV_0 e^{-\left[\frac{(a(x^2+y^2)+b z^2)}{2R^2} \right]} + H_R + H_D \quad (1)$$

with

$$H_R = \frac{\alpha_R}{\hbar} \left[\boldsymbol{\sigma} \times \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right) \right]_Z, \quad (2)$$

$$H_D = \frac{\beta_D}{\hbar} \left[\sigma_x \left(p_x + \frac{e}{c} A_x \right) - \sigma_y \left(p_y + \frac{e}{c} A_y \right) \right]. \quad (3)$$

In Eq. (1), $e(m^*)$ refers to the charge (Bloch mass) of the electron, $\mathbf{r}(x, y, z)$ represents the position of the electron, $\mathbf{p}(p_x, p_y, p_z)$ its momentum, $\mathbf{D}$ is the position of the D^0 impurity, ε is the dielectric constant of the medium, $V_0(R)$ represents the depth (range) of the confinement potential, $\mathbf{A}$ denotes the vector potential defined by the equation: $\mathbf{B} = \nabla \times \mathbf{A}$, where $\mathbf{B}(0, 0, B)$ is the magnetic field applied in the z -direction, I is a unit matrix of order 2 and H_R and H_D describe respectively the Rashba and Dresselhaus interactions. In Eq. (2) and Eq. (3), $\sigma_x, \sigma_y, \sigma_z$ are the Pauli spin matrices, α_R and β_D denote the RSOI and DSOI constants. We use the symmetric gauge and choose: $\mathbf{A} = B(-y/2, x/2, 0)$.

We first deal with the SOI's. In order to incorporate the effect of SOI's, we apply on $\mathcal{H}$ a unitary transformation: $U = e^S$ with $S = i(m^*/\hbar^2) [\alpha_R(y\sigma_x - x\sigma_y) + \beta_D(x\sigma_x - y\sigma_y)]$. This transformation was first used by Aleiner and Falco [53] and later by Rodriguez *et al.* [54] and Kumar *et al.* [55]. This diagonalizes the Hamiltonian in the spin space to order α_R^2 and β_D^2 . In the transformed frame, the eigenstates are orbitals with well-defined spin and orbital angular momentum. In this method, terms higher than α_R^2 and β_D^2 are neglected and we get

$$\begin{aligned} \tilde{\mathcal{H}} = & \left(\frac{p^2}{2m^*} + \frac{1}{8} m^* \omega_c^2 \rho^2 - \frac{e^2}{\varepsilon |r - D|} \right) I - IV_0 e^{-\frac{a(x^2+y^2)+b z^2}{2R^2}} - \frac{m^*}{\hbar^2} (\alpha_R^2 + \beta_D^2) I - \\ & - \frac{m^*}{2\hbar^3} (\alpha_R^2 - \beta_D^2) [\omega_c \sigma_z \rho^2 + 2L_z] \sigma_z + \frac{\omega_c}{2} L_z, \end{aligned} \quad (4)$$

where $\omega_c = (eB/m^*c)$, $\rho^2 = (x^2 + y^2)$ and $L_z = -i\hbar(\partial/\partial\varphi)$. We are interested in a variational GS of $\tilde{\mathcal{H}}$ and so we adopt an appropriate variation ansatz: $\psi(\mathbf{r}) = [1 + \gamma e^{-\alpha(r-D)}] e^{-\beta r^2 - im\varphi}$, where γ, α and β are to be selected by the optimization process. The proposed variational ansatz has been designed to adequately describe the dominant physical characteristics of the GS of (2). Let $E(e^-)$ and $E(D^0)$ denote the lowest energy states of a single electron and a neutral donor complex, respectively, confined within the AGQD. We also calculate the magnetic moment (M) and susceptibility (S) of the D^0 complex, which are defined as: $M = -(\partial E/\partial B)$; $S = (\partial M/\partial B)$.

3. Quantitative findings and discussion

Although the formalism developed here is fairly broad in scope and applicable to any QD system, we specifically consider a GaAs QD dot for concreteness. All physical quantities will be expressed in SI units, with energy in meV and length in nm. For GaAs, the electrical permittivity is taken as $\varepsilon = 12.4$ and the electron band mass as $m^* = 0.06m_0$, where m_0 denotes the free electron mass. The magnetic field is given in Tesla (T), and the SOI parameters are given in meV·nm.

Figure 1 illustrates how the GS energy (E) of an off-centre donor D^0 within a GaAs AGQD evolves relative to the donor position (D), comparing three distinct pairs of asymmetry parameters a and b . As D enhances, E rises and gradually approaches a constant value at large D . This behaviour can be interpreted using a straightforward semiclassical framework where the effective potential function on minimization provides the system's lowest energy. The GS energy decreases with decreasing asymmetry along the z -direction. Furthermore, in cases when D^0 is separated farther from the confinement centre, the influence of asymmetry becomes increasingly significant.

Figure 2 demonstrates how E changes with V_0 in the case of a GaAs AGQD for different values of α_R and β_D and a certain value of D ($D = 10$ meV). The GS energy decreases with increasing V_0 , which is consistent with expectations. Additionally, both RSOI and DSOI lower the GS energy, with the RSOI contribution being more significant.

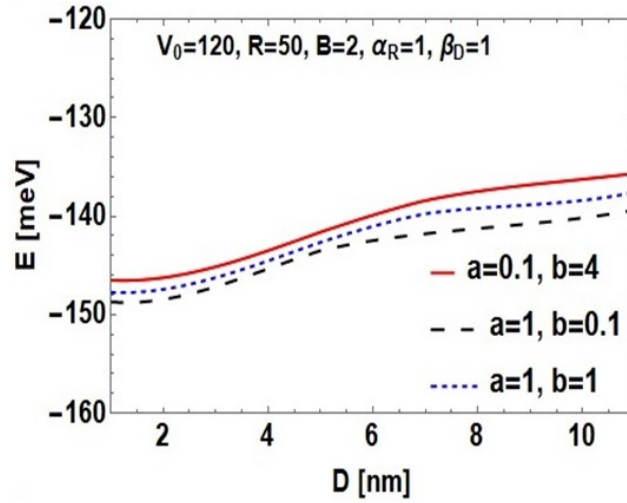


FIG. 1. Plot showing the variation of the GS energy E (in meV) of an off-centre D^0 impurity within a GaAs AGQD with respect to the distance of D^0 from the stable equilibrium potential minimum (D in nm) for three sets of asymmetry parameters

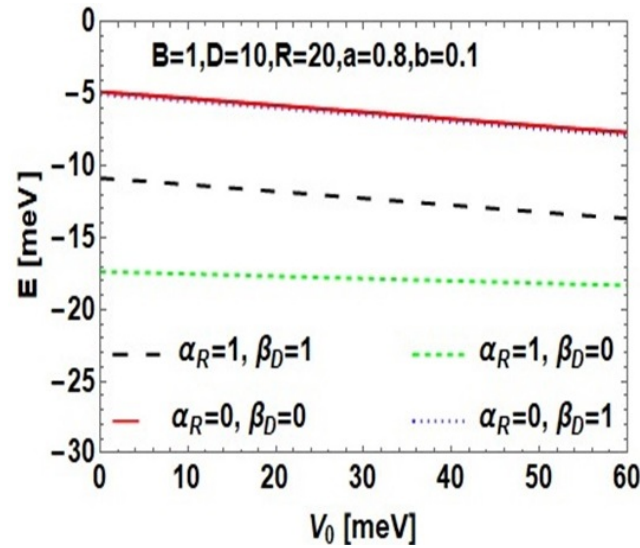


FIG. 2. Plot showing the variation of GS energy E with respect to V_0 for a D^0 impurity within GaAs AGQD with $D = 10$ nm and for four sets of SOI parameters

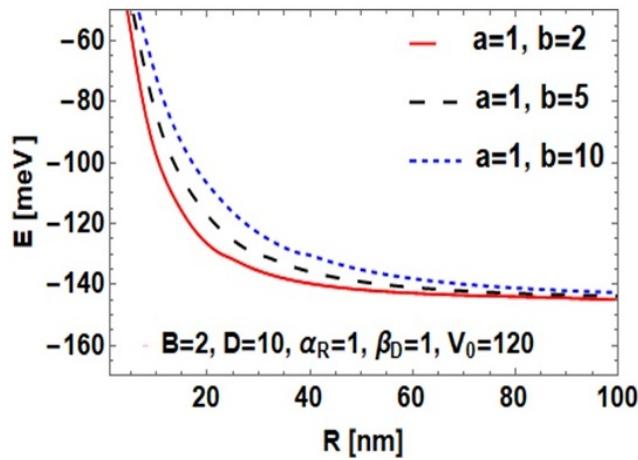


FIG. 3. Plot of E against R in the case of a D^0 impurity in a GaAs AGQD for a few sets of asymmetry parameters

Figure 3 illustrates the dependence of E on R in the case of a GaAs AGQD for a three sets of asymmetry parameters with the impurity position $D = 10$ meV. The values of other parameters are specified within the figure. The figure shows that for small QD sizes, the effect of the asymmetry parameter is not very significant. However, as the QD size increases, the GS energy is impacted by the asymmetry parameter in a more pronounced way. The graph, of course, also demonstrates the accepted behavior that the GS energy rises with increasing QD size.

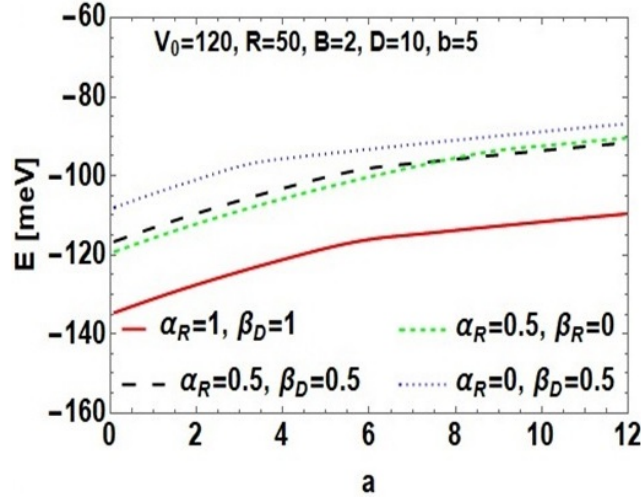


FIG. 4. Plot showing how E depends on the asymmetry parameter a in the case of an off-centre hydrogenic complex within a GaAs AGQD

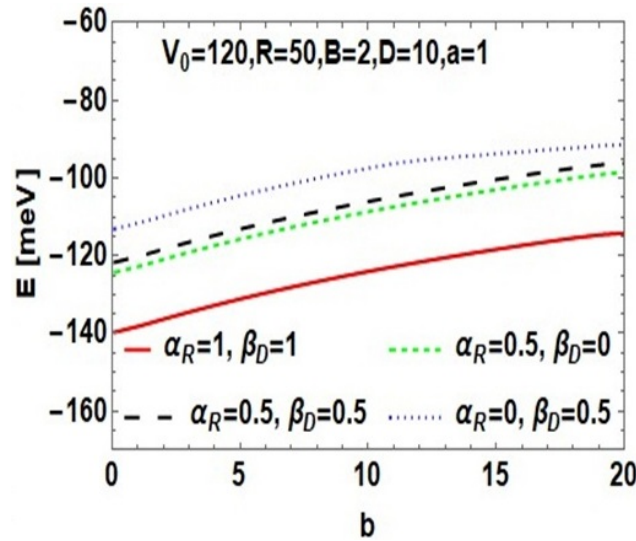


FIG. 5. Plot showing how E depends on the asymmetry parameter b in the case of an off-centre hydrogenic complex within a GaAs AGQD

Figure 4 and Fig. 5 describe how E depends on the asymmetric parameters a and b for four pairs of values of α_R and β_D with $V_0 = 120$ meV, $R = 50$ nm, $D = 10$ nm and $B = 2T$. The graphs indicate that the energy is a growing function of the asymmetry parameters a and b . Furthermore, the directional asymmetry along the Z exhibits a more pronounced impact in lowering the energy than the x-y asymmetry. The combined impact of RSOI and DSOI gives rise to a further reduction in the GS energy in both cases.

Figure 6 displays the trend of the GS energy against B for $V_0 = 300$ meV, $D = 4$ nm, $R = 10$ nm, $\alpha_R = 1$, $\beta_D = 1$ with different values of the asymmetry parameters. In all cases, a positive correlation is observed between E and B . Moreover, reduction in asymmetry along the z-direction results in lower energy.

Figure 7 exhibits how the nature of the moment (M) is governed by B for $V_0 = 300$ meV, $D = 4$ nm, $R = 10$ nm and $\alpha_R = 1$ and $\beta_D = 1$ and for three sets of asymmetry parameters. The behaviour distinctly indicates the diamagnetic nature of M . The figure also suggests that $|M|$ is a monotonically increasing function of B . It is also visible that a lower asymmetry along the z-direction results in an increased magnitude of magnetization. However, for small B values, the dependence of M on the QD potential asymmetry is rather feeble.

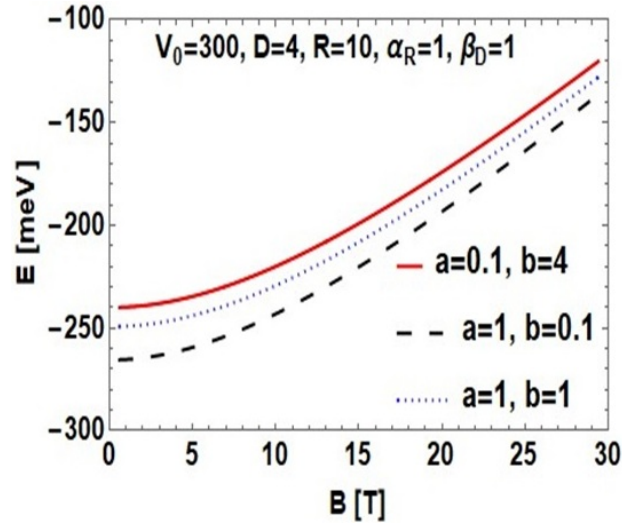


FIG. 6. Dependence of E on B in the case of an off-center hydrogenic complex in a GaAs AGQD for a few sets of asymmetry parameters

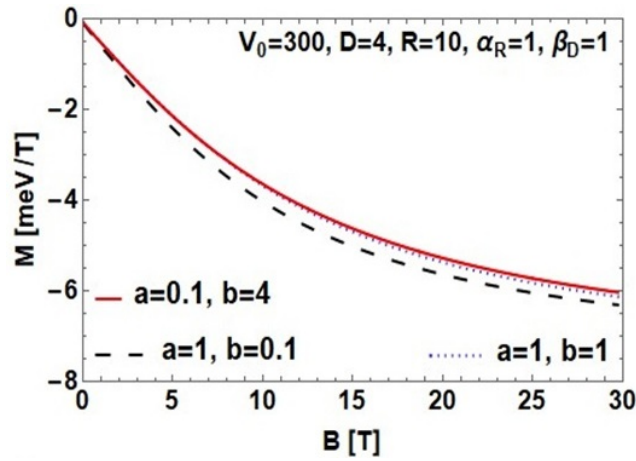


FIG. 7. Dependence of magnetic moment (M) of an off-center impurity in a GaAs AGQD on the applied field B for three sets asymmetry parameters

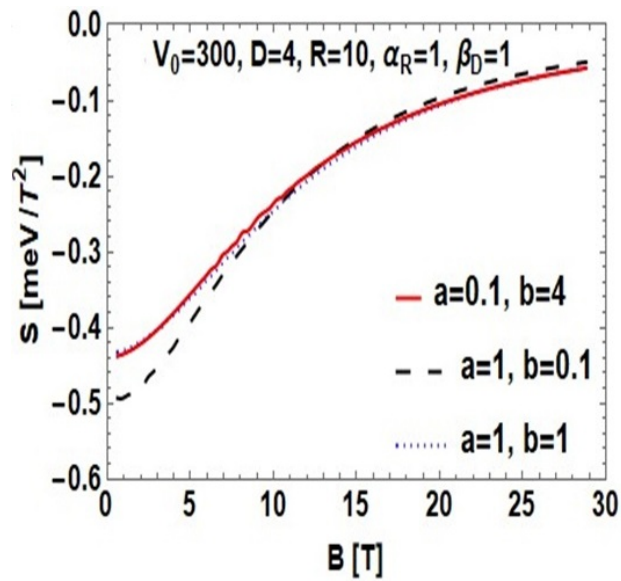


FIG. 8. Correlation between the Magnetic susceptibility (S) and B for an off-center system in a GaAs AGQD for three sets of asymmetry parameters

Figure 8 presents the correlation between the magnetic susceptibility (S) and the applied field B in the case of an off-centre D^0 system in a GaAs AGQD. The figure distinctly demonstrates the diamagnetic behaviour of the susceptibility S . In addition, the impact of the asymmetry parameters on S is significant at low small B , but becomes negligible as B increases. The susceptibility increases as a function of B for all asymmetry parameters and exhibits a gradual saturation at higher magnetic fields.

4. Conclusion

We have examined how the GS energy (E), Magnetization and the susceptibility (S) of an off-centre D^0 complex in a GaAs AGQD are influenced by the depth, range and the asymmetry parameters of the QD potential under a magnetic field. It is observed that E increases with the increase in the impurity distance D and the asymmetry parameters of the QD potential. It is furthermore found that deepening or widening the potential well results in a lower bound-state energy, the effect of the range being much more stronger. We finally demonstrate that the magnetic field enhances the energy and also the magnetization strength and susceptibility.

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Submitted 9 May 2026; revised 18 May 2026; accepted 25 May 2026

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Conflict of interest: the authors declare no conflict of interest.

Laser-enhanced activated carbon from Jericho date stones: unified evidence from multi-model structural, textural, and surface analyses

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ABSTRACT Activated carbon from date stones is a promising material for energy, environmental and catalytic applications due to its high carbon yield, renewable nature, and tunable porosity. This paper presents an extensive comparative study of potassium hydroxide-activated carbon (AC) vs. Nd:YAG laser post-treated activated carbon (LAC), both derived from Jericho date stones. Comprehensive analyses – XRD, SEM, FTIR, nitrogen sorption (BJH, Horvath-Kawazoe, DFT, DR, DA), BET, Langmuir, and t-plot – show striking improvement in LAC's microporosity, mesoporosity, surface area, and surface chemistry. Benchmarking against published literature, these findings demonstrate unified agreement across models and characterization methods, thus supporting laser post-treatment as an effective complementary strategy for tailoring the textural and surface properties of biomass-derived activated carbon and may offer a promising pathway for further development of sustainable porous carbon materials.

KEYWORDS activated carbon, laser carbonization, laser-assisted activated carbon, date stones, DFT, PSD, adsorption kinetics

FOR CITATION Jabr A., Saadeddin I., Hamouz A.E., Qamhieh Z., Jung H., Park J.W. Laser-enhanced activated carbon from Jericho date stones: unified evidence from multi-model structural, textural, and surface analyses. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 346–356.

1. Introduction

Activated carbon (AC) is integral to adsorption, catalysis, water purification, and energy storage systems due to its high surface area, hierarchical porosity, and functional surface chemistry [1]. The shift toward sustainable materials has emphasized the use of agricultural waste as carbon precursors, with date stones emerging as a key renewable source, particularly in regions with extensive palm cultivation [2, 3]. As a biomass feedstock, date stones possess a high fixed carbon content, low ash, and dense structure suitable for conversion into high-performance AC.

The preparation of AC generally follows either physical or chemical activation routes. Among chemical activators, potassium hydroxide (KOH) exhibits superior ability to develop micro-mesoporous networks and enhance textural characteristics [4–6]. Activation temperature, impregnation ratio, and precursor structure collectively determine the pore architecture and surface area. Recent reports demonstrated date stone-derived AC achieving specific surface areas typically in the range of 700 – 1100 m²/g under optimized KOH treatment [7, 8]. Enhanced methods involving mixed alkali activation (KOH/NaOH), stepwise pyrolysis, and hybrid acid-base activation have achieved further improvements by modulating carbon lattice disorder and oxygen surface chemistry [9, 10].

With the drive to maximize surface accessibility and tailor surface functionalities for energy and catalysis applications, post-synthesis processing techniques such as laser treatment have gained attention. Laser irradiation can introduce nanometer-level modifications, create defects, and increase the density of reactive oxygen-containing sites [11, 12]. The use of pulsed and continuous-wave lasers has been reported to modify the microstructure of carbon electrodes, carbon nanofibers, and biomass-derived carbons to tune wettability, nano-porosity, and conductivity [13–15]. Recent studies have shown the potential of laser irradiation to produce hierarchically structured carbon nanomaterials with enhanced adsorption and electrochemical performance [16].

In this study, we develop and evaluate KOH-activated carbon derived from Jericho date stones and investigate further modification through Nd:YAG laser post-treatment. The work integrates multi-scale analyses – XRD, SEM, FTIR, and multiple gas adsorption models – to establish a unified understanding of structural and surface property enhancement. At the nanoscale, laser treatment introduces surface activation, defect engineering, and oxygenation, which collectively strengthen its applicability in adsorption and catalysis. This study defines a scalable route for producing nanostructured sustainable carbon materials from renewable agricultural waste.

2. Literature survey and benchmarking of date stone-derived activated carbon

The valorization of date stones into activated carbon has become an increasingly important research pathway for sustainable nanomaterials production. Date stones, a lignocellulosic byproduct of the date industry, are particularly suitable due to their high fixed carbon and favorable composition [2, 3]. Multiple studies have addressed both physical (CO₂, steam) and chemical (KOH, ZnCl₂, H₃PO₃) activation, the latter being preferred for achieving optimally microporous and mesoporous carbons [5, 6, 8].

Haimour and Emeish [3] reported AC prepared via CO₂ activation with a surface area of approximately 700 m²/g optimized for heavy metal adsorption. Alhamed and Bamufleh [2] achieved values of 800 – 950 m²/g using KOH activation for sulfur removal. Foo et al. [7] demonstrated that microwave-assisted KOH activation provides better energy efficiency and pore uniformity, while Jabbar [8] and Bamerdhah et al. [9] reported structure–performance sensitivity to ionic strength, impregnation ratio, and activation temperature. Recent works have demonstrated significant textural variation when combining KOH and NaOH activators or varying pyrolysis temperatures between 700 – 900 °C [17].

Laser-based processes introduce a new dimension to post-activation surface tuning, transforming carbon structures by localized nanothermal and photochemical mechanisms [13, 15, 16, 18]. Laser irradiation of bio-derived carbons has been shown to induce nitrogen or oxygen enrichment, restructure sp² networks, and enhance electrochemical behavior [14, 18]. Studies of laser-induced carbonization from polymers and biomass precursors reveal formation of nanoscale carbon architectures, including carbon nanospheres, fibers, and porous films that vastly improve the density of active sites [19, 20].

Despite their promise, few works have explored laser post-treatment on date-stone-derived carbons. The present study bridges this gap by experimentally evaluating Nd:YAG laser modification as a route to develop hierarchical porosity and nanoscale defects while benchmarking its performance against the best chemical activation routes reported in literature. A comprehensive comparison of published data and this work's outcomes is provided in Table 1.

TABLE 1. Timeline and comparative properties of date stone-derived activated carbons

Activation method	Surface area (m ² /g)	Key Application	Ref.	Year
Physical (CO ₂)	~700	Heavy metal adsorption	[3]	2005
Chemical (KOH)	800 – 950	Sulfur removal	[2]	2009
Microwave + KOH	900	Dye adsorption	[1]	2011
KOH, ZNCl ₂ , H ₂ SO ₄	950 (KOH)	Dye removal	[8]	2020
Optimized KOH	763 – 910	Gas, dye adsorption	[9]	2025
Chemical (KOH)	1900+		This work	2025
KOH + Laser	2100 – 2200+		This work	2025

The substantial increase in measured surface area seen in Table 1, micropore volume, and functional group density seen in this work – corroborated by multiple analytical models – represents a significant advancement over the current literature. The synergy between chemical and laser activation sets a new benchmark for bio-based AC materials. These findings are expected to result in enhanced behaviors if this synergy is applied in different areas like gas adsorption, dye removal, heavy metal removal and energy storage.

3. Materials and methods

3.1. Raw material sourcing and pre-treatment

Date stones were collected from local agricultural waste in Jericho, thoroughly washed with boiling deionized water to remove adhering fruit residues and dust. After then, date stones were sun-dried, followed by overnight oven-drying at 110 °C to remove moist. The dried stones were ground using a grind mill then meshed using an 80 mesh to separate granules from powders on which different tests were carried.

3.2. Carbonization and chemical activation

The powder was subjected to carbonization in a muffle-tube furnace at 500 °C (ramp rate: 10 °C/min) under a constant flow of nitrogen purge (100 mL/min) for 2 hours. The resulting biochar was mixed with potassium hydroxide (KOH, ≥98 %) in a 2:1 weight ratio (KOH:Char) and gently stirred in deionized water to produce a homogeneous slurry then left for 24 hours. The impregnated mixture was oven-dried overnight at 110 °C and then activated in a muffle-tube furnace at 800 °C for 2 hours (ramp rate: 15 °C/min) under nitrogen flow of (100 mL/min) yielding about 30 % char after pyrolysis.

After activation, the carbon was directly quenched in deionized water, stirred and repeatedly washed with deionized water to eliminate residual potassium and inorganic ash. The washed carbon was dried again overnight at 110 °C yielding approximately 27 % of the original mass prior pyrolysis before further processing.

3.3. Laser post-treatment

Half gram of KOH-activated carbon was mixed in 50 ml deionized water using magnetic stirrer for 30 min and then irradiated using a pulsed Nd:YAG laser (1064 nm, 10 Hz, 2-hour exposure) under continuous stirring resulting in laser-treated activated carbon (denoted LAC). Laser fluence was optimized to induce effective surface restructuring and defect creation without excessive graphitization. The laser-treated activated carbon was separated from treatment water, washed, and oven-dried overnight at 110 °C yielding about 93 % of the original KOH-activated sample being subjected to laser. LAC was compared to chemically activated material without laser treatment (denoted AC).

3.4. Characterization techniques

XRD diffraction measurements for carbonized material (C), (AC) and LAC powder samples were investigated using X-ray diffractometer (Ultima IV, Rigaku) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. FTIR spectra were obtained using Benchtop Thermo-Fisher Nicolet IS5 FTIR spectrometer to verify functional group change due activation process and laser irradiation of AC sample. Surface Morphology for samples was conducted by FE-SEM (JSM-7100F, JEOL) allowing quantification of particle size and surface roughness.

N₂ adsorption–desorption isotherms at liquid nitrogen temperature (77 K) were carried up with a high precision surface area analyzer (BELsorp-mini II, Microtrac) to analyze pore parameters. BET surface area, pore volumes/distributions (BJH for mesopores, HK for micropores, DFT/DFT-Modified for full profile) were computed using standard Micromeritics ASAP 2020 Plus software. Isotherm Modeling indices for (Langmuir, t-plot, Dubinin-Radushkevich (DR), Dubinin-Astakhov (DA), Maximum adsorption capacities and porosity) were extracted and all fits evaluated by R² and compared against literature benchmarks.

4. Results

4.1. Crystallography: XRD analysis

Figure 1 shows the X-ray diffraction (XRD) patterns for the AC and LAC samples.

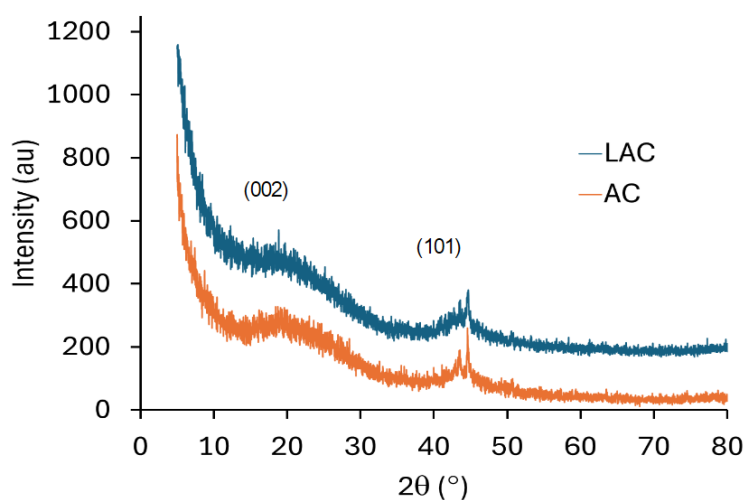


FIG. 1. XRD patterns for AC and LAC

As seen in Fig. 1, both AC and LAC patterns show broad bands centered at $2\theta \approx 24^\circ$ and 44° , corresponding, respectively, to the (002) and (101) planes of turbostratic carbon, as is typical for biomass-derived and KOH-activated carbons [21–23]. The prominence and breadth of these peaks reveal the predominantly disordered arrangement of graphene-like layers, lacking significant crystalline graphite domains. This amorphous nature is a hallmark of high porosity activated carbons and matches previous findings for both date stone and other lignocellulosic precursors [2, 5].

A closer comparison of the diffraction patterns reveals that the broad feature centered at approximately $44^\circ - 45^\circ$, commonly assigned to the (100)/(101) reflection of turbostratic carbon, exhibits reduced intensity in the LAC sample relative to AC. This attenuation indicates that laser modification does not introduce new crystalline phases but instead alters the short-range ordering of carbon layers [6].

In disordered carbon materials, the (100)/(101) reflection is highly sensitive to in-plane coherence length and defect density within sp^2 domains. A reduction in intensity in this region can therefore be associated with increased structural heterogeneity, fragmentation of aromatic domains, or disruption of in-plane ordering, all of which are consistent with localized, rapid thermal effects induced by laser irradiation. Similar reductions or broadening of the $\sim 43 - 45^\circ$ carbon reflection have been reported in activated carbons and laser-treated carbons where increased defect density and microstructural disorder are introduced without the formation of long-range graphitic order [42].

Comparative reports for XRD of KOH-activated carbons from other precursors consistently identify broad (002) and (101) peaks, minimal graphitization, and occasional K_2CO_3 peaks that can persist if activation temperature is low or washing is incomplete [5,22,24]. Advanced treatments such as laser modification, chemical post-treatments, or secondary carbonization are known to reduce these byproducts and enhance disorder, which is linked to improved electrochemically active surface area and adsorption behavior [7, 19].

4.2. Morphology: SEM analysis

Figure 2 shows SEM micrographs for AC and LAC samples at $\times 5000$ magnification. Fig. 2(a) reveals that AC as compact, smooth-edged particles, while Fig. 2(b) LAC is notably fragmented, exhibiting higher surface roughness, abundant edges, and micro/nano-sized debris. These results are consistent with laser-induced surface ablation, defect formation, and increased pore volume and area, mirroring recent literature for laser carbon modification. Such features promote greater adsorption site exposure and are expected to correlate with observed changes in porosity and surface chemistry.

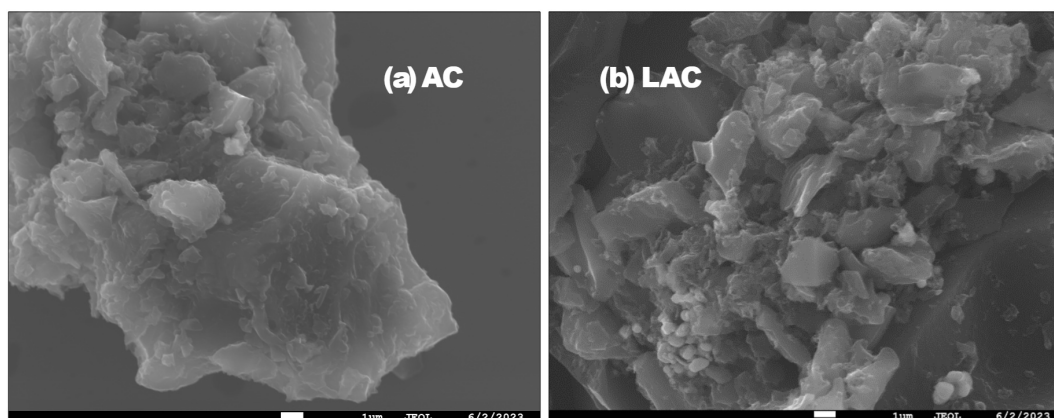


FIG. 2. SEM micrographs for (a) AC and (b) LAC samples at $\times 5,000$

4.3. Surface functionalization: FTIR analysis

Figure 3 shows the baseline-corrected and normalized FTIR spectra for AC and LAC samples. As seen in Fig. 3, laser treatment significantly intensifies the O–H stretching features ($3630 - 3700\text{ cm}^{-1}$), C=O stretching ($1690 - 1560\text{ cm}^{-1}$), and C–O stretching ($1200 - 1350\text{ cm}^{-1}$) bands, indicating an increased density of oxygen-containing functional groups at the carbon surface [11,25]. This enhancement is critical because oxygen-containing groups including hydroxyl, carboxyl, and carbonyl moieties play a key role in adsorption efficiency for polar contaminants and improved catalytic activity [26, 27].

The diminished intensity of aromatic C–H stretches and associated signals reflects partial fragmentation or disruption of the graphene-like domains typical of highly aromatic activated carbons, which occurs both during KOH activation and is further amplified by laser processing [28,29]. Such structural modifications promote the creation of defect sites and enhance the material's surface polarity [11, 13]. Comparative studies confirm that KOH activation reliably increases the density and diversity of oxygenated functional groups, raising the content of carbonyl and carboxylic acid groups in a precursor-dependent fashion [26,30].

Laser modification further amplifies these effects; recent reports demonstrate an even greater increase in O–H and C–O functionalities after laser-induced carbonization, which translates to superior wettability and ionic conductivity [12,31]. Loss of aromatic signals and rise of oxygenated bands have been confirmed in FTIR studies of laser-treated graphene and amorphous carbons, with direct links to improved adsorption, electrochemical performance, and catalytic selectivity for a variety of contaminants and intermediates [11,27,32]. In some works, high-resolution FTIR analysis reveals the relative loss or shift of peaks associated with aromatic C–H as oxygen functional groups gain dominance [32].

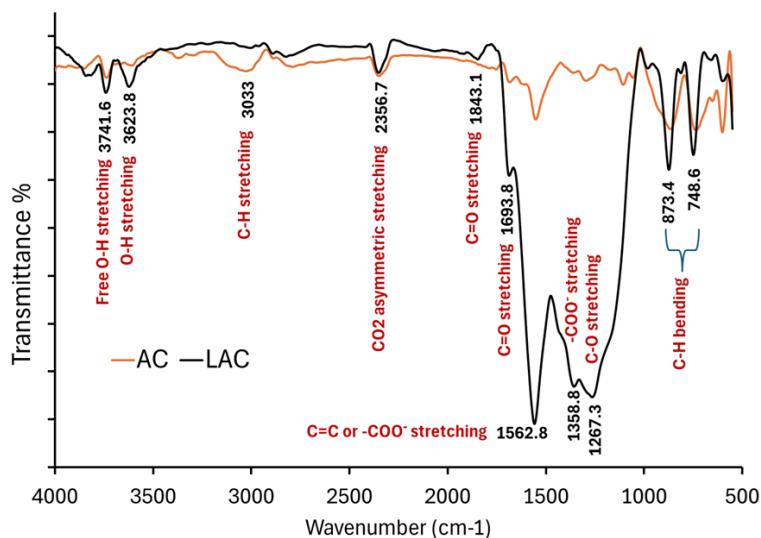


FIG. 3. FTIR spectra for AC and LAC samples

4.4. Pore size distribution and total porosity

Figure 4 shows DFT pore size and cumulative pore volume distributions for AC and LAC samples versus pore width. As seen in Fig. 4, both materials have a sharp, dominant peak in the micropore region around 1 nm, a characteristic of KOH-activated carbons prepared from biomass precursors [27, 33].

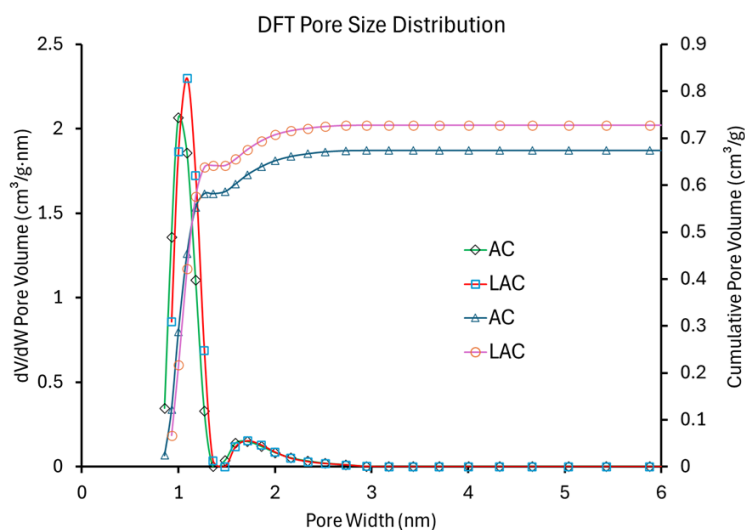


FIG. 4. DFT Pore size distribution of AC and LAC

The cumulative pore volume for LAC is notably higher across the measured range, evidencing that laser post-treatment successfully augments micro/meso-porosity beyond conventional activation. This enhancement is well correlated with recent reports on advanced laser modification of activated carbons, where densification of defect sites and fragmentation of residual byproducts yield greater developed pore volumes and surface areas [11].

Horvath–Kawazoe cumulative pore volumes for AC and LAC samples were plotted versus pore width as seen in Fig. 5.

Horvath–Kawazoe cumulative pore volume deepens the comparison, showing that LAC achieves a larger cumulative volume at all pore widths compared to AC counterparts as seen in Fig. 5. This is indicative of both; increased micropore accessibility and efficient connectivity between micro- and mesopores. Such shifts have been reported for carbons undergoing sequential activation processes, particularly when strong alkali activation (KOH) is followed by additional thermal or physical treatments [34, 35]. For date stone-derived and other lignocellulosic activated carbons, higher pore connectivity and cumulative volume are directly linked to improved adsorption, especially for molecular contaminants and small gas molecules [36].

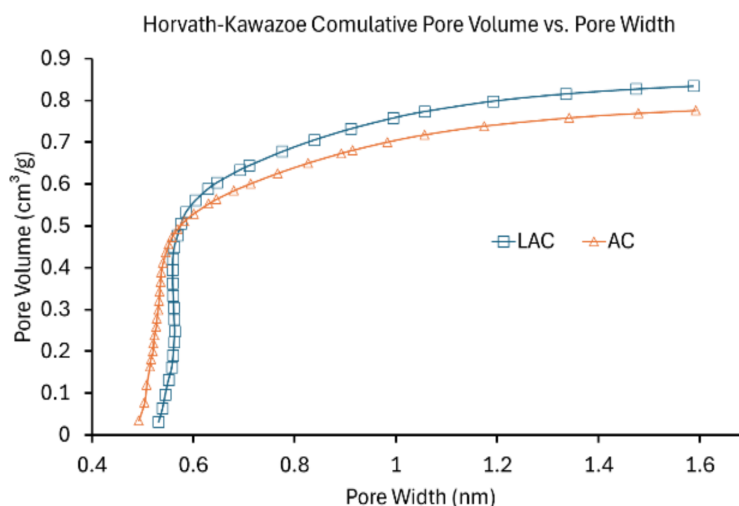


FIG. 5. Horvath–Kawazoe cumulative pore volume for AC and LAC

Figure 6 shows Horvath–Kawazoe differential pore volumes for AC and LAC samples as plotted versus pore width. Horvath–Kawazoe differential pore volume profiles seen in Fig. 6 demonstrate that both AC and LAC possess a primary micropore peak in the (0.5 – 0.6 nm), consistent with the ideal adsorption window for small polar molecules and ions [11, 37]. The peak is a sharp, massively intense and more symmetrical in LAC (0.56 nm) compared to a wide less intense (0.5 – 0.55 nm) peak in AC, suggesting more uniform pore formation due to laser post-treatment.

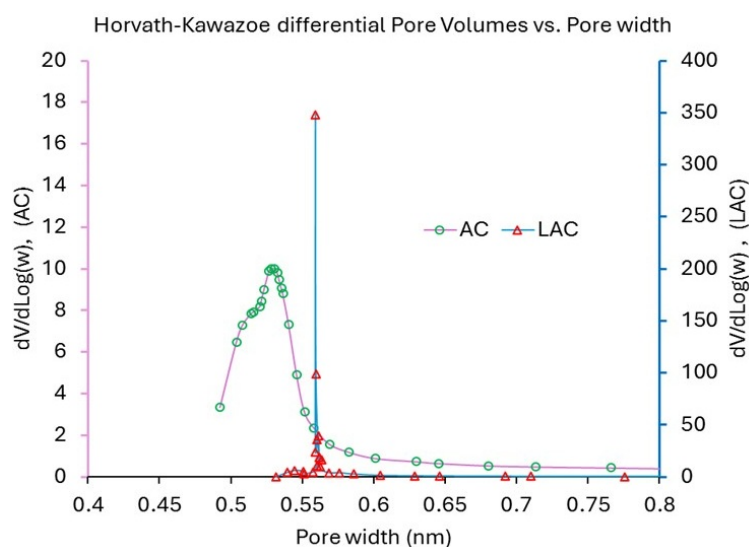


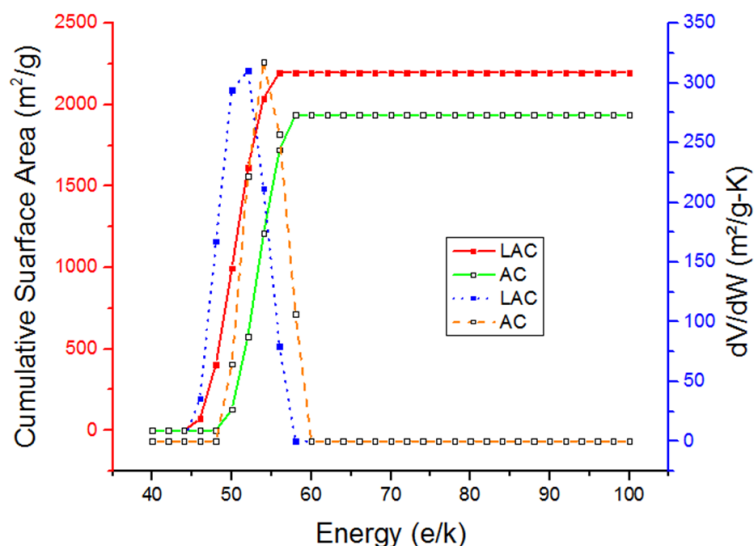
FIG. 6. Horvath–Kawazoe differential pore volume for AC and LAC

Literature on pore engineering of activated carbon confirms that narrower, more uniform micropores are achieved when activation protocols are precisely controlled, and that post-activation laser processing can further reduce heterogeneity and broaden the accessible pore range [38].

Overall, LAC shows increased dV/dw values and cumulative volume, reflecting a higher density of adsorption sites and more open pore structure. This is directly associated with higher BET surface area and enhanced performance in adsorption and catalysis [12, 27]. Comparative studies using both DFT and Horvath–Kawazoe models underscore the critical role of activation sequence and post-treatment in controlling pore structure, as seen in various recent nanomaterial carbon investigations [11, 12, 38].

As Fig. 7 shows, Both AC and LAC display an activated carbon characteristic rapid increase of cumulative surface area as adsorption energy increases, corresponding to micropore filling. The LAC sample attains a substantially higher cumulative surface area ($\sim 2100 - 2200 \text{ m}^2/\text{g}$) compared to AC ($\sim 1900 \text{ m}^2/\text{g}$), consistent with enhanced pore development by laser post-treatment [11, 27].

The differential surface area plot (dV/dW) of Fig. 7 shows sharper, higher peaks for LAC, indicating a more homogeneous distribution of pore energies and consequently more uniform microporosity.

FIG. 7. N₂ Modified DFT energy Plot for AC and LAC

Such enhanced microporosity and uniform energetic distribution are critical for adsorption performance, enhancing the capacity and kinetics for polar gas and vapor adsorption [11, 34]. Notably, DFT analysis surpasses traditional BET or DR methods by combining molecular simulations with classical thermodynamics, enabling the capture of a more realistic pore environment in carbon materials [39, 40].

Comparisons with recent studies on laser-modified biomass-derived carbons reinforce these findings. Laser processing modifies surface chemistry and pore structure sequentially to create a tailored nanoscale environment favorable for selective adsorption and catalysis applications [12, 13]. The superior micropore volume and uniform energy distribution observed post laser treatment promote improved adsorbate binding strength and faster diffusion within the porous network [41].

4.5. Comprehensive adsorption analysis: BET, Langmuir, and t-plot

Comparative adsorption results between laser-treated activated carbon (LAC) and conventional activated carbon (AC), both derived from date stones through KOH activation are presented in Table 2.

TABLE 2. BET, Langmuir, t-plot analysis for AC and LAC samples

Sample Method	SA (BET)	C	$Q_{\max}$ (BET)	SA (Langmuir)	$Q_{\max}$ (Langmuir)	V_{mic} (t-plot)	S_{mic} (t-plot)	S_{mes} (BJH)	S_{ext} (t-plot)
LAC	2109.6	920.9	484.7	2508.7	576.3	0.707	1804.9	108	304.6
AC	1962.8	825.8	450.9	2325.9	534.4	0.643	1645.3	101	317.5
Enh. %	7.5	11.5	7.5	7.9	7.8	10.0	9.7	6.98	-4.1

Findings shown in Table 2 reveal pronounced improvements across key surface textural parameters following laser post-treatment. This quantitative analysis demonstrates that the BET surface area for LAC increases to 2109.6 m²/g from 1962.8 m²/g for AC, corresponding to a 7.5 % enhancement. Similarly, the maximum adsorption capacity determined by the BET method ($Q_{\max}$ BET) rises by 11.5 %, indicating a significant increase in overall pore volume. Langmuir model analysis corroborates these findings, with a 7.9 % increase in surface area and a 7.8 % boost in maximum adsorption capacity for LAC relative to AC. These gains reflect a more accessible and finely developed pore structure, beneficial for adsorption-driven applications.

Micropore analysis using the t-plot method shown in Table 2 demonstrates nearly 10 % increases for both micropore volume and surface area in LAC (0.707 and 1804.9 m²/g) compared to AC (0.643 and 1645.3 m²/g), signifying that the porosity enhancements are concentrated in the microporous fraction. Notably, the external surface area (S_{ext}) exhibits a modest decrease of about 4 % for LAC, implying that the textural evolution induced by laser processing predominantly favors micropore generation over meso- and macropores. BJH analysis shows clearly about 7 % increment in mesoporosity surface area after laser post treatment of activated carbon.

These improvements are directly attributable to the effects of laser post-treatment, which has been shown in analogous recent studies to facilitate additional pore formation, increase graphitic ordering, and further activate the carbon matrix for enhanced electrochemical and adsorptive behavior. The overall enhancements presented in all major porosity metrics support the assertion that LAC offers greater adsorption capacity and a higher proportion of microporous structure, while the slight reduction in external surface area suggests a focused modification within the carbon matrix.

This set of results establishes laser post-activation as a moderate step in the synthesis of activated carbon from agricultural waste sources, with particular benefit for supercapacitor electrodes and advanced adsorbents where high microporosity and surface area are critical for high-performance operation. Thus, incorporating laser post-treatment into the activation pathway delivers tangible advancements in carbon quality, positioning LAC as a good candidate for sustainable energy storage and environmental remediation applications.

4.6. Micropore models: DR and DA comparison

Dubinin–Radushkevich (DR) parameters deduced from AC and LAC samples are presented in Table 3.

TABLE 3. Dubinin–Radushkevich (DR) parameters for AC and LAC samples

Sample	Equivalent surface area (m^2/g)	Limiting micropore capacity (cm^3/g STP)	Limiting micropore volume (cm^3/g)	Characteristic energy (kJ/mol)
LAC	4542.19	1043.56	1.61	10.18
AC	3562.13	818.39	1.26	11.97

As seen in Table 3, LAC exhibited markedly enhanced porous structure compared to AC where surface area increases from $3562 \text{ m}^2\text{g}^{-1}$ (AC) to $4542 \text{ m}^2\text{g}^{-1}$ (LAC) indicating that laser treatment promotes additional surface development beyond chemical activation alone. This substantial increase suggests the generation of new accessible surface area, likely through the opening of previously blocked pores and the creation of additional micro- and ultra micropores through localized heat deposition and shockwaves.

Consistent with this observation, the limiting micropore capacity increases from $818 \text{ cm}^3 \text{ g}^{-1}$ STP for AC to $1044 \text{ cm}^3 \text{ g}^{-1}$ STP for LAC, accompanied by an increase in limiting micropore volume from 1.26 to $1.61 \text{ cm}^3\text{g}^{-1}$. These results indicate that laser modification enhances both the quantity and accessibility of micropores, rather than merely enlarging existing pores.

In contrast, Table 3 shows a decrease in characteristic energy from $11.97 \text{ kJ mol}^{-1}$ (AC) to $10.18 \text{ kJ mol}^{-1}$ (LAC). This reduction suggests a broader micropore size distribution and a partial shift toward wider micropores in the LAC sample, which is consistent with localized thermal effects of laser irradiation that can induce pore widening and structural rearrangement without collapsing the carbon framework.

Analogous behavior is seen when deducing Dubinin–Ashtekhov (DA) parameters for AC and LAC samples as seen in Table 4.

TABLE 4. Dubinin–Ashtekhov (DA) parameters for AC and LAC samples

Sample	Equivalent surface area (m^2/g)	Limiting micropore capacity (cm^3/g STP)	Limiting micropore volume (cm^3/g)	Modal pore width (nm)
LAC	1928.34	549.25	0.849	1.728
AC	1638.83	449.7	0.695	1.665

Overall, textural analysis demonstrates that laser treatment significantly enhances surface area and micropore volume while slightly reducing adsorption energy, supporting the conclusion that laser modification introduces additional porosity and structural heterogeneity. These findings are consistent with the XRD results, which show preserved amorphous carbon structure with increased short-range disorder rather than the formation of long-range graphitic order.

4.7. Unified cross-technique consistency

All the provided crystallographic, structural, morphological, surface functionality and model implications show that laser post-treatment of activated carbon results in higher surface area, greater micropore/mesopore development, enhanced energetically uniform adsorption sites, more abundant/accessible functional groups. Altogether emphasizes greater potential of LAC for selective adsorptive, catalytic, or separation applications in addition to supercapacitor applications.

Comparative review with Table 1 demonstrates the leap in material performance over all previously reported date stone ACs, making LAC a next-generation functional carbon.

5. Discussion

The comparative results across analytical probes and adsorption model robustly demonstrate that Nd:YAG laser treatment provides measurable and meaningful enhancement of KOH-activated date stone carbon. The increase in overall surface area, pore volume, and the broadening of pore distributions – as observed in BET, BJH, HK, DFT, DR, DA, and t-plot analyses – are direct consequences of new defects, fragmentation, and surface restructuring driven by laser ablation and local heating.

Laser post-activation not only generates more and broader pores but also exposes new edges and surfaces and introduces additional oxygen-containing functional groups – crucial for effective adsorption, catalysis, and ion-exchange capabilities. These changes match with increased disorder and reduction of crystallite phase intensity in XRD, indicating the material's conversion from mere KOH-activated carbon to an advanced multifunctional adsorbent.

By integrating surface and porosity enhancement, the material achieves simultaneous improvements in capacity ($Q_{\max}$), selectivity (micropore distribution profiles), and accessibility (higher external surface and mesopore fraction), all while remaining consistent with or exceeding the physical/chemical benchmarks set in the latest literature.

5.1. Benchmarking against published works

Relative to the date stone-derived activated carbons summarized in Table 1, the laser-activated carbon (LAC) produced in this study exhibits comparatively high surface area (nitrogen BET/DFT: 2100 – 2500 m²g⁻¹), increased monolayer adsorption capacity and a balanced micro/mesopore contribution. In many previous reports, surface areas below approximately 950 m²g⁻¹ and predominantly narrow pore size distributions were obtained. In contrast, the present approach yields a carbon material that combines pronounced microporosity with a measurable mesoporous fraction and enhanced surface functionality within a single processing route.

These results suggest that laser post-treatment can be an effective complementary strategy for tailoring the textural and surface properties of biomass-derived activated carbon and may offer a promising pathway for further development of sustainable porous carbon materials.

5.2. Applications and future potential

The observed enhancements in surface area, pore structure, and energetic characteristics have practical implications beyond fundamental materials characterization. The coexistence of high surface area with a hierarchical pore network comprising both micro- and mesopores, together with a relatively uniform distribution of adsorption sites, renders the laser-activated carbon (LAC) a promising candidate for a range of adsorption- and energy-related applications. In particular, the dominant microporosity is favorable for the adsorption of small gas molecules such as CO₂, H₂, and CH₄, while the presence of mesopores can facilitate improved mass transport and accessibility of active sites, which are important for both gas separation and liquid-phase pollutant removal.

Furthermore, the incorporation of oxygen-containing surface functionalities may enhance interactions with polar molecules and contribute to improved wettability and charge transfer in electrochemical environments. In this context, the combined micro/mesoporous architecture and surface chemistry are expected to support faster ion diffusion and more efficient electrolyte penetration, which are beneficial for applications such as supercapacitors and as supports in heterogeneous catalysis. Collectively, these characteristics suggest that laser post-treatment provides a versatile approach for tuning the functional performance of biomass-derived activated carbons, thereby broadening their potential applicability in environmental and energy-related technologies.

6. Conclusion

Laser post-treatment of KOH-activated date stone carbon produces a next-generation sustainable adsorbent and catalyst support. Multi-model consistency across XRD, SEM, FTIR, BJH, HK, DFT, DR, DA, BET, Langmuir, and t-plot analyses confirm major improvements in surface area, pore architecture, and surface chemistry. Compared with traditional methods and previous literature, laser-enhanced AC achieves record-setting porosity (>2100 m²/g), broader micropore and mesopore distributions, higher adsorption capacity, and more favorable surface functionalities.

These unified findings, validated by experimental and theoretical probes, demonstrate marked advantages for gas capture, pollutant removal, and catalytic applications. Laser processing should be further explored to fine-tune pore size distributions and optimize energy efficiency, advancing the field towards scalable green material technologies.

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Submitted 12 October 2025; revised 8 February 2026; accepted 19 May 2026

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Conflict of interest: the authors declare no conflict of interest.

Cationic organic dyes adsorption on few-layer graphene produced by self-propagating high-temperature synthesis

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PACS 68.43.-h

ABSTRACT The effectiveness of carbon nanomaterials in purifying water from organic dyes has been proven over the previous decade. However, the problem of industrial application of carbon nanomaterials has not yet been solved. This is primarily due to the high cost and low productivity of carbon nanomaterials synthesis methods. This article presents the thermodynamic and kinetic data of rhodamine 6G and methylene blue adsorption on few-layer graphene. Few-layer graphene was obtained by self-propagating high-temperature synthesis from cellulose. It is a promising method which is inexpensive and easy to scale. It was found that the studied few-layer graphene has a high adsorption capacity for both dyes, and the obtained values of adsorption capacity are higher than most of the studied carbon materials, such as carbon nanotubes or activated carbon. The most common adsorption models were used to describe the thermodynamics of the process. The kinetics of the process are described by a pseudo-second-order equation, which is quite common in graphene materials. The proposed adsorption mechanism is based on hydrophobic interaction between adsorbent and adsorbate with the formation of H- π and π - π bonds.

KEYWORDS Few-layer graphene, graphene, SHS, adsorption, rhodamine 6G, methylene blue.

ACKNOWLEDGEMENTS The study was performed under state assignment of Ioffe Institute FFUG-2024-0019.

FOR CITATION Podlozhnyuk N.D., Vozniakovskii A.A., Voznyakovskii A.P., Kidalov S.V. Cationic organic dyes adsorption on few-layer graphene produced by self-propagating high-temperature synthesis. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 357–366.

1. Introduction

Organic dyes are widely used in the textile, paper, and cosmetics industries. Dyes make it possible to achieve stable coloring of most materials and their production is constantly increasing. Organic dyes are classified according to their structure. Most of them are bulky molecules containing aromatic groups and heteroatoms. However, organic dyes are dangerous to the environment and humans, even in extremely low concentrations [1]. The effect of dyes on organisms is still at the research stage due to the synthesis of new dyes [2]. That's why, one of the problem of industries using dyes is to treat their wastewater.

One of the most common methods of purifying water from organic dyes is adsorption due to its fairly simple and relatively cheap implementation method. Various carbon materials can be adsorbents, such as activated carbon [3], carbon black [4], highly dispersed graphite [5], carbon nanotubes [6], as well as natural materials – sawdust [7]. However, industry development led to an increase in the volume of wastewater, and treatment cannot be carried out with proper efficiency using classical adsorbents. Therefore, the adsorption properties of new materials are actively studied including nanomaterials. For these purposes, graphene and its derivatives can be used. It has been shown that graphene-based materials can act as an effective adsorbent for many substances, for example, dyes [8,9], gases [10,11], aromatic solvents [12], and metal ions [13]. One of the characteristics of graphene nanostructures is the number of layers, which can also influence on adsorption efficiency. However, there is currently no consensus in the literature regarding the detailed influence of the number of layers in graphene-based materials on their adsorption efficiency. The theoretical value of the specific surface area of single-layer graphene is 2600 m²/g and by increasing the number of layers the specific surface area will decrease. It should also be noted that in addition to the specific surface area, attention should be paid to the pore volume, type and degree of surface functionalization. The use of graphene materials for adsorption purposes is still limited by the high cost and low productivity of synthesis methods [14,15]. The complexity of the synthesis of carbon nanomaterials may cast doubt on their use as adsorbents. Thus, for the real use of carbon nanomaterials in adsorption

processes, in addition to increasing the adsorption capacity, it is also necessary to look for more accessible methods of synthesis.

In our previous works, it was shown that few-layer graphene obtained by self-propagating high-temperature synthesis [16] is an effective adsorbent for purifying water from radionuclides [17] and mycotoxins [18]. We have also previously shown that FLG obtained by the SHS method from a mixture of cellulose and ammonium nitrate in a mass ratio of 1/1 is capable for adsorption of rhodamine 6G [19]. In this work, we selected the optimal composition of the mixture for FLG synthesis by the SHS method for the effective adsorption of organic dyes – rhodamine 6G (Rh6G) and methylene blue (MB). Rh6G and, in particular, MB are fairly common objects in the study of organic dye adsorption. They are also cationic and suitable for objects with oxygen-containing groups. The main difference between these dyes can be considered their geometry and size, which will be discussed below. Self-propagating high-temperature synthesis can be used for obtaining few-layer graphene from wastes and products containing carbohydrates - cellulose, lignin, starch, etc., which is utilized for processing waste from the pulp and paper industry. The productivity of the method in laboratory is 500 g/hour, while the low cost of the product is due to cheap reagents and the simplicity of the synthesis process.

2. Experimental part

2.1. FLG synthesis

Few-layer graphene (FLG) was synthesized by self-propagating high-temperature synthesis from cellulose (99.9 %, Sigma-Aldrich, no. 9004-34-6) according to [16]. A mixture of cellulose and ammonium nitrate was added to a steel reactor in a mass ratio of 30/70, respectively. The mixture was heated to 250 °C, at which point the decomposition of ammonium nitrate began, and the reaction started. After the end of the exothermic reaction, the product was washed with demineralized water and isopropyl alcohol and then dried in air at 120 °C. Dried FLG was homogenized in a drum mill for 20 min (BPR 50/1).

2.1.1. Annealing in vacuum. To investigate the adsorption mechanism, FLG was annealed in vacuum. 1 g FLG was placed in a vacuum oven (VTSh-K52-250, Octan), after which the atmosphere was pumped out to a pressure of $6.6 \cdot 10^{-3}$ Pa. Then, the furnace was heated to 1100 °C at a heating rate of 15 °C/min, the sample was annealed at 1100 °C for 2 hours.

2.2. Characterization of FLG

Images of the samples were obtained by scanning electron spectroscopy (SEM) using a Mira-3M scanning electron microscope (TESCAN). To obtain SEM images, a sample of FLG was applied to double-sided electrically conductive carbon tape 8 mm wide (TED PELLA, INC.). X-ray phase analysis was carried out on a Rigaku SmartLab 3 X-ray diffractometer ($\text{CuK}\alpha$, wavelength $\lambda = 0.154051$ nm). The particle sizes of FLG were determined by laser diffraction using Mastersizer 2000 (Malvern Instruments). For measurements, a 50 mg sample was used, which was dispersed in 50 ml of deionized water by stirring for 1 minute. FTIR spectra of FLG were obtained using an Infracum FT-08 spectrometer (Lumex-Marketing LLC). Raman spectra of FLG were obtained using a “Ntegra Spectra” (NT-MDT). Zeta potential measurements were performed using a Zetasizer Nano ZS (Malvern Instruments). pH- measurement was carried out using a laboratory ion meter I-160 (Antech). To determine the specific surface area of FLG samples, we used the ASAP 2020MP automated system (Micromeritics), designed to measure the characteristics of the adsorption capacity by the volumetric method using various gases. The studies were carried out using the method of low-temperature nitrogen adsorption (77 K).

2.3. Adsorption of organic dyes

Rh6G analytical grade “GK Interhim” and MB analytical grade “GK Interhim” were used. To study the adsorption capacity of FLG towards organic dyes, standard solutions of Rh6G with a concentration of 100 mg/dm³ and MB with a concentration of 1 g/dm³ were prepared in demineralized water. All other solutions were obtained by dilution standard solutions. The adsorption study was carried out in 250 cm³ flat-bottomed flasks. An organic dye with a known concentration and FLG was added to the flask after that the mixture was kept under the studied conditions on an S-3.02 20M auto-shaker (ELMI). FLG was separated from solution by centrifugation at 4000 rpm for 10 min. The equilibrium concentration of organic dye solutions was determined by absorbance at 520 nm and 660 nm for Rh6G and MB, respectively, using a UV-1800 ECOVIEW spectrophotometer (Shanghai Mapada Instruments Co., Ltd.). The specific adsorption capacity q_e was calculated using equation (1).

$$q_e = \frac{C_0 - C_e}{m} \times V, \quad (1)$$

where C_0 is the concentration of the dye before adsorption (mg/dm³), C_e is the concentration of the dye after adsorption (mg/dm³), m is the mass of FLG (g), V is the volume of the solution (dm³).

2.4. Effect of pH

The effect of pH on adsorption was studied from 3 to 11 pH in a 100 cm³ solution of Rh6G and MB with concentrations of 40 mg/dm³ and 200 mg/dm³ respectively, and 50 mg of FLG. HNO₃ (70 %, Sigma-Aldrich, no. 7697-37-2), diluted with demineralized water to 1 %, and NaOH (98 %, Sigma-Aldrich, no. 1310-73-2) in the form of 1 were added to vary pH of the solution.

2.5. Effect of temperature

To study the thermodynamics of adsorption, 50 mg of FLG was added to 100 cm³ of an organic dye solution with initial concentrations from 5 to 100 mg/dm³ and from 5 to 800 mg/dm³ for Rh6G and MB respectively, at temperatures of 293 and 333 K. Temperature was controlled by water thermostat.

2.6. Adsorption kinetics

The kinetic of adsorption was carried out using a solution 40 mg/dm³ and 800 mg/dm³ of Rh6G and MB, respectively, and 50 mg of FLG. The contact time was varied from 10 to 1350 min (24 h) on an S-3.02 20M autoshaker (ELMI).

3. Results and discussion

3.1. FLG structure

Using SEM method, it was shown that the particles of FLG obtained by self-propagating high-temperature synthesis are plates with torn edges (Fig. 1A). Using the EDX-analysis, it was found that FLG contains nitrogen (5 %) and oxygen (10 %) atoms on the surface due to the synthesis technique. X-ray diffraction studies were carried out to estimate the number of layers in FLG (Fig. 1B). Using the Scherrer equation, the crystallite size was determined (12.1 Å). Based on the data on the width of the 002 peak at half maximum and in conjunction with data on the interplanar distance (4.07 Å), it was established that the number of layers in the FLG does not exceed 3 [20]. The X-ray image also contains low-intensity broad peaks (10 °2θ, 44 °2θ) that are the result of software processing.

The Raman spectrum (Fig. 1C) contains three characteristic bands of graphite materials: D – 1380 cm⁻¹, G – 1601 cm⁻¹ and 2D – 2834 cm⁻¹. The obtained Raman spectrum is similar for graphene oxide and reduced graphene oxide [21, 22]. The presence of the D-band indicates various defects in the aromatic structure - vacancies, sp³-hybridized carbon atoms, and incorporation of oxygen atoms into the aromatic structure. The G-band characterizes planar vibrations of sp²-hybridized carbon atoms. The D+G band should also be present in the 2D-band area, but it is not detected. These bands characterize structural electronic defects [23, 24]. However, as was shown in [25], the synthesized FLG does not contain Stone-Wales defects, unlike graphene nanostructures synthesized using alternative methods.

The FTIR spectrum of FLG (Fig. 1D) contains bands at 1170 cm⁻¹, 1540 cm⁻¹, 2360 cm⁻¹, 2850 cm⁻¹, 2934 cm⁻¹ and 2966 cm⁻¹. The band at 1170 cm⁻¹ corresponds to the vibration of the carboxyl bond (C–O), band at 1540 cm⁻¹ can be attributed to the vibration of the C=C bond, band at 2360 is due to carbon dioxide from the air, and bands at 2850 cm⁻¹, 2934 cm⁻¹ and 2966 cm⁻¹ refers to C-H vibrations in the methyl group [26]. From EDX, Raman spectroscopy and FTIR data, it can be concluded that the structure of FLG obtained by self-propagating high-temperature synthesis is close to the structure of reduced graphene oxide.

The average particle size determined by laser diffraction was 1 μm (Fig. 2A). The most significant volume contribution was made by particles 20 – 28 μm (Fig. 2B).

3.2. Adsorption of organic dyes

To investigate the adsorption mechanism of cationic organic dyes, FLG was annealed in vacuum at 1100 °C. As a result of annealing, the specific surface area of FLG decreased from 661 m²/g to 377 m²/g, the pore volume (*V_{pore}*) from 0.397 to 0.263, and the micropore volume (*V_{micropore}*) from 0.263 to 0.126 (Tabel 1). Also, as a result of annealing, the zeta potential (ζ) from –30 mV became almost equal to zero and the content of “O” heteroatoms decreased from 10 at.% to 8 at.% and “N” from 5 at.% to 0 at.%. A decrease in the concentration of heteroatoms leads to a decrease in the content of functional groups, which in turn becomes practically impossible to detect by FTIR spectrometry (Fig. 3). A series of experiments were carried out on the adsorption of Rh6G and MB with FLG particles and FLG annealed in vacuum at 1100 °C. From Fig. 4 it can be seen that the adsorption capacity of FLG annealed in vacuum is almost two times lower than that of the original FLG for both dyes.

If we consider the process of adsorption of cationic organic dyes on the FLG surface from the point of view of electrostatic forces that is positively charged particles are attracted to a negatively charged surface, then the reduction of ζ to almost zero (from –30 to –1 mV) after annealing in a vacuum should almost eliminate the possibility of cationic dyes adsorption on FLG annealed in vacuum. If we consider the process of adsorption of cationic organic dyes on the FLG surface from the point of view of hydrophobic interactions – dye molecules interact with areas of the FLG surface with the formation of H-π or π-π bonds, thereby reducing the surface energy, then the adsorption capacity should depend from the specific surface of the adsorbent. In general, such a dependence is observed in this case. Annealing FLG in vacuum leads to a decrease in specific surface area by 42.9 %, while the adsorption capacity decreases by 38.7 % and 44.9 % for Rh6G

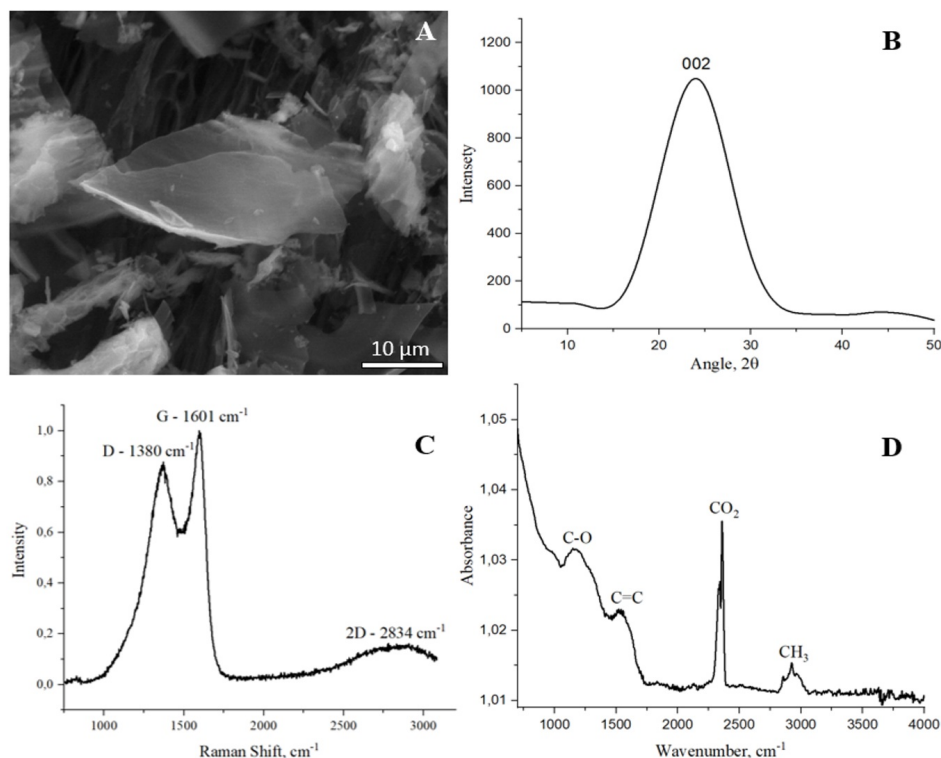


FIG. 1. (A) SEM image of the FLG, (B) X-Ray diffraction of the FLG, (C) Raman spectrum of the FLG, (D) FTIR spectrum of the FLG

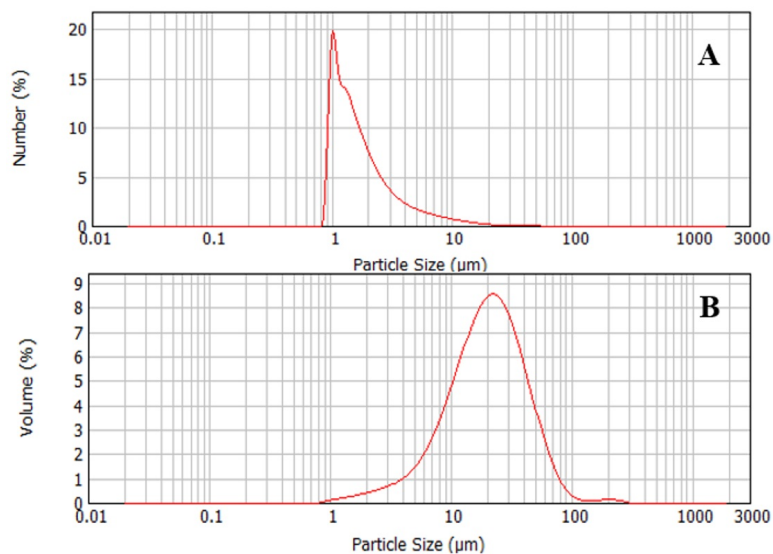


FIG. 2. Distribution of FLG particles by (A) number and (B) volume after milling

and MB, respectively. Of course, in a real process, all of the above interactions between the adsorbent and the adsorbate may occur, but the specific surface area has the greatest influence on the adsorption capacity.

3.2.1. Effect of pH. The pH of the aqueous solution is one of the most important factors in adsorption studies. The adsorption of Rh6G and MB at different pH values of the solution are shown in Fig. 5. As can be seen from Fig. 5, the acidity of the solution has little effect on the adsorption of both dyes. Increasing pH from 2 to 11 leads to a slight increase in sorption capacity by 8 and 11 % for Rh6G and MB, respectively. An approximately similar result was observed in [8], where non-functionalized graphene was used for MB adsorption. When using graphene oxide, the acidity of the medium strongly affects the adsorption of cationic organic dyes, as was shown in [27]. This difference is due to the presence of a huge number of oxygen-containing functional groups – carboxyl and hydroxyl – on the surface of graphene oxide. This makes adsorption possible due to electrostatic interaction, and as the pH of the solution increases, additional ionization of

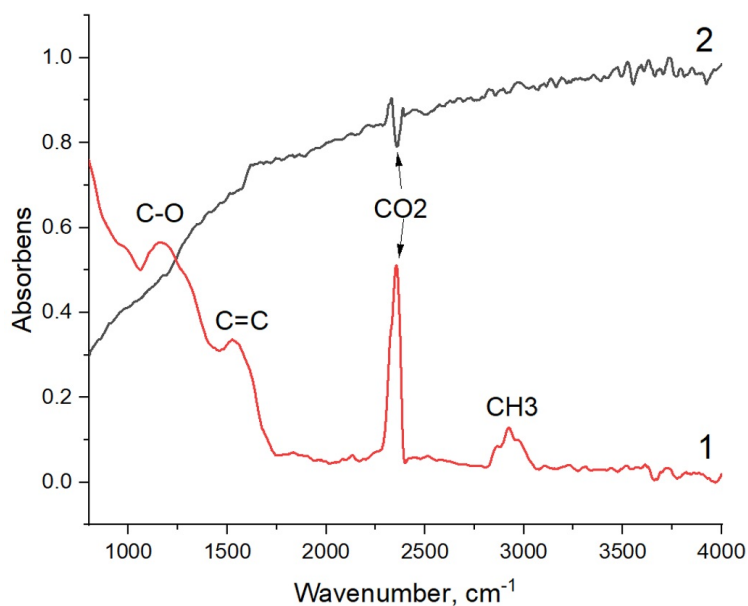


FIG. 3. FTIR spectrum of FLG (1) and FLG annealed in vacuum 1100 °C (2)

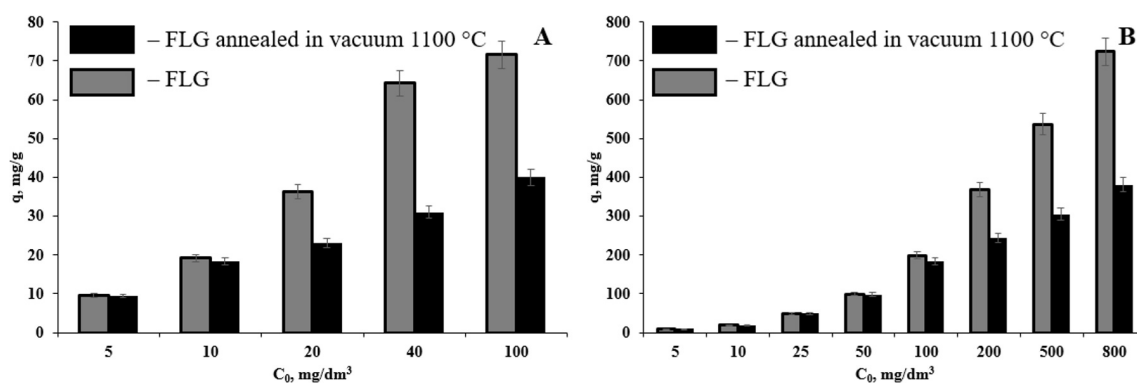


FIG. 4. Dependence of FLG and FLG annealed in vacuum 1100 °C adsorption capacity on the initial dye concentration: (A) Rh6G, (B) MB

these groups occurs, which further stimulates adsorption by this mechanism. In the case of FLG, the obtained dependence confirms the conclusion made earlier that the adsorption of the studied dyes on the FLG surface is due predominantly to the hydrophobic interaction of the adsorbate with the adsorbent due to the low content of functional groups.

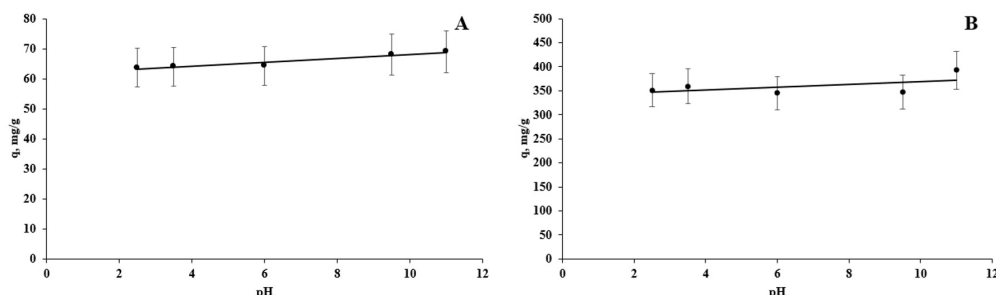


FIG. 5. pH effect on adsorption capacity of FLG (A) Rh6G, (B) MB

3.2.2. Adsorption isotherms. The solution temperature is another important factor in adsorption studies. In Fig. 6. adsorption isotherms of Rh6G and MB at 20 and 60 °C are presented. It can be seen that the adsorption capacity increases as the temperature increases. The maximum adsorption capacity increases from 71,6 to 76,1 mg/g for Rh6G and from 723 to 969 for MB with the increase in temperature from 293 to 333 K. These results demonstrate that Rh6G and MB

adsorption onto FLG is endothermic. The more significant effect of increasing adsorption capacity for MB with increasing temperature can be associated with the size and shape of the dye molecules. In Rh6G, the xanthene part is rotated relative to the benzoyl part by almost 90° [28], and the Rh6G molecule is bigger than the MB molecule. Thus, the Rh6G molecule can create enormous steric hindrances when filling adsorption sites.

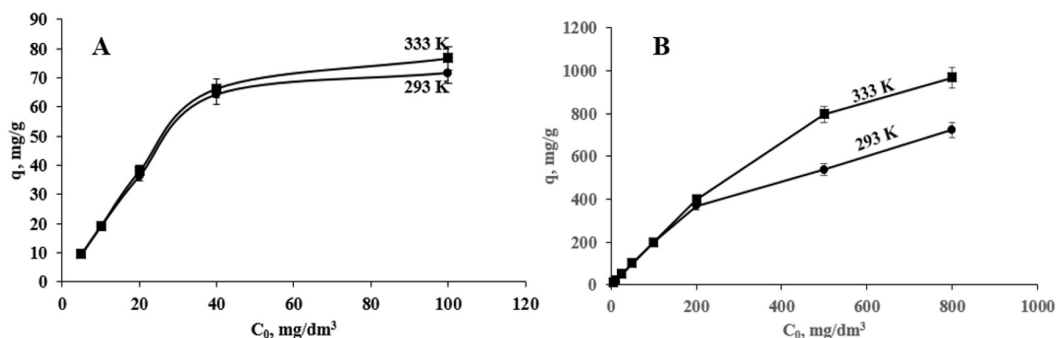


FIG. 6. Adsorption isotherms of (A) Rh6G and (B) MB at 293 and 333 K on FLG

In Tabel 1, the obtained results were compared with other works on this topic. It can be concluded that the resulting FLG obtained by self-propagating high-temperature synthesis has potential for use in water purification from cationic organic dyes. Moreover, the simplicity of synthesis may allow it to find its industrial application as an adsorbent.

TABLE 1. Comparison with other adsorbents

Material	Adsorptive	Conditions	$q_{\max}$ (exp)	Reference
FLG	Rh6G	293 K, pH6	71.6	This work
	MB		723.8	
FLG	Rh6G	293 K, pH 6	9.4	Our previous work [19]
AC	MB	293 K pH 2.8	625	[3]
CNT	MB	333 K, pH 7	60	[6]
Graphene	MB	333 K, pH 7	205	[8]
AC-PEI-SAA	Rh6G	298 K, pH 4.45	122.5	[30]
AC	MB	333 K	324.4	[31]
GO	MB	298 K, pH 7	570.4	[22]
AC	MB	298 K, pH 7	19.5	[32]
GO	Rh6G	–	23.3	[33]
RGO-Fe ₃ O ₄	Rh6G	298 K, pH 7	30	[34]

Langmuir, Freundlich, and Temkin models were used to describe adsorption isotherms. The Langmuir model assumes that adsorption is monomolecular and occurs on a homogeneous surface; adsorbed molecules do not interact with each other [35, 36]. The Langmuir isotherm is a straight line described by equation (2):

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \times k_L \times C_e}, \quad (2)$$

where C_e is the equilibrium concentration of the solution after sorption (mg/dm^3), $q_{\max}$ is the maximum adsorption capacity (mg/g), k_L is the Langmuir constant, characterizing the interaction of the adsorbate and the adsorbent (dm^3/mg).

The Freundlich equation is empirical (3) and describes adsorption on a heterogeneous surface [36, 37].

$$\lg(q_e) = \lg(k_F) + \frac{1}{n} \times \lg(C_e) \quad (3)$$

where k_F is the Freundlich constant (dm^3/mg), characterizing the adsorption capacity, $1/n$ is an empirical parameter characterizing the intensity of adsorption.

Temkin's model assumes that the heat of adsorption of all molecules in a layer decreases linearly as the layer is filled, while adsorption occurs with a uniform distribution of maximum binding energy. However, it does not describe data well at very high and very low concentrations [38], equation (4) expresses this model in linear form.

$$q_e = B_t \times \lg(K_t) + B_t \times \lg(C_e), \quad (4)$$

where K_t is the Temkin constant (dm^3/mg), characterizing the adsorption capacity, B_t is a constant, characterizing the heat of adsorption (J/mol).

The constants calculated using these models are given in Tabel 2. The highest value of R^2 is observed in isotherms calculated using the Langmuir model, however, the calculated values of the adsorption capacity of the monolayer ($q_{\max}$) are less than the experimental ones by 9 and 14 % at 293 and 333 K, respectively, for Rh6G and by 44 and 6 % at 293 and 333 K, respectively, for MB. Langmuir adsorption is monomolecular and the adsorption capacity of a monolayer ($q_{\max}$) is a limiting value that must be greater than or equal to the experimental value of the adsorption capacity. This fact indicates that the Langmuir model cannot adequately describe the process of adsorption of organic dyes on FLG. The calculated Freundlich isotherms have the lowest R^2 values among used models, while an increase in temperature leads to an increase in K_F , which is consistent with experiment. Isotherms calculated using the Temkin model have a fairly high value of R^2 , the nature of the change in the constant B_t , which takes into account the effect of temperature, is consistent with the experiment – an increase in temperature has little effect on the Rh6G adsorption process and significantly affects to MB adsorption process.

TABLE 2. Calculated constants based on adsorption models

Model	Parameters	Rh6G		MB	
		293 K	333 K	293 K	333 K
Langmuir model	$q_{\max}$ (mg/g)	67.57	65.36	500	909.09
	k_L (dm^3/gm)	0.94	1.28	1.25	1.38
	R^2	0.99	0.99	0.98	0.99
Freundlich model	k_F (dm^3/gm)	23.81	26.13	181.89	341.43
	$1/n$	0.34	0.33	0.22	0.1859
	R^2	0.89	0.84	0.95	0.91
Temkin model	B_t (J/mol)	11.2	11.5	74.05	10.7
	K_t (dm^3/gm)	15.75	22.35	14.79	20.78
	R^2	0.95	0.92	0.96	0.95

3.2.3. Adsorption kinetics. An increase in temperature accelerates the adsorption process, and an inflection in the graph occurs at 20 minutes for Rh6G (Fig. 7A). The adsorption process also slows down due to a significant decrease in adsorption centers and steric difficulties created by bulky molecules. Adsorption of MB at 293 K also slows down significantly after 1.5 hours, and a further slight change in adsorption capacity indicates complete saturation of the adsorbent (Fig. 7B). At 333 K, MB adsorption curve also has an inflection at 90 min. An increase in temperature increases the mobility of MB molecules, which allows them to more actively occupy adsorption sites, and because MB molecules create less steric hindrance, we observe an increase in adsorption capacity.

Adsorption kinetics can be described by pseudo-first (5) and pseudo-second (6) order kinetic models [39]. The limiting factor in the pseudo-first-order model is physical adsorption, and in the pseudo-second-order model, the limiting stage is chemical adsorption [40].

$$\lg(q_e - q_t) = \lg(q_e) - \frac{k_1 \times t}{2.303}, \quad (5)$$

$$\frac{t}{q_e} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e}, \quad (6)$$

where q_t and q_e (mg/g) are dye concentrations in the sorbent at the time (t) and equilibrium, respectively, k_1 is the adsorption rate constant in the pseudo-first-order model, k_2 is the adsorption rate constant in the pseudo-second-order model, t is adsorption time (min).

The pseudo-first-order model does not allow the calculation of the adsorption capacity with sufficient accuracy (Table 3). The deviation of the experimental value of the adsorption capacity from the calculated is 25 and 64 % at 293 and

333 K for Rh6G and 64 and 53 % at 293 and 333 K, respectively, for MB. The deviation of the experimental value of the adsorption capacity calculated by the pseudo-second-order equation is 12 and 21 % at 293 and 333 K for Rh6G and 1 and 3 % at 293 and 333 K, respectively, for MB. Thus, the pseudo-second-order kinetic model better describes the process of adsorption of Rh6G and MB on the FLG surface.

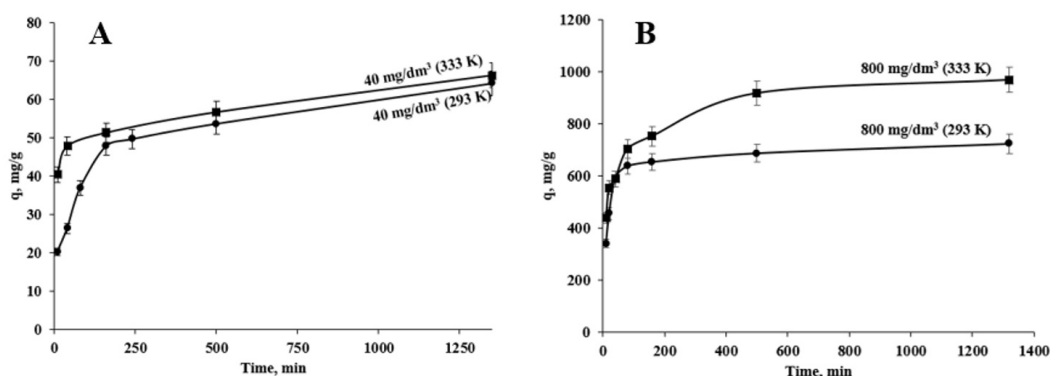


FIG. 7. The dependence of FLG adsorption capacity on time (A) rhodamine 6G, (B) MB

TABLE 3. Parameters of organic dyes adsorption on the FLG surface, calculated using pseudo-first and pseudo-second order kinetic models

Model	Parameters	Rh6G		MB	
		293 K	333 K	293 K	333 K
Pseudo-first-order kinetic model	q_{exp} (mg/g)	64.29	66.32	723.83	969.5
	q_{cal} (mg/g)	47.81	24.02	202.82	456.14
	k_1 (1/min)	$1.26 \cdot 10^{-3}$	$6.08 \cdot 10^{-4}$	$7.38 \cdot 10^{-4}$	$8.25 \cdot 10^{-4}$
	R^2	0.97	0.98	0.69	0.98
Pseudo-second-order kinetic model	q_{exp} (mg/g)	64.29	66.32	723.83	969.5
	q_{cal} (mg/g)	56.18	52.36	714.29	1000
	k_2 (g/mg/min)	$5.42 \cdot 10^{-4}$	$5.69 \cdot 10^{-3}$	$9.95 \cdot 10^{-5}$	$3.55 \cdot 10^{-5}$
	R^2	0.99	0.99	0.99	0.99

4. Conclusions

FLG obtained by self-propagating high-temperature synthesis can be used as an effective sorbent for cationic dyes – rhodamine 6G and methylene blue. Based on EDX, Raman spectroscopy and FTIR data, it can be concluded that the structure of FLG obtained by self-propagating high-temperature synthesis is close to the structure of reduced graphene oxide.

The adsorption of the studied cationic organic dyes on the FLG surface is due to hydrophobic interaction with the formation of π – π and H– π bonds between the adsorbent and the adsorbate. The smaller the size of the dye molecule, the greater the adsorption capacity for this dye.

The adsorption process of cationic dyes is endothermic and it is better described by the Temkin model. This model assumes a polymolecular type of adsorption. The possibility of dimers formation for dyes used in this work also satisfies this position in the Temkin model.

The pseudo-second-order kinetic equation satisfactorily interprets the kinetics of the process, which is quite common in graphene materials. The FLG adsorption capacity value of rhodamine 6G and methylene blue is higher or comparable to the already studied analogs. FLG obtained by self-propagating high-temperature synthesis can be an industrial organic dye adsorbent, considering the simplicity and easily scalable synthesis method.

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Submitted 17 November 2025; revised 17 February 2026; accepted 9 June 2026

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Conflict of interest: the authors declare no conflict of interest.

Fe-Mo/Al₂O₃ catalyst for methane decomposition synthesized by solution combustion technique using oxalic acid

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ABSTRACT This work reports the synthesis of 80%Fe–10%Mo/10% Al₂O₃ catalysts via solution combustion synthesis using oxalic acid as fuel. The catalysts were tested in methane decomposition at 850 °C and 1 atm for 6 h. The synthesized samples were characterized by X-ray diffraction, transmission electron microscopy, photosedimentation analysis, etc. The specific carbon yield ranged from 5.8 to 8.4 g/gcat and the hydrogen yield from 1.0 to 1.4 mol/g_{cat}, respectively. Catalytic decomposition of methane over Fe–Mo/Al₂O₃ led to the formation of mixture of bamboo-like carbon nanotubes and multi-walled carbon nanotubes. It was found that the highest yield of MWCNTs was reached at fuel-to-oxidizer ratio of 0.022.

KEYWORDS catalysis; solution combustion; methane; catalyst; Fe-Mo-catalyst.

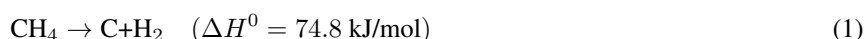
ACKNOWLEDGEMENTS This work was partially supported by State task of Ministry of Higher Education and Science of Russian Federation (code no. FSUN-2026-0006).

FOR CITATION Kurmashov P.B., Shishin A.A., Golovakhin V., Danilenko M.A., Shpakova S.A., Belov N.A., Gudyma T.S., Ukhina A.V., Ishchenko A.V., Bannov A.G. Fe-Mo/Al₂O₃ catalyst for methane decomposition synthesized by solution combustion technique using oxalic acid. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 367–374.

1. Introduction

Currently, the development of technology for processing of associated petroleum gas (APG), natural gas and other gases containing C₁–C₄ hydrocarbons is a pressing issue for many oil-producing companies. Solving this problem will improve the environmental situation in Russia. A modern and economically efficient method for their processing is low-temperature pyrolysis, which occurs at temperatures up to 1000 °C. This process is simple to operate, easily scalable, and the reaction products are free of carbon oxides, making it a “CO_x-neutral” method. Furthermore, the process leads to the formation of hydrogen and nanostructured carbon. The production of the latter, as a product with specific added value, is considered an advantage from an economic perspective due to its wide range of applications [1]. Hydrogen can be used in metallurgy, hydrogen energy, petrochemicals, the chemical industry, etc. Carbon nanomaterials can be applied in environmental protection (as sorbents, in gas sensing) [2–5], as additives for composite materials [6–9], in electrochemical devices (supercapacitors, batteries) [10, 11], among other uses.

Low-temperature pyrolysis can be implemented over a wide range of temperatures (500–1000 °C) and pressures (1–10 atm) in the presence of catalysts containing metals such as Ni, Fe, Co, etc [12–16]. In this technology, the catalyst plays a primary role; its composition affects the process temperature, and its synthesis method impacts the catalyst production cost. The formation of hydrogen and carbon nanofibers is based on the decomposition reaction of the initial methane into carbon, hydrogen is passing according the reaction (1) [17–20].



The solution combustion synthesis (SCS) can be used for synthesis of catalysts for methane decomposition and related processes [21–24]. This method is relatively simple, rapid, and is a single-step process. It is based on a redox reaction between metal nitrates and reducing agents (so-called fuels), such as urotropine, glycine, oxalic acid, etc. [18].

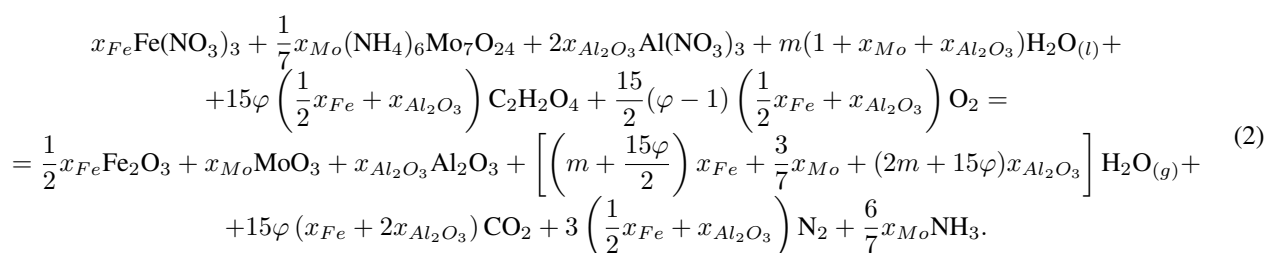
The oxalic acid-based SCS is applied for synthesis of Ni-containing catalysts [25, 26], CoCr_2O_4 ceramic pigment nanoparticles [27], hexagonal WO_3 [28], CuO [29] and other materials. However, the results of the use of oxalic acid for SCS of Fe-Mo/ Al_2O_3 for decomposition of methane and even for production of multi-walled carbon nanotubes (MWCNTs) are almost absent. The system is typically applied for synthesis of MWCNTs [30–32].

This work is devoted to investigation of the Fe-Mo/ Al_2O_3 catalysts using oxalic acid as a fuel for the methane decomposition reaction. The catalysts were tested and characterized at different fuel-to-oxidizer ratios. An analysis of the catalytic activity, crystallite size, phase composition, particle size of the resulting carbon nanomaterial was conducted.

2. Materials and methods

A series of 80%Fe–10%Mo/10% Al_2O_3 catalyst for the synthesis of MWCNTs was synthesized. Oxalic acid was used as the fuel in the catalyst systems under investigation. The implementation of catalyst synthesis via the SCS technique requires the calculations of fuel-to-oxidizer ratio φ . For this purpose, an approach based on thermodynamic calculations of the redox reaction is employed. The combustion reaction in an oxygen-containing environment, involving a metal nitrates, ammonium paramolybdate, and oxalic acid (fuel), can be derived by combining the decomposition reactions of metal nitrates to metal oxides in the presence of water, according to the reactions below.

Thus, the general combustion equation for the system under consideration can be obtained (Equation 2).



The investigation of the kinetic patterns of the process for producing carbon nanofibers and hydrogen via the catalytic decomposition of C1–C4 hydrocarbons was carried out using the catalyst samples described above. The testing was performed in a laboratory-scale quartz reactor at atmospheric pressure. The concentrations of the reagents and reaction products were measured using a Khromos GC-1000 gas chromatograph. A schematic diagram of the setup is shown in Fig. 1.

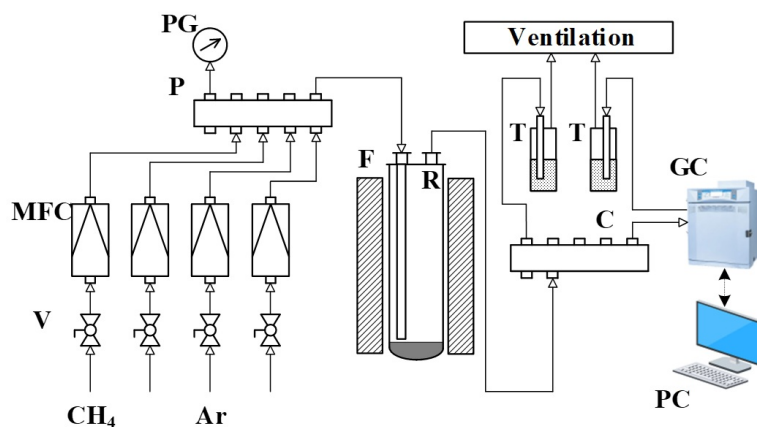


FIG. 1. Schematic diagram of the catalytic setup equipped with a quartz reactor: PG – Pressure Gauge; P – pipeline; MFC – Mass flow controller; V – Valve; F – Furnace (500–1000 °C); R – Reactor; T – Water trap; GC – Gas chromatograph; PC – Personal Computer

The quartz reactor is a vertical flask with an internal diameter of 28 mm and a height of 220 mm, which is hermetically sealed to a metal housing via a swage nut with a gasket made of thermally expanded graphite.

Due to the presence of iron and molybdenum oxides, the catalysts of the system 80 wt.% Fe – 10 wt.% Mo / 10 wt.% Al_2O_3 were pre-reduced in a hydrogen flow at 430 °C for 1 h. Although nickel-containing systems obtained by SCS can be initiated without reduction with hydrogen [33], the 80 wt.% Fe – 10 wt.% Mo / 10 wt.% Al_2O_3 system, which is oriented more towards the production of MWCNTs, becomes active only after reduction with H_2 . On one hand, this is a disadvantage for the industrial implementation of the process; on the other hand, it is typical behavior for Fe-containing systems [34,35]. The operating temperature was 850 °C. The use of higher temperatures is not advisable from an economic point of view, as the process must be conducted with minimal costs, which is important for its piloting and semi-industrial testing. To accelerate the testing, the typical duration of the catalytic experiment was set at 6 h.

Transmission electron microscopy (TEM) was performed using a JEOL JEM-2200 FS-CS instrument with a resolution of up to 0.1 nm. The accelerating voltage was 80–200 kV.

3. Results and Discussion

The considered 80 wt.% Fe – 10 wt.% Mo/10 wt.% Al₂O₃ catalysts exhibited catalytic activity only after a preliminary reduction stage in a hydrogen flow at 430 °C (for 1 h). The hydrogen concentration value reaches its maximum level at the initial moment, ranging from approximately 11–20 vol.% (Fig. 2a), which is explained by the completion of the catalyst reduction stage and the initiation of its operation. Over time, the hydrogen concentration in the reaction medium gradually decreases, reaching values of approximately 8–14 vol.% (Fig. 2b). Subsequently, the catalyst deactivation rate decreases significantly, and a smooth decline is observed over 4 h, with the hydrogen concentration stabilizing at a level of approximately 4–6 vol.%. Varying the fuel excess had an insignificant effect on the catalyst's activity. It can be noted that compared to other common fuels (e.g., urea, glycine), the use of oxalic acid leads to a higher adiabatic combustion temperature during solution combustion synthesis due to its more negative enthalpy of formation. However, oxalic acid generates the smallest amount of gaseous products upon combustion, which in turn affects the porosity and specific surface area of the resulting catalysts.

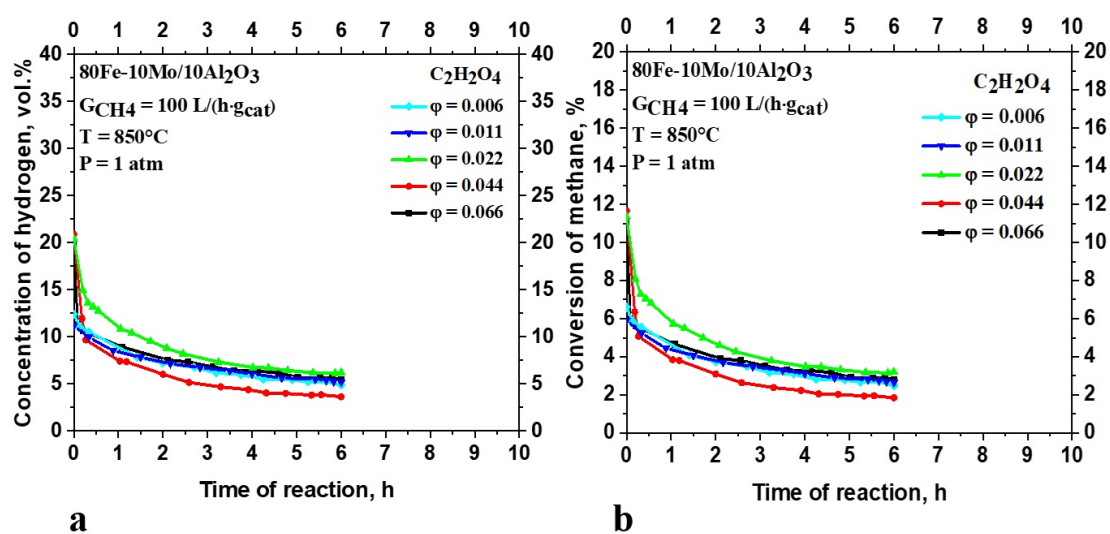


FIG. 2. (a) Hydrogen concentration and (b) methane conversion versus reaction time for the 80 wt.% Fe – 10 wt.% Mo / 10 wt.% Al₂O₃ catalyst (fuel: oxalic acid; LHSV = 8.9 h⁻¹)

Table 1 presents the results of the catalytic tests for the catalysts in the laboratory quartz reactor for the methane decomposition reaction.

TABLE 1. The results of catalytic tests

No	φ	Catalytic tests		
		t , h	Y_C , g/g _{cat}	Y_{H_2} , mol/g _{cat}
1	0.006	6	6.1	1.0
2	0.011		5.8	1.0
3	0.022		8.4	1.4
4	0.044		5.8	1.0
5	0.066		6.9	1.1

A clear optimum of catalytic activity is observed at $\varphi = 0.022$. At this value, the yields of carbon and hydrogen are maximum (8.4 g/g_{cat} and 1.4 mol/g_{cat}). This indicates that it is with this rather low fuel ratio that the most favorable conditions are created for the formation of a highly active catalytic phase. The highest rate of carbon formation was 1.4 g/(g_{cat}*h).

TEM images (Fig. 3a-c) of the catalysts represented the aggregated structures, which significantly different from the one obtained by sol-gel, impregnation and other techniques [36–39]. This is caused by high temperature reached during

combustion and the smelted-like particle morphology is typical for SCS-based powders. The diameter of nanoparticles ranged within 5–10 nm.

The Fe–Mo/ Al_2O_3 catalyst at 850 °C forms classical structures characteristic of multi-walled carbon nanotubes (MWCNTs) and bamboo-like carbon nanotubes (Fig. 3d-f).

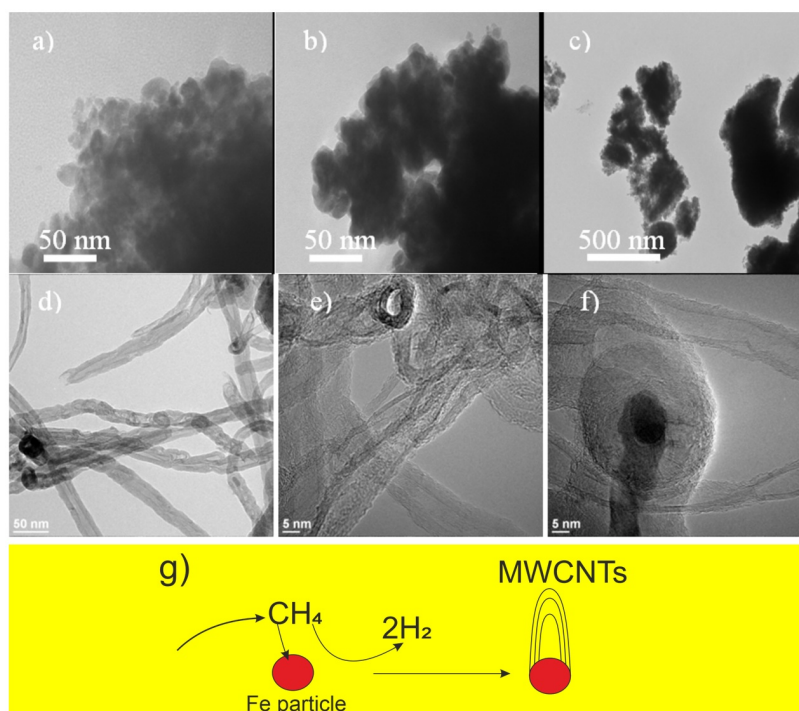


FIG. 3. TEM images of the (a-c) catalyst ($\varphi = 0.022$) and (d-f) carbon nanomaterial grown over 80 % Fe – 10 % Mo/ Al_2O_3 catalyst (850 °C, 1 atm), mechanism of methane decomposition and MWCNTs growing (g)

This suggests that tip-growth mechanism operate simultaneously during methane decomposition over the Fe–Mo/ Al_2O_3 catalyst (Fig. 3g) [40,41].

According to X-ray diffraction patterns, the catalysts of the 80 wt.% Fe – 10 wt.% Mo / 10 wt.% Al_2O_3 system synthesized with oxalic acid consisted fully of the $\text{Fe}_2(\text{MoO}_4)_3$ phase (JCPDS 31-642, monoclinic) (Fig. 4).

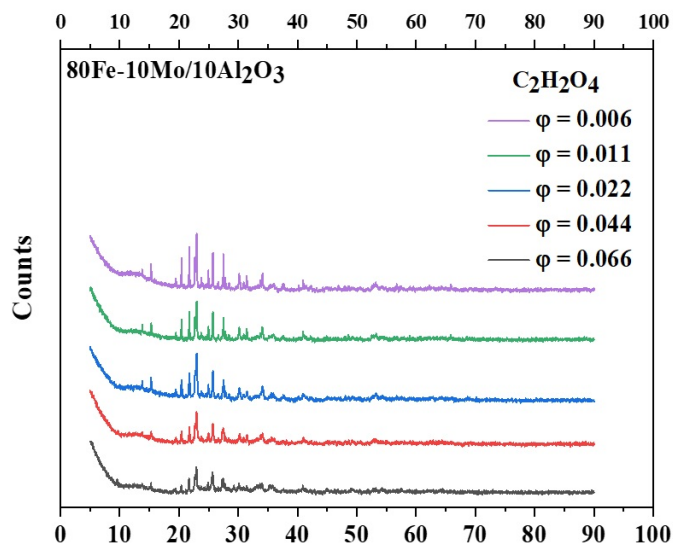


FIG. 4. X-ray diffraction patterns of the synthesized 80 wt.% Fe – 10 wt.% Mo / 10 wt.% Al_2O_3 catalysts using oxalic acid (Cu $K\alpha$ radiation, 1.54 Å)

It was found that the phase composition depends on the fuel-to-oxidizer ratio. Reflections related to the fuel are almost entirely absent, although elemental analysis of virtually all catalysts obtained by combustion synthesis typically

indicates residues of the fuel or compounds formed during its transformation (ranges within 2–4 wt.% according to energy-dispersive X-ray spectroscopy). This latter aspect has been investigated very little, and such studies represent a subject for separate research due to the complexity of the task, the vast number of compounds that fuels can form with elements in the initial mixture, and especially in the case of bi- and trimetallic systems, where the range of such compounds (and the problem of their identification) increases significantly.

For Fe₂(MoO₄)₃ the crystallite size generally increases with increasing φ (from 83.2 nm at $\varphi = 0.066$ to more than 100 nm (the large grains is not possible to determine due to high error) at $\varphi = 0.022$ –0.044). The exception is the sample with $\varphi = 0.066$, where the growth in φ induced the lower crystallite size. It is hypothesized that the most active catalyst ($\varphi = 0.022$) has a relatively high crystallite size. Therefore, it can be supposed, that this value does not bring a linear effect on the operation of the catalyst. Probably, the catalysts with fine grains operated at higher methane conversion during first minutes of process and the majority of active sites blocked during initial period. Therefore, usually, the catalysts with high crystallite size possessed higher time until reaching deactivation and higher yield of carbon and hydrogen. The relatively low crystallite size at $\varphi = 0.006$ –0.011 indicated the low-temperature synthesis and the growth in fuel-to-oxidizer ratio led to sharp growth in crystallite size caused by fuel-driven temperature increase. Further growth ($\varphi > 0.044$) induced the decrease in crystallite size, but the change in lattice parameters compared to other samples (Table 2). Even when the lattice of sample $\varphi = 0.066$ under stress state, the activity of such catalyst is not so high.

Typically, the particle size of the catalysts is large enough and somehow correlates with the compounds synthesized by SCS, representing the smelted powder of micron size particles [42–45]. It is important to note that these data represent catalyst agglomerates, not the primary particles of the active Fe-Mo phase. The analysis of $\varphi = 0.22$ sample was carried out. The photo-sedimentation analysis reveals a broad particle size spectrum ranging from 1.00 to 120.0 μm . The key statistical parameters indicate a median diameter (d_{50}) of 65.1 μm . The distribution is multimodal, with distinct peaks identified at 2.8, 10.2, 18.2, 50.3, and 67.2 μm . The granular composition is characterized by a high content of particles larger than 10.0 μm , constituting 93.4% of the sample, while only 11.5% of particles are finer than 14.0 μm . Compliance with technical specifications was confirmed by the characteristic percentiles: $d_3 = 116.8 \mu\text{m}$, $d_{50} = 65.1 \mu\text{m}$, and $d_{94} = 9.7 \mu\text{m}$. In summary, the catalyst is a polydisperse powder with a predominant fraction in the medium size range around 65 μm and a non-uniform, multimodal distribution, which is a typical characteristic for materials synthesized by the solution combustion method.

TABLE 2. Results of the X-ray diffraction of the synthesized catalyst samples

φ	Crystallite size of Fe ₂ (MoO ₄) ₃ phase, nm	Lattice parameters, Å		
		a	b	c
0.006	83.2±5	15.6828±0.004	9.2278±0.002	18.2146±0.004
0.011	66.3±5.2	15.6826±0.008	9.2296±0.002	18.2121±0.008
0.022	> 100	15.6850±0.004	9.2302±0.0012	18.2152±0.003
0.044	> 100	15.6863±0.0012	9.2303±0.0008	18.2157±0.0016
0.066	60.4±6.6	15.6968±0.014	9.2375±0.006	18.2245±0.012

TABLE 3. Comparison of yield of CNTs obtained over various catalysts

Reference	Catalyst	Gas (feedstock)	Carbon yield (time on stream), g/g _{cat}
[46]	50%Fe-50%Co (non-supported)	CH ₄	0.6 g/g _{cat} (7 h)
[47]	40%(Fe ₂ Mo)/Al ₂ O ₃	C ₂ H ₄	7.7 g/g _{cat} (n/a)
[48]	FeMo/MgO	CH ₄	5.77 g/g _{cat} (n/a)
[49]	Fe-Co/TiO ₂	C ₂ H ₂	3.4 g/g _{cat} (n/a)
This work	80%Fe-10%Mo/Al ₂ O ₃	CH ₄	8.4 g/g _{cat} (6 h)

Although the crystallite size of Fe₂(MoO₄)₃ varied significantly with φ (from 60 to more than 100 nm), no direct correlation with the catalytic activity was observed. This can be attributed to several factors. First, the Fe₂(MoO₄)₃ phase is reduced to metallic Fe(Mo) nanoparticles under H₂ at 430 °C, and the size of these active particles does not necessarily reflect the initial crystallite dimensions. Second, the Al₂O₃ formed during combustion synthesis, acts as a

structural promoter that inhibits sintering of the metallic phase, thereby stabilizing a wide range of particle sizes. Third, the presence of Mo enhances the metal–support interaction and may alter the growth mechanism of carbon nanotubes. Finally, the catalyst particles are polydisperse (1–120 μm) with complex internal porosity, so the accessibility of active sites is governed by textural properties rather than the primary crystallite size. The highest activity observed at $\varphi = 0.022$ is therefore attributed to an optimal unit cell parameters and high crystallite size of $\text{Fe}_2(\text{MoO}_4)_3$ phase.

For comparison, similar works on Fe-containing catalysts were analyzed and presented in Table 3 and showing the efficiency of the catalyst under study. However, direct comparison of carbon yields in Table 3 should be made with caution, as the data originate from different feedstocks (CH_4 , C_2H_4 , C_2H_2) and reaction conditions (temperature, pressure, time on stream), which significantly affect catalyst performance.

4. Conclusions

The SCS method with oxalic acid as a fuel has proven its effectiveness for obtaining Fe–Mo/ Al_2O_3 catalysts for the decomposition of methane. The catalysts showed activity and produced bamboo-like carbon nanotubes and hydrogen. The fuel-to-oxidizer ratio (φ) is a critically important parameter that determines the phase composition, the size of crystallites and, as a result, the catalytic activity. It was found that there is an optimal value of $\varphi = 0.022$. The catalytic activity (carbon yield of 8.4 g/g_{cat}) depends non-linearly on φ . Fe-based catalysts require a longer pre-reduction stage, which is a disadvantage for industrial applications compared to some Ni-catalysts. There is also a gradual deactivation during the reaction. The results obtained are of great value for optimizing the synthesis of catalysts by the SCS method.

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Submitted 2 December 2025; revised 22 April 2026; accepted 10 June 2026

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Conflict of interest: the authors declare no conflict of interest.

Ni/CeO₂ catalysts synthesized by SCS with a porous γ -Al₂O₃ support for efficient H₂ production via aqueous-phase glycerol reforming

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PACS 82.65.+r

ABSTRACT Aqueous-phase reforming (APR) of glycerol for H₂ production was evaluated over a supported Ni/CeO₂ (CeNi) catalyst prepared by introducing a porous γ -Al₂O₃ support into the reaction mixture during solution combustion synthesis. This approach enables the preparation of a catalyst with improved pore volume and average pore size, which is crucial for facilitating reactant diffusion. Unlike the bulk CeNi system, the presence of alumina increases the availability of active nickel nanoparticles and enhances ceria and nickel dispersion. The glycerol APR results show that CeNi/ γ -Al₂O₃ provides higher glycerol conversion and hydrogen yield compared to the bulk system. Notably, halving the active component content leads to a 2.3-fold increase in activity, which is independent of the feed flow rate and, consequently, of the extent of diffusion limitations. The catalyst obtained in this study outperformed known analogs in terms of H₂ formation rate, while maintaining high glycerol conversion and H₂ selectivity.

KEYWORDS nickel, ceria, alumina, solution combustion synthesis, aqueous-phase reforming, glycerol, hydrogen

ACKNOWLEDGEMENTS This research was funded by the Russian Science Foundation (grant number 25-73-00276, <https://rscf.ru/project/25-73-00276/>).

FOR CITATION Matveyeva A.N., Omarov Sh.O., Tenevich M.I. Ni/CeO₂ catalysts synthesized by SCS with a porous γ -Al₂O₃ support for efficient H₂ production via aqueous-phase glycerol reforming. *Nanosystems: Phys. Chem. Math.*, 2026, **17** (3), 375–386.

1. Introduction

Crude glycerol is the main by-product of biodiesel production, resulting from the transesterification of plant-based substances (100 g of glycerol *per* 1 kg of biodiesel) [1, 2]. Increased biodiesel manufacturing capacity is driving efforts to recycle glycerol to improve profitability and reduce waste, aided by lower glycerol prices [3, 4].

Aqueous phase reforming (APR) of glycerol [5] is one of the efficient and promising methods for converting it into valuable hydrogen, which is the main energy source of the future world [6]. In APR, reactants remain in the liquid phase, unlike steam reforming (SR), thus avoiding an energetically demanding vaporization-step [7]. In an ideal APR reaction, up to 7 moles of H₂ can be obtained from one mole of glycerol [8] by combining glycerol decomposition followed by the water-gas shift (WGS) reaction [9]. Mild APR conditions (200 – 260 °C; 20 – 50 bar) promote the WGS reaction [6, 10], which prevents the formation of excess CO [7]. Nevertheless, the immaturity of this technology requires ongoing research into active and stable catalysts that will increase the attractiveness of the process for industry [7, 11].

In order to facilitate the cleavage of C–C, C–H and O–H bonds in the glycerol molecule during the APR process, the catalyst should contain noble metals or nickel [7]. Nickel-based systems, known for their high availability and cost-effectiveness, have also attracted considerable attention as an alternative to more expensive metals. In addition to the main APR reaction, Ni nanoparticles are effective in C–O hydrogenolysis and CO/CO₂ methanation [12], because under H₂-rich conditions, the metal sites rapidly hydrogenate these fragments to alkanes [13]. Collectively, this diminishes the production of hydrogen and consequently mitigates the necessity for regulating the distribution and accessibility of nickel particles.

The efficiency of this process is ensured by the selection of an appropriate catalyst support material. In particular, the use of CeO₂ is the most promising due to the increased oxygen mobility and the acceleration of the WGS reaction instead of methanation [12]. It was previously shown that the Ni–Ce–O system can successfully compete with noble metal-based catalysts (Pt/ γ -Al₂O₃) in glycerol APR [5]. This was achieved using the solution combustion method (SCS) with a high glycine-to-oxidizer ratio. A similar advantage of this method over classical catalyst preparation methods (co-precipitation, impregnation) for glycerol APR was shown in [14], as well as in [15–20] for other processes. Moreover, this method ensures high dispersion and homogeneity of nanoparticles, as well as a spongy porous structure.

However, APR involves numerous side reactions: oxidation to dihydroxyacetone/glyceraldehyde/glyceric acid [21], hydrogenolysis into glycols [22], etherification [23], and esterification [24–26]. These reactions lead to the consumption

of H_2 , which is formed during the main reaction. This requires the development of a more selective catalyst with respect to H_2 -forming reactions. Furthermore, intense agglomeration of the material during SCS leads to sintering of the primary nanoparticles into dense conglomerates, which reduces the availability of active Ni nanoparticles and destroys useful open porosity [27]. To improve the economic efficiency of the APR process, it is essential to reduce the amount of active Ni/CeO₂ without compromising H_2 yield.

These problems can be solved by switching from a bulk Ni/CeO₂ catalyst to supported catalysts in combination with the SCS method. This is achieved by introducing an external microstructural template (a porous oxide support), into the SCS reaction mixture. Using a template allows to significantly moderate combustion by reducing the maximum temperature and to localize the reaction in nanodomains between particles and in the nanopores of the support [28]. It has previously been shown that deposition of CeFeO₃ and LaFeO₃ perovskites on γ -Al₂O₃ improves CO₂ hydrogenation catalyst performance. γ -Al₂O₃ acted as a support with a large surface area, which promotes finer dispersion of crystallites, increases oxygen defectiveness, and enhances the adsorption capacity for H_2 and CO₂ [29, 30]. This combination of approaches made it possible to reduce the amount of active ferrite without losing catalytic activity and stability. More complex diffusion phenomena in the APR process, occurring in a three-phase system, are an additional argument in favor of using porous supports. Thus, this study aims to assess the potential of the solution combustion method for producing a Ni/CeO₂ catalyst in combination with a porous γ -Al₂O₃ support to improve the efficiency of H_2 production by aqueous-phase reforming of glycerol.

2. Experimental

2.1. Synthesis

NiO/CeO₂-based systems (denoted as CeNi), both supported and bulk, were prepared by solution combustion synthesis (SCS) using glycine and nitrates. γ -Al₂O₃, obtained by calcining AlOOH (Pural SB Lot. N. 233,144, Sasol) at 700 °C for 2 hours, was used as the support.

In a wide glass beaker (250 mL), an appropriate amount of glycine (99.2 %, LenReactiv, Russia) and the corresponding metal nitrates (Ni(NO₃)₂·6H₂O (99.0 %, NevaReactiv, Russia) and Ce(NO₃)₃·6H₂O (99.1 %, LenReactiv, Russia)) were dissolved in deionized water (1 ml *per* 1 g of precursors) to obtain 1 g of NiO/CeO₂. The theoretical NiO content was 30.3 wt % (or 23.8 wt % Ni). The fuel-to-oxidizer ratio (φ) was taken 2 and calculated through the reducing and oxidizing valence states according to [5]. In the supported system, in addition to nitrates and glycine, 1 g of γ -Al₂O₃ (and 1 ml of water) was added to the initial solution, resulting in lower nickel concentration in final CeNi/ γ -Al₂O₃. The aqueous solution or suspension with alumina was heated on an electric plate (1 kW) until boiling, after which spontaneous combustion occurred. In the final stage, the samples were heat treated at a temperature of 350 – 450 °C to burn off most of the remaining fuel and nitrates.

2.2. Characterization

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a DTG-60A analyzer (Shimadzu, Japan) by heating the sample in static air at a heating rate of 10 °C/min.

Infrared transmission spectra were determined using an IRTracer-100 spectrophotometer (Shimadzu, Japan) in the range from 4000 to 350 cm⁻¹. One to two mg of each solid sample were mixed with 200 – 210 mg of vacuum-dried IR-grade KBr. The mixture was dispersed in an agate mortar and then formed into tablets under 12 tons of pressure and vacuum pumping in a steel die 13 mm in diameter.

X-ray diffraction (XRD) analysis was performed on an XRD-6100 diffractometer (Shimadzu, Japan) equipped with a Fe filter and a CoK α radiation source ($\lambda_1 = 1.78897$ Å). The settings included 40 kV voltage, 30 mA current, a scan speed of 1 °/min, a step width of 0.02 °, and D(divergence):S(scatter):R(receiving) = 1:1:0.3. The diffraction data were analyzed using Crystallographica Search-Match ver. 2.0.3.1. The mean crystallite size was calculated using the Scherrer equation.

N₂ physical adsorption was carried out using an Autosorb-6iSA instrument (Quantachrome, USA) (for the supported CeNi/ γ -Al₂O₃ and alumina) and an ASAP 2020 device (Micromeritics, USA) (for bulk CeNi). The samples were pre-degassed at 200 – 250 °C in vacuum. The specific surface area and total pore volume were determined using the BET equation. The NLDFT method was used to calculate pore size distributions.

To obtain high-resolution images and conduct elemental microanalysis of solid samples, a VEGA 3 SBH microscope (Tescan, Czech Republic) equipped with an EDS INCAx-act detector (Oxford Instruments, England) was used.

Temperature-programmed reduction with hydrogen (H_2 -TPR) and temperature-programmed desorption of H_2 (H_2 -TPD) were performed on a SOLO Chemosorb unit (Russia) equipped with a thermal conductivity detector and a MC7-200D quadrupole mass analyzer (Institute for Analytical Instrumentation of Russian Academy of Sciences).

In H_2 -TPR tests, from 13 to 42 mg of a powder was reduced from 70 – 150 to 800 °C at a 10 °/min rate under 20 mL/min of 10 vol % H_2 /Ar (99.9999 vol % purity) in the presence of a water vapor trap.

In H_2 -TPD, 50 – 100 mg of a sample was first reduced *in situ* by a H_2 /Ar flow (50:50 vol %, 40 mL/min) at a ramp rate of 20 °/min to 450 or 550 °C (for supported systems) and 10 °/min to 500 or 600 °C (for supported systems) and held

for 30 min. Then it was cooled to 60 °C and saturated with H₂ (H₂/Ar flow, 50:50 vol %, 20 mL/min) for 20 min. The removal of physically adsorbed H₂ was monitored using a mass spectrometer by purging with argon (20 mL/min), after which the sample was heated to 600 °C at a ramping rate of 10 °C/min.

The nickel dispersion (%), specific metal surface area (m²/g-Ni), and the average Ni diameter (nm) were calculated by assuming a stoichiometry ratio of H/Ni using equations from [5].

2.3. Catalytic tests

Catalyst tests in aqueous phase reforming (APR) of glycerol (99.3 %, NevaReactiv, Russia) were carried out using a fixed bed reactor in the downflow (top-down) mode. The reactor was a cylindrical stainless-steel tube 46 cm in length, with an inner diameter of 4 mm, and a wall thickness of 1 mm. A two-zone furnace was used to heat and expand the isothermal zone of the reactor. The separator volume is 47 ml.

The required amount of catalyst granules (660±3 mg) of fraction 0.1 – 0.3 mm was mixed with quartz granules of fraction 0.45 – 0.90 mm to a total volume of 2 mL. The upper unfilled part of the reactor was packed with quartz granules of the same fraction. The installation was considered hermetically sealed if the pressure drop in it did not exceed 0.10 bar in 10 minutes at an excess pressure of 39.00 bar for N₂.

Before testing, the samples were preliminarily reduced in H₂ flow (40 mL/min) for 30 min at a temperature in accordance with the results of H₂-TPR. All tests were performed at an excess pressure of 35.00 ± 0.05 bar and a temperature of 231 ± 2 °C measured under the catalyst bed. For all tests, the reactor was fed with a flow of N₂ (99.999 vol % purity, 32 mL/min) and liquid feedstock (a mixture of 10 wt % of glycerol and water; total liquid flow 0.05 or 0.12 mL/min). Liquid sampling was performed after 3 hours of accumulation at a feed flow rate of 0.05 ml/min, and after 1 hour of accumulation at 0.12 mL/min.

2.4. Method for determining the composition of APR products

A Test-1 gas analyzer (BONER, Russia) was used for online monitoring of H₂, CO₂, and CO concentrations in the gaseous products. The detailed composition of the gaseous products was analyzed using a Crystallux-4000M gas chromatograph (Meta-Chrom, Russia) equipped with two thermal conductivity detectors and two packed columns: a CaA column (3 m × 3 mm) and a Haysep Q column (3 m × 2 mm). Hydrogen and argon were used as carrier gases, and the column temperature was maintained constant at 80 °C throughout the analysis. The following compounds were detected in the chromatograms: H₂, CO₂, CO, CH₄, C₂H₆, and C₃H₈.

The method for calculating glycerol conversion into gaseous products ($X(G)_{gas}$, %), the yield of hydrogen ($Y(H_2)$, % of stoichiometry), and selectivity ($S(i)$, %) is similar to that used in the previous study [5, 15, 31].

The residual concentration of glycerol in the liquid products was determined using the external standard method on the same gas chromatograph, equipped with a TRB WAX capillary column (30 m × 0.32 mm × 0.5 μm) and a flame ionization detector. The method described in [32] was used as the reference conditions. The residual glycerol concentration, $C(G)_\tau$, in liquid APR products was determined using the known concentration of 1,4-butanediol in the sample and a dilution factor.

The total conversion of glycerol $X(G)_{sum}$ was calculated as:

$$X(G)_{sum} = \frac{C(G)_0 - C(G)_\tau}{C(G)_0}, \quad (1)$$

where $C(G)_0$ is the initial concentration of glycerol in the feedstock (10 wt %).

3. Results and discussion

3.1. Combustion efficiency and surface functional groups

The total weight change upon heating in air (Fig. 1) and IR spectroscopy data (Fig. 2) indicate that some amount of unburned fuel and nitrates remained in the as-prepared bulk and supported NiO–CeO₂ systems (designated as CeNi and CeNi/ γ -Al₂O₃, respectively). Overall, excluding physical water, the residual glycine-nitrate precursor ranged from 2.1 to 3.7 wt % (Fig. 1). Combustion in the presence of alumina leads in increased weight loss compared to the bulk CeNi system. This phenomenon can be explained by a decrease in the peak combustion temperature as a result of partial absorption of the released heat by the support. Accordingly, DTA revealed a shift of the exothermic peak upon the addition of alumina from 323 to 314 °C attributed to the combustion-type decomposition of free glycine and its complexes [33]. Water desorption is accompanied by thermal degradation of nitrate ions at a temperature of approximately 163 °C.

Prior to FTIR analysis, the samples were further heat-treated at 350 – 450 °C to remove the majority of residual fuel and nitrates. The presence of the most intense absorption bands in the far-infrared region indicates the formation of metal–oxygen bonds (Fig. 2). For the bulk nanocomposite, an absorption band was found at 414 cm^{−1}, which can be attributed to O–Ce–O stretching vibrations [34, 35]. For the alumina-based system, two peaks can be identified at 452 and 733 cm^{−1}, which are associated with vibrations of the Al–O bonds in octahedral [AlO₆] and tetrahedral units [AlO₄], respectively [36, 37]. It is clear that nickel and cerium oxides provide a significant signal enhancement in the region of 452 cm^{−1} relative to the 733 cm^{−1} peak, which is not typical for pure alumina.

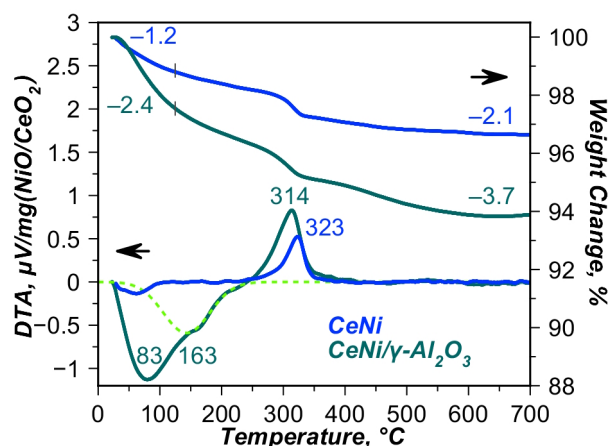


FIG. 1. DTA–TGA data of the as-prepared bulk and alumina-supported CeNi-based samples obtained by glycine-nitrate combustion method (SCS)

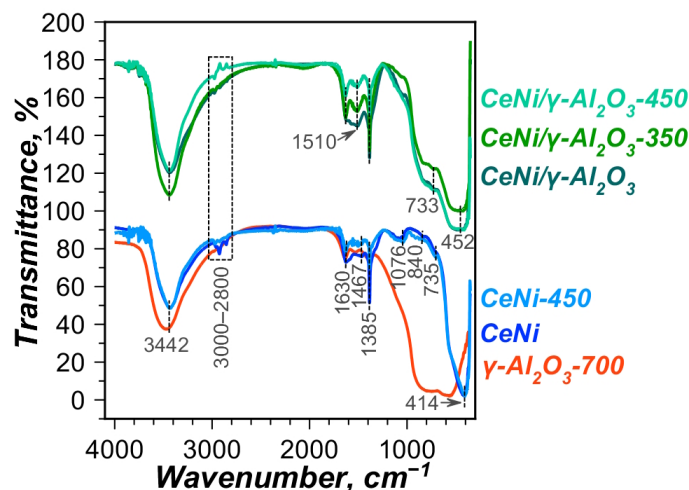


FIG. 2. IR spectra of the as-prepared and calcined samples produced using glycine-nitrate combustion (SCS)

Peaks observed in the ranges of 1630 and 3442 cm^{-1} are due to bending and stretching vibrations of surface hydroxyl groups or molecular water. The presence of nitrate groups is confirmed by peaks at 840, 1385, and 1510 cm^{-1} . The bands at 1467 and 2800–3000 cm^{-1} indicate the presence of stretching and bending vibrations of aliphatic C–H bonds, while the peak at 1076 cm^{-1} confirms the absorption of the amino acid group.

3.2. Phase composition and crystallinity

Figure 3 shows XRD patterns of bulk and supported CeNi systems, as well as $\gamma\text{-Al}_2\text{O}_3$. In the CeNi-alumina system, no noticeable shift in the position of the 440 peak was detected, indicating minimal structural changes in the crystal lattice of alumina. Based on the obtained values of the average size of CeO_2 crystallites (Table 1), it can be concluded that the combustion of nickel–ceria in the presence of alumina occurs under milder conditions (than for the bulk CeNi system, confirmed by DTA–TGA), which makes it possible to obtain smaller particles.

TABLE 1. Peak positions and average crystallite size for the synthesized materials

Sample	CeO_2 (111)		NiO (200)	
	Peak position, $2\theta^\circ$	Crystallite size, nm	Peak position, $2\theta^\circ$	Crystallite size, nm
CeNi-350	33.227	6.2	50.692	5.0
CeNi/ $\gamma\text{-Al}_2\text{O}_3$ -350	33.342	2.8	51.248	5.2

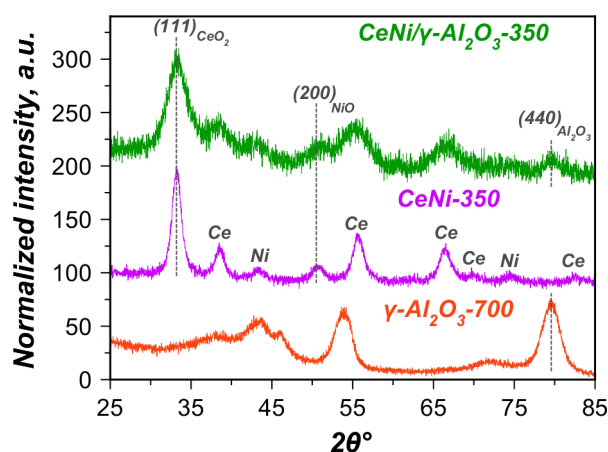


FIG. 3. XRD patterns of γ -alumina and materials synthesized by the glycine-nitrate combustion method (SCS) (additionally calcined at 350 °C), where reflections designated as Ni and Ce represents their oxides according to PDF cards No. 44-1159 (cubic) and 75-120 (cubic), respectively

3.3. Morphology and porosity

Alumina and all synthesized samples exhibit an IUPAC type IV(a) isotherm, characteristic of a mesoporous structure (Fig. 4a). The small total pore volume ΣV_{pores} (0.09 cm³/g) and moderate specific surface area S_{BET} (27 m²/g) in the bulk CeNi sample is probably due to secondary porosity and aggregation of small crystalline particles. This is also confirmed by the H4 hysteresis loop, a phenomenon often observed in aggregated crystals. In contrast, the support exhibits an H1-type loop (almost parallel vertical adsorption and desorption branches), which is typical for materials with well-defined cylindrical mesopores or a narrow pore size distribution.

In the supported CeNi system obtained by the SCS method, a combined hysteresis loop of H1 and H4 is observed, because parallelism is broken at high relative pressures, and at $P/P_0 = 0.4$, compared to alumina, a characteristic sharp step-down the desorption branch appears. In this case, a decrease in S_{BET} and ΣV_{pores} is also observed (Table 2).

TABLE 2. Textural characteristics of the obtained CeNi-based systems and comparison with alumina and literature data

Sample	Synthesis method	Temperature calcination, °C	Ni, wt %	Ce, wt %	S_{BET} , m ² /g	ΣV_{pores} , cm ³ /g	Average pore diameter, nm
γ -Al ₂ O ₃ -700	—	700	0	0	200	0.50	10.0
CeNi	SCS with glycine, $\varphi = 2$	—	23.8	56.8	27	0.09	13.3
CeNi/ γ -Al ₂ O ₃ -450	SCS with glycine, $\varphi = 2$	450	11.9	28.4	119	0.38	12.8
Ni/Al ₂ O ₃ [38]	Wet impregnation	600	15	0	175	0.57	—
Ni ₂₀ Al ₂ O ₃ -M [39]	Microwave method	400	20	0	163	0.49	10.0
Ni ₂₀ Al ₂ O ₃ -I [39]	Improved impregnation	400	20	0	144	0.42	12.3
NiCeAl (R=4) Ce:Al = 4.9 [40]	EISA method	700	7	10.8	64	0.24	11.5
Ni/10Ce-Al [41]	Incipient wetness impregnation	600	10	9.1	198	0.36	6.8
Ni/CeAl [42]	Wet impregnation	500	10.0	14.8	141	0.31	6.1
Ni-IS [43]	Impregnation	500	20	9.8	121	0.21	7.0

The pore size distribution for the bulk CeNi system is relatively wide compared to the system containing alumina (Fig. 4b). It is evident that wider pores of alumina become clogged more strongly than smaller ones. In addition, in the alumina-supported CeNi system, the pore distribution pattern repeated the long tail of the bulk system at large diameters (Fig. 4c).

A comparison with literature data shows that cerium-free samples have higher surface areas (144 – 175 m²/g) and pore volumes (0.42 – 0.57 cm³/g); these values, however, depend on the alumina properties, synthesis conditions, and

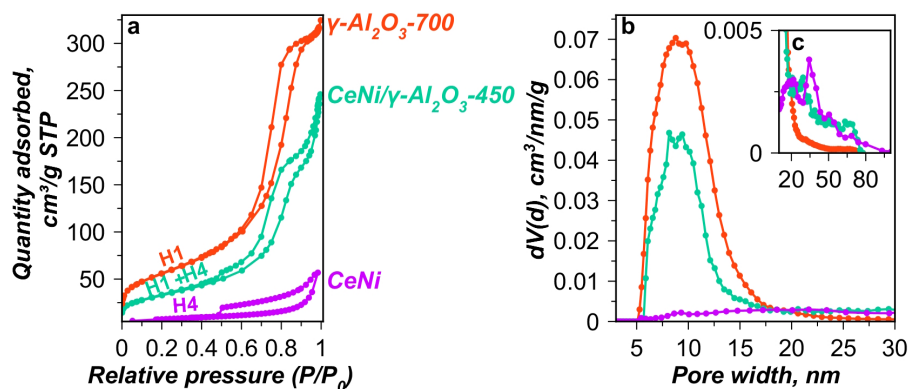


FIG. 4. N_2 adsorption–desorption isotherms (a) and DFT pore size distribution (b,c) for CeNi-based systems and alumina support

nickel content (Table 2). Compared to Ni/Al_2O_3 , ΣV_{pores} of cerium-containing systems drops more significantly, falling to 0.21 – 0.36 cm^3/g . An even more significant influence was observed for the average pore diameter, which diminished to mostly 6 – 7 nm. This is in contrast to $CeNi/\gamma-Al_2O_3-450$ synthesized in this study, which has an average pore diameter of 12.8 nm. Therefore, the SCS method including the support is preferable to retain the significant pore volume and average pore size of $CeNi/\gamma-Al_2O_3$, which may be crucial to facilitate the diffusion of reactants.

According to SEM and EDX mapping of morphologically distinct regions, the $CeNi/\gamma-Al_2O_3$ sample consisted of dense dark sub-round particles and a light foam-like phase (Fig. 5b,c). Foam was observed around and on the surface of dark particles with high aluminum and low nickel-cerium content compared to light particles (Fig. 5b, Table 3), which suggests the formation of a variable-thickness Ce–Ni–O layer on the alumina surface. Analysis of the distribution of elements in numerous particles reveals large areas where alumina predominates (Fig. 5d).

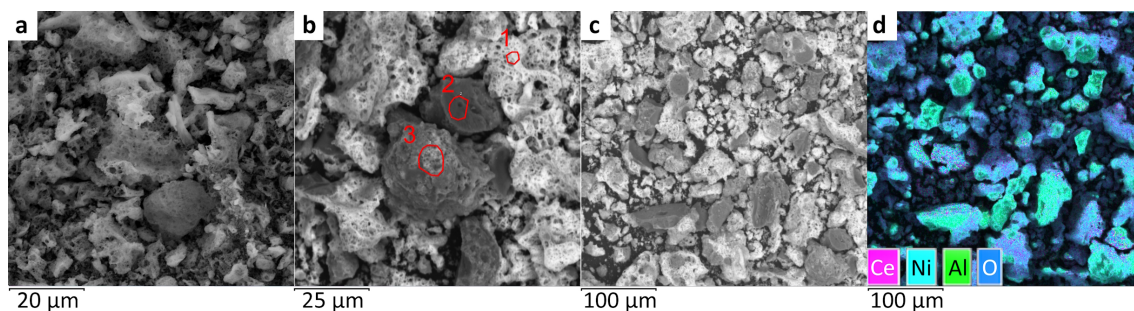


FIG. 5. SEM images (a–c) and EDX elemental mapping (d) and of bulk (a) and alumina-supported (b–d) NiCe-based systems obtained by SCS

TABLE 3. EDX results for different areas of $CeNi/\gamma-Al_2O_3-350$ presented in Fig. 5b

Area	Ni	Ce	Al	O
1	19.2	47.7	4.2	28.9
2	18.2	40.4	18.7	22.8
3	10.4	25.3	30.3	34.1

3.4. Reducibility and nickel dispersion

H_2 -TPR analysis clearly shows that the obtained bulk and supported CeNi-based systems begin to react with hydrogen at 150 – 200 °C (Fig. 6a). The most symmetrical peak of hydrogen consumption with a maximum of 329 °C is observed in the bulk CeNi system, which is even 15 °C less than that of the reference NiO obtained from nickel nitrate by calcination. Increasing the heat treatment temperature from 350 to 450 °C cleans the surface of the studied systems from residual organic compounds or incompletely decomposed nitrates, which changes H_2 -TPR profiles. In contrast, $CeNi/\gamma-Al_2O_3$ exhibits more complex reduction spectra with peaks shifted towards higher temperatures. Moreover, when normalized by NiO/CeO_2 mass, the bulk composite system exhibits a peak intensity 1.8 times higher than the alumina-based system.

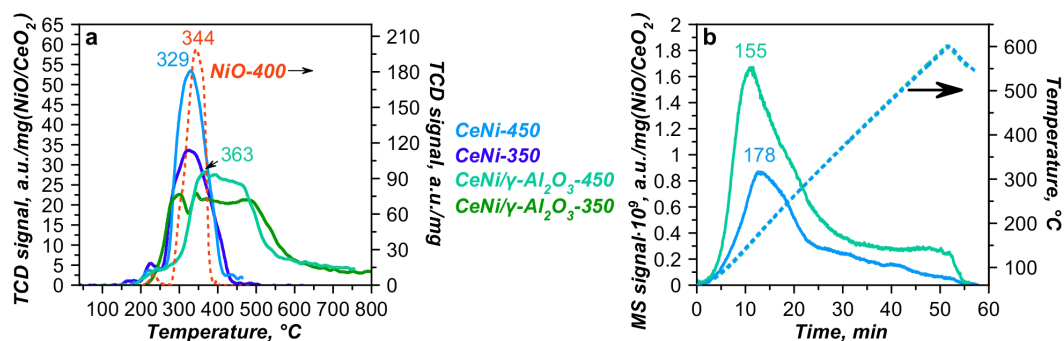


FIG. 6. H₂-TPR profiles (a) and H₂-TPD spectra (b) for calcined samples produced using SCS. Nickel oxide reference was prepared from nickel nitrate by calcination at 400 °C

To further investigate the influence of support presence on the H₂ adsorption capacity, an H₂-TPD analysis was performed (Fig. 6b). The results show that the main temperature range of desorption occurs for weakly bound hydrogen. The desorption intensity in the bulk system is significantly lower compared to the system containing alumina. Thus, the SCS synthesis using alumina ensured high accessibility of the active sites. The principal difference between the bulk and supported systems is in the region of strongly bound hydrogen (above 200 °C). The large signal areas observed for the supported system indicate that nickel is dispersed as smaller nanoparticles, unlike the bulk system.

Direct comparison of the samples shows that using of alumina has a positive effect on nickel dispersion (Table 4). In the unsupported system, the Ni dispersion decreases sharply to 7.1 %, while the particle size increases to 14.3 nm, highlighting the important role of γ -Al₂O₃ as a spatial spacer to achieve a highly dispersed state of nickel. The larger particle sizes of Ni detected by H₂-TPD compared to NiO determined by XRD indicate that although individual Ni crystallites are small, they aggregate together.

TABLE 4. Ni dispersion, particle size, and surface area for the obtained CeNi-based samples and comparison with literature data

Sample	Synthesis method	Temperature calcination, °C	Ni, wt %	Ce, wt %	Ni dispersion, %	Ni surface area, m ² /g	Ni particle size, nm
CeNi-450	SCS with glycine, $\varphi = 2$	450	23.8	56.8	7.1	47.3	14.3
CeNi/ γ -Al ₂ O ₃ -450	SCS with glycine, $\varphi = 2$	450	11.9	28.4	13.8	92.1	7.3
Ni/Al ₂ O ₃ -450 [44]	Wet impregnation	450	9.6	0	4.3	—	12.6
Ni/Al ₂ O ₃ [38]	Wet impregnation	600	15	0	4.3	4.3	23.7
Ni ₂₀ Al ₂ O ₃ -M [39]	Microwave method	400	20	0	25.3	—	10
Ni ₂₀ Al ₂ O ₃ -I [39]	Improved impregnation	400	20	0	16.6	—	15
Ni/CeO ₂ -Al ₂ O ₃ (N-N) [46]	Incipient wetness impregnation	500	9.9	2.5	3.2	21.4	—
NiCeAl (R=4) Ce:Al = 4.9 [40]	EISA method	700	7	10.8	11.7	1.9	6.2
Ni/10Ce-Al [41]	Incipient wetness impregnation	600	10	9.1	23.7	—	2.7
20 %Ni/CeO ₂ -Al ₂ O ₃ [45]	Wet impregnation	400	20	42.5	1.2	7.7	—

It is evident that cerium-free conventional impregnation leads to low dispersion (4.3 %) and the generation of large nickel particles (12.6 nm) [44]. Under more severe conditions (600 °C and higher loading), the particle size increases further to 23.7 nm [38]. The effect of cerium inclusion on nickel dispersion is not straightforward. In the Ni/10Ce-Al sample with 9.1 % Ce [41], a very high dispersion (23.7 %) and extremely small nickel particle size (2.7 nm) are achieved, which is explained by the ability of CeO₂ to stabilize the metal and prevent sintering. Nevertheless, achieving such high

dispersion entails a trade-off in the form of diminished transport properties. With a significant excess of cerium (42.5 % in the study [45]), dispersion decreases to 1.2 %, presumably because ceria layers cover the nickel surface and block the active sites. Microwave synthesis and improved impregnation method of Ni/Al₂O₃ [39] in the absence of cerium yield high dispersion of 16.6 – 25.3 % and particle size of 10 – 15 nm, demonstrating that there are alternative routes to obtain highly dispersed nickel without the addition of Ce.

The CeNi/ γ -Al₂O₃-450 sample synthesized in this study occupies an intermediate position: it exhibits moderate dispersion with the most favorable pore properties of all cerium-containing materials. This makes it attractive for practical applications requiring a combination of good active site accessibility and efficient mass transfer, such as steam/aqueous-phase reforming or hydrodesulfurization reactions involving large molecules.

3.5. Catalytic performance in APR

The results obtained from testing the synthesized catalysts in APR are shown in Fig. 7 and Table 6. These data clearly indicate that CeNi/ γ -Al₂O₃-450 achieved the highest conversion of glycerol into gaseous products (Fig. 7a) and the highest hydrogen yield (Fig. 7b). Accounting for the absolute nickel content, the H₂ formation rate (Fig. 7c) enables a more meaningful catalyst activity comparison. It is evident that halving the active component loading resulted in a 2.3-fold increase in activity that was unaffected by WHSV and, hence, by the extent of diffusion limitations. Thus, the combination of SCS method and porous support provided a synergistic effect on the catalytic activity in APR.

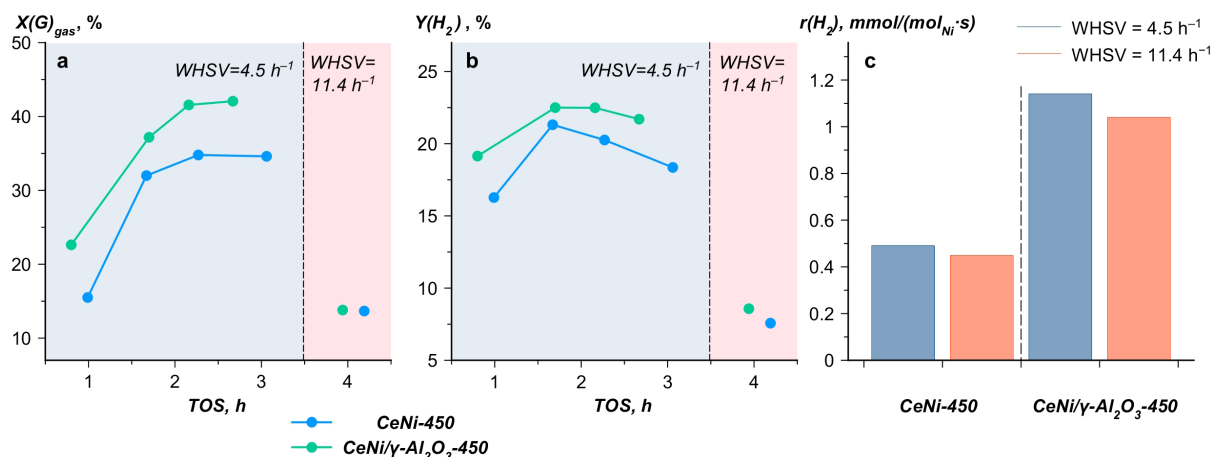


FIG. 7. Glycerol conversion into gaseous products (a), hydrogen yield (b) over time-on-stream and the rate of H₂ formation *per* mole of Ni (c)

Table 5 presents a comparison of the catalyst behavior of CeNi/ γ -Al₂O₃-450 catalyst with literature analogues. Catalysts containing similar active components and support were selected under comparable APR testing conditions ($T = 225 - 250$ °C, $P = 20 - 41$ bar, 10 – 15 wt % glycerol in the feedstock). Clearly, the catalyst obtained in this study outperformed known analogs in terms of H₂ formation rate $r(H_2)$, while maintaining high glycerol conversion and H₂ selectivity. Moreover, this advantage remained consistent across various feed flow rates.

As expected, increasing WHSV led to lower values for total glycerol conversion, conversion of glycerol into gaseous products, and hydrogen yield. This phenomenon is due to the reduced role of the primary reaction between glycerol and water, which produces H₂ and CO₂, a characteristic of glycerol transformation processes [5, 31]. In addition, there was also a general increase in $S(H_2)$ and $S(CO_2)$, but selectivity towards other products decreased (Table 6).

Two factors explain the above-mentioned effect. Firstly, increasing the pressure with an excess H₂ relative to CO₂ promotes an increase in the yield of methane [51]. This route is also supported by the fact that methane formation increases with increasing conversion of glycerol to gaseous products during glycerol SR [5, 31]. The same trend is seen in the present study when comparing glycerol conversion and $S(CH_4)$ at varying feed flow rates (Table 6). However, this route does not explain the formation of other hydrocarbons [52]. Therefore, secondly, CO and hydrocarbons can be by-products in a complex chain of consequence-parallel reactions of glycerol (de)hydrogenation and dehydration [5, 10, 53] involving metallic nickel nanoparticles and the acid sites of the catalyst. During glycerol SR, the formation of ethane and propane occurs predominantly with decreasing conversion of glycerol to gaseous products [5, 31]. In this study, as glycerol conversion diminished, selectivity to CO and hydrocarbons also declined. This finding underscores the significant influence of liquid by-products on selectivity.

Therefore, with increasing the feed flow rate, the observed increase in $S(H_2)$ and $S(CO_2)$ can be explained by a decrease in the contribution of CO₂ hydrogenation to CH₄ and CO, as well as a decrease in H₂ consumption for the hydrogenation of intermediate liquid products. Evidently, the decrease in $S(H_2)$ and $S(CO_2)$ coupled with the increase

TABLE 5. The catalyst performance of CeNi/ γ -Al₂O₃-SCS-450 in APR compared with literature data

Catalyst	Synthesis method	Ni ⁰ , nm	Reactor and reaction conditions	Results	Reference
11.9 %34.9 %CeO ₂ / γ -Al ₂ O ₃ -450	SCS, $\varphi = 2$	7.3 (H ₂ -TPD)	Fixed bed, 231 °C, 35 bar, 2 – 2.5 h, 4.5 h ⁻¹ , 10 wt % glycerol	$X(G)_{\text{sum}} = 100 \%$; $X(G)_{\text{gas}} = 42.1 \%$; $Y(\text{H}_2) = 21.7 \%$; $r(\text{H}_2) = 1.14 \text{ mmol}/(\text{mol}_{\text{Ni}} \cdot \text{s})$; $S(\text{H}_2) = 54.1 \%$	This study
11.9 %34.9 %CeO ₂ / γ -Al ₂ O ₃ -450	SCS, $\varphi = 2$	7.3 (H ₂ -TPD)	Fixed bed, 231 °C, 35 bar, 3.9 h, 11.4 h ⁻¹ , 10 wt % glycerol	$X(G)_{\text{sum}} = 25 \%$; $X(G)_{\text{gas}} = 13.8 \%$; $Y(\text{H}_2) = 8.6 \%$; $r(\text{H}_2) = 1.04 \text{ mmol}/(\text{mol}_{\text{Ni}} \cdot \text{s})$; $S(\text{H}_2) = 61.9 \%$	This study
14.24 %Ni/CeO ₂ [47]	Precipitation	5.3 (XRD)	Fixed bed, 250 °C, 20 bar, 20 h, 5 h ⁻¹ , 15 wt % glycerol	$X(G)_{\text{gas}} = 17.3 \%$; $S(\text{H}_2) = 95.7 \%$	[47]
33.2 %Ni/ γ -Al ₂ O ₃ [48]	Sol-gel	25.7 (XRD)	Batch, 250 °C, 41.4 bar, 3.9 h, 1.8 wt % glycerol	$X(G)_{\text{gas}} = 49.0 \%$; $Y(\text{H}_2) = 31.0 \%$; $S(\text{H}_2) = 62.0 \%$	[48]
NiAl ₂ O ₄ (33.2 % Ni) [49]	Precipitation	16.0 (XRD)	Fixed bed, 235 °C, 35 bar, 3 h, 24.5 h ⁻¹ , 10 wt % glycerol	$X(G)_{\text{sum}} = 65.0 \%$; $X(G)_{\text{gas}} = 27.0 \%$; $Y(\text{H}_2) = 8.0 \%$; $r(\text{H}_2) = 0.68 \text{ mmol}/(\text{mol}_{\text{Ni}} \cdot \text{s})$; $S(\text{H}_2) = 37.0 \%$	[49]
1.3 %Ni4.6 %Co/6.0 %CeO ₂ -Al ₂ O ₃	CCMU	—	Fixed bed, 225 °C, 25 bar, 2.5 h, 4.9 h ⁻¹ , 10 wt % glycerol	$X(G)_{\text{sum}} = 23 \pm 1.2 \%$; $r(\text{H}_2) = 0.12 \text{ mmol}/(\text{mol}_{\text{Ni}} \cdot \text{s})$; $S(\text{H}_2) = 83.0 \%$	[50]

TABLE 6. Gas product selectivity in the APR process

Sample	$X(G)_{\text{sum}}, \%$	$S(\text{H}_2), \%$	$S(\text{CO}_2), \%$	$S(\text{CH}_4), \%$	$S(\text{C}_2\text{H}_6), \%$	$S(\text{C}_3\text{H}_8), \%$	$S(\text{CO}), \%$
$WHSV = 4.5 \text{ h}^{-1}$ and TOS = 2 – 2.5 h							
CeNi-450	100	58.2	70.3	15.8	1.4	1.8	10.7
CeNi/ γ -Al ₂ O ₃ -450	100	54.1	68.0	20.9	1.0	0.9	9.3
$WHSV = 11.4 \text{ h}^{-1}$ and TOS = 3.9 – 4.2 h							
CeNi-450	39.3	55.1	74.2	15.0	1.2	1.4	8.1
CeNi/ γ -Al ₂ O ₃ -450	25.0	61.9	74.6	17.1	0.5	0.5	7.4

in $S(\text{CH}_4)$ observed for CeNi/ γ -Al₂O₃-450 can be attributed to the increased dispersion of nickel particles, which in turn enhanced the hydrogenation function of the catalyst.

The importance of the various catalyst functions also becomes apparent when assessing its deactivation. This is difficult to determine definitively, as glycerol conversion to gaseous products does not decrease with increasing TOS. The drop in hydrogen yield observed with increasing TOS can be explained by the increasing role of RWGS, which produces CO. This is supported by the observed increase in $S(\text{CO})$ and decrease in $S(\text{CO}_2)$ as a function of TOS (data not shown). An additional contribution could potentially come from side reactions of hydrogenation of liquid intermediates; however, the decrease in selectivity to ethane and propane indicates deactivation of acid sites responsible for these reactions. The smallest decrease in hydrogen yield and formation of undesirable hydrocarbons are observed over CeNi/ γ -Al₂O₃-450.

The catalyst test results show a distinct period of increasing conversion and hydrogen yield. This effect is primarily due to the filling of the catalytic unit volume with gaseous products of the APR process, which has also been shown in other studies [5, 50]. However, the varying periods of stabilization of the parameters in Fig. 7 suggest an additional effect associated with an induction period of catalysts under process conditions.

4. Conclusions

The methods used to develop catalysts significantly influence their structure, surface properties, and catalytic performance. Solution combustion synthesis (SCS) has proven to be a reliable and versatile method for the rapid production of catalytic materials, allowing the creation of highly dispersed and porous structures that are crucial for achieving high catalytic efficiency in complex chemical reactions. Specifically, in aqueous-phase reforming (APR) of glycerol for hydrogen production, the Ni/CeO₂ (CeNi) system developed using this method shows potential to compete with noble metal-based catalysts.

In this study, glycerol APR was evaluated over a supported Ni/CeO₂ catalyst prepared by introducing a porous γ -Al₂O₃ support into the SCS reaction mixture. This approach enables the preparation of a catalyst with improved pore volume and average pore size, which is crucial for facilitating reactant diffusion. Unlike the bulk CeNi system, the presence of alumina increases the availability of active nickel nanoparticles and enhances nickel dispersion. This underscores the important role of γ -Al₂O₃ as a spatial spacer for achieving a highly dispersed nickel state. Because the support partially absorbs the released heat, the peak combustion temperature is reduced, thereby explaining this phenomenon.

The glycerol APR results show that CeNi/ γ -Al₂O₃ provides higher glycerol conversion and hydrogen yield compared to the bulk system. Notably, halving the active component content leads to a 2.3-fold increase in activity, which is independent of the feed flow rate and, consequently, of the extent of diffusion limitations. The catalyst obtained in this study outperformed known analogs in terms of H₂ formation rate, while maintaining high glycerol conversion and H₂ selectivity. Thus, reducing the amount of Ni/CeO₂ without reducing the H₂ yield increases the economic efficiency of the APR process.

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Conflict of interest: the authors declare no conflict of interest.

Paper abstracts in Russian / Аннотации статей

Пороговые резонансы и дискретный спектр гамильтониана двух бозонов с молекулярным каналом на одномерной решётке

Лакаев Ш.С.

В работе исследуется двухканальный решёточный гамильтониан в секторе фиксированного числа частиц на одномерной решётке Z . Модель состоит из молекулярного канала, связанного с бозонным двухчастичным каналом с локальным взаимодействием. В импульсном представлении трансляционная инвариантность приводит к семейству редуцированных гамильтонианов $H_{\gamma,\lambda}(K)$ параметризованных полным квазиимпульсом $K \in T$, каждый из которых действует в пространстве $C \oplus L_e^2(T)$. Для контактного взаимодействия каждый редуцированный гамильтониан является возмущением ранга два свободного диагонального оператора. С помощью метода Липпмана–Швингера задача о собственных значениях вне существенного спектра сводится к системе линейных уравнений размерности 2×2 и эквивалентному условию обращения в нуль явного скалярного определителя Фредгольма. Исследованы пороговые свойства определителя и получены критерии существования собственных значений и пороговых резонансов.

Ключевые слова: решёточный гамильтониан, двухканальная модель, сектор фиксированного числа частиц, определитель Фредгольма, уравнение Липпмана–Швингера, дискретный спектр, пороговая асимптотика, пороговый резонанс.

Новые критерии осцилляции нелинейных возмущенных дифференциальных уравнений с запаздыванием второго порядка

Рамья Б., Шринивасан Р.

В данной работе рассматривается класс возмущенных дифференциальных уравнений второго порядка с запаздыванием вида $(\eta(\kappa)u'(\kappa))' + f_1(\kappa, u(\tau(\kappa))) = f_1(\kappa, u'(\kappa))$. С помощью метода преобразований исследуемое уравнение преобразуется в биномиальное, а затем с использованием преобразования Риккати, теоремы сравнения и метода интегрального усреднения получают новые критерии осцилляции. Приводятся примеры, демонстрирующие важность и новизну основных результатов.

Ключевые слова: дифференциальные уравнения второго порядка с возмущениями, задержка, колебания.

Заклинивание на границе раздела фаз и механический гистерезис в нанопузырьках, стабилизированных поверхностно-активными веществами: Прогностическая кинетическая модель стабильности при флотации и в других областях

Ху Л., Ли Х.

Представлена минимальная 0D кинетическая модель для межфазного заклинивания нанопузырьков, стабилизированных поверхностно-активными веществами. Модель связывает кинетику адсорбции Лангмюра с геометрической концентрацией и механическим равновесием. В

плоскости (средство Лангмюра, скорость десорбции) существует резкая граница заклинивания; коммерческие бутиловые и изобутиловые ксантаты находятся глубоко внутри заклиненной области при типичных дозах флотации (вероятность Монте-Карло 1,00). Энергия гистерезиса составляет от 10^{-14} до 10^{-9} Дж, а критическая объемная концентрация для заклинивания колеблется от 8.2×10^{-6} до 0.35 моль·м $^{-3}$. Граница предсказуемо смещается в зависимости от объемной концентрации, давления и времени цикла, но нечувствительна к модулю оболочки. Подтверждена численная сходимость, а показатель расходимости за один цикл достигает пика при $+0.42$ с $^{-1}$ вблизи перехода. Модель представляет собой инструмент прогнозирования для нанопузырьков, стабилизированных поверхностно-активными веществами, в процессах флотации, катализа и биомедицинских наносистем.

Ключевые слова: нанопузырьки, межфазное заклинивание, гистерезис, кинетика Лангмюра, флотация.

Вычисление характеристик субнанометровых дельта-легированных слоёв в алмазе в квазиклассическом приближении

Кукушкин В.А., Кукушкин Ю.В.

Показано, что характеристики субнанометровых дельта-легированных бором слоёв в химически осаждённых из газовой фазы алмазных плёнках могут быть вычислены в квазиклассическом приближении как в равновесии, так и во внешнем электромагнитном поле, ионизирующем легирующие атомы бора. Найдены соответствующие решения, в первом случае – аналитически, во втором – численно. Использование квазиклассического приближения позволяет существенно упростить математическое моделирование алмазных структур с субнанометровыми дельта-легированными слоями, необходимое для их использования в нанoeлектронике, например в быстродействующих полевых транзисторах.

Ключевые слова: дельта-легированные слои, квазиклассическое приближение, химически осаждённый из газовой фазы алмаз.

Условия возникновения вольт-амперных характеристик джозефсоновского типа в углеродных материалах при комнатной температуре и нормальном давлении

Ионов А.Н., Бугров А.Н.

В данной работе показано, что взаимодействие хлопьев высокоориентированного пиролитического графита и графеновых пленок с алканами является необходимым, но недостаточным условием для наблюдения в них джозефсоновской вольт-амперной характеристики, которая, как известно, присуща всем сверхпроводящим материалам. Другим ключевым фактором является создание деформационного поля в материале на основе графена.

Ключевые слова: высокоориентированный пиролитический графит, графен, алканы, механические напряжения, сверхпроводимость.

Оптическое поглощение и рамановская спектроскопия ферробората $\text{HoFe}_3(\text{BO}_3)_4$: экспериментальное исследование с термодинамическим анализом

Шарипов М., Низомова Ш., Файзиев Ш., Джураев Д.

Вибрационные и оптические свойства монокристаллов $\text{HoFe}_3(\text{BO}_3)_4$ были исследованы с помощью рамановской спектроскопии и измерений оптического поглощения. Рамановский спектр, записанный при комнатной температуре, выявляет четко выраженные фононные моды, связанные с колебаниями решетки и внутренними модами структурных единиц. Интенсивные полосы в диапазоне $1200 - 1450 \text{ см}^{-1}$ приписываются внутренним колебаниям групп BO_3 , в то время как особенности в области $400 - 700 \text{ см}^{-1}$ обусловлены октаэдрами FeO_6 . Спектр оптического поглощения, измеренный в диапазоне $190 - 1100 \text{ нм}$, демонстрирует слабые узкие полосы в видимой и ближней инфракрасной областях, соответствующие внутри- $4f$ переходам ионов Ho^{3+} , и выраженный край поглощения в ультрафиолетовой области, связанный с переходами переноса заряда $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$. Оптическая ширина запрещенной зоны оценивается в $3,3 - 3,5 \text{ эВ}$. Установлена корреляция между колебательными и оптическими свойствами, демонстрирующая роль групп BO_3 и октаэдров FeO_6 в определении электронной структуры и оптического отклика материала. Результаты обеспечивают согласованную экспериментальную характеристику $\text{HoFe}_3(\text{BO}_3)_4$ и указывают на его потенциал для оптических и магнитооптических применений.

Ключевые слова: $\text{HoFe}_3(\text{BO}_3)_4$, ферробораты редкоземельных элементов, рамановская спектроскопия, оптическое поглощение, оптическая ширина запрещенной зоны, переходы с переносом заряда, электронные переходы $4f$, колебательные свойства.

Вариационное исследование электронной теплопроводности модели решетки Андерсона: применение к манганитам с конфигурацией CMR ($\text{Re}_{1-x}\text{A}_x\text{MnO}_3$)

Рахул Саини, Сунил Панвар

Используя вариационный метод, мы исследовали температурную зависимость электронной теплопроводности (КЭ) в редкоземельных манганитах, легированных ионами щелочноземельных металлов, которые демонстрируют хорошо известное поведение КМР (кандидомагнитного магнитосопротивления). Анализ основан на двухзонном ($l-b$) гамильтониане модели решетки Андерсона, подходящем для режима сильной электронно-решеточной связи Яна–Теллера (ЯТ), согласующемся с двухжидкостными описаниями, включающими ($l-b$) гибридизацию. Ключевые параметры модели включают кулоновское отталкивание U , сильную связь Хунда J_H между спинами e_g и t_{2g} и гибридизацию V между l -поляронами и d -электронами одного и того же спина. В ферромагнитной металлической фазе расчеты показывают, что КЭ увеличивается с повышением температуры, а вблизи температуры перехода $T_c \approx 400 \text{ К}$ наблюдается минимум или провал КЭ при фиксированных значениях V , J_H и x . Результаты, полученные для келина, демонстрируют типичный кристаллический характер, при этом рассеяние на границах зерен является основным механизмом, ограничивающим теплопередачу в этих соединениях.

Ключевые слова: гамильтониан модели решетки Андерсона, манганиты CMR, электронная теплопроводность, вариационный метод.

Молекулярное моделирование вязкости гибридных наножидкостей с углеродными нанотрубками и медными наночастицами

Рудяк В.Я., Краснолуцкий С.Л., Лежнев Е.В., Рафальская Т.А.

Методом молекулярной динамики изучены коэффициенты вязкости гибридных наножидкостей на основе бензола с одностенными углеродными нанотрубками и наночастицами меди. Исследована зависимость вязкости этих наножидкостей от концентрации углеродных нанотрубок и наночастиц, а также от их морфологии. Показано, что вязкость всех исследованных наножидкостей значительно выше, чем у базовой жидкости и обычных крупнодисперсных жидкостей. Коэффициент вязкости наножидкости с углеродными нанотрубками при заданной концентрации увеличивается с увеличением их длины. При одинаковых концентрациях вязкость гибридных наножидкостей значительно превышает вязкость наножидкости с наночастицами или углеродными нанотрубками и увеличивается с уменьшением размера наночастиц. Одним из основных факторов, ответственных за наблюдаемое увеличение вязкости наножидкости, является структурирование молекул базовой жидкости вблизи наночастиц или углеродных нанотрубок.

Ключевые слова: Вязкость, гибридные наножидкости, метод молекулярной динамики, наножидкости, наночастицы, структура наножидкости, углеродные нанотрубки.

Распад и зарождение скирмионов в синтетических антиферромагнитных островках с закрепленными границами

Поткина М.Н.

Магнитные скирмионы в синтетических антиферромагнетиках являются перспективными наноразмерными элементами, но их применимость зависит от того, насколько надежно сохраняется и может быть создана записанная пара. Используя сокращенную решеточную модель, мы вычислили пути с минимальным перепадом энергии для коллапса антиферромагнитно связанной пары скирмионов и для обратного зарождения из закрепленного антиферромагнитного референсного состояния. При антиферромагнитно закрепленных границах энергия наибольшего седлового состояния лишь незначительно изменяется с размером островка, в то время как энергия пары скирмионов в начальном минимуме имеет сильно зависящую от размера островка граничную поправку. Для крупных островков коллапс происходит последовательно по слоям и может проходить через промежуточный минимум со скирмионом в одном слое всякий раз, когда это состояние удовлетворяет критерию релаксации. Гораздо больший обратный барьер для нуклеации демонстрирует сильную асимметрию с коллапсом в той же модели закрепленной границы и согласуется с послойной последовательной записью с помощью вспомогательных средств.

Ключевые слова: высокоориентированный пиролитический графит, графен, алканы, механические напряжения, сверхпроводимость.

Влияние спин-орбитальных взаимодействий на смещенную от центра примесь D^0 в асимметричной квантовой точке под действием магнитного поля

Саини П., Мукхопадхай С., Попов И.Ю., Чаттерджи А.

Мы оцениваем энергию основного состояния смещенной кулоновской примеси в асимметричной гауссовой квантовой точке GaAs в постоянном магнитном поле. Используя унитарное преобразование, мы учитываем комбинированный эффект взаимодействий Рашбы и Дрессельхауса, рассматривая члены связи до квадратичного порядка. Затем мы рассматриваем преобразован-

ный гамильтониан, используя вариационный подход с подходящей анзац-формой. Результаты показывают, что энергия основного состояния увеличивается с увеличением расстояния примеси от центра ограничения и с увеличением асимметрии потенциала. Наконец, мы исследуем, как асимметрия в гауссовом ограничении влияет на магнитный момент и восприимчивость примеси.

Ключевые слова: асимметричная квантовая точка GaAs, энергия смещенной примеси, спин-орбитальные взаимодействия, магнитное поле и восприимчивость.

Углерод, полученный методом лазерной обработки из финиковых косточек Иерихона: объединенные данные, полученные в результате многомодельного структурного, текстурного и поверхностного анализа

Ахмад Джабр, Ияд Саадеддин, Амер Эль-Хамуз, Заид Камхия, Хён Чжон, Чон Вон Пак

Активированный уголь из косточек фиников является перспективным материалом для энергетических, экологических и каталитических применений благодаря высокому выходу углерода, возобновляемому характеру и регулируемой пористости. В данной статье представлено обширное сравнительное исследование активированного угля (АК), полученного с использованием гидроксида калия, и активированного угля (ЛАУ), обработанного лазером Nd:YAG, оба материала получены из косточек фиников сорта «Иерихон». Комплексный анализ – рентгенодифракционный анализ (XRD), сканирующая электронная микроскопия (SEM), инфракрасная спектроскопия с преобразованием Фурье (FTIR), адсорбция азота (BJH, Horvath-Kawazoe, DFT, DR, DA), метод БЕТ, метод Лангмюра и t-график – показывает значительное улучшение микропористости, мезопористости, площади поверхности и химического состава поверхности ЛАУ. Сравнивая полученные результаты с опубликованными данными, можно отметить единое соответствие между моделями и методами характеристики, что подтверждает эффективность лазерной постобработки как дополнительной стратегии для целенаправленного изменения текстурных и поверхностных свойств активированного угля, полученного из биомассы, и может открыть перспективный путь для дальнейшего развития устойчивых пористых углеродных материалов.

Ключевые слова: Активированный уголь, лазерная карбонизация, активированный уголь, полученный с помощью лазера, косточки фиников, DFT, PSD, кинетика адсорбции.

Адсорбция катионных органических красителей на малослойном графене, полученном методом самораспространяющегося высокотемпературного синтеза

Подложнюк Н.Д., Возняковский А.А., Возняковский А.П., Кидалов С.В.

Эффективность углеродных наноматериалов для очистки воды от органических красителей была доказана на протяжении последнего десятилетия. Однако проблема промышленного применения углеродных наноматериалов до сих пор не решена. Это связано в первую очередь с высокой стоимостью и низкой производительностью методов синтеза углеродных наноматериалов. В данной статье представлены термодинамические и кинетические данные адсорбции родамина 6G и метиленового синего на малослойном графене. Малослойный графен был получен методом самораспространяющегося высокотемпературного синтеза из целлюлозы. Этот метод является перспективным, недорогим и легко масштабируемым. Было установлено, что исследуемый малослойный графен обладает высокой адсорбционной способностью по отно-

шению к обоим красителям, причём полученные значения адсорбционной ёмкости превышают показатели большинства изученных углеродных материалов, таких как углеродные нанотрубки или активированный уголь. Для описания термодинамики процесса были использованы наиболее распространённые модели адсорбции. Кинетика процесса описывается уравнением псевдовторого порядка, что довольно часто встречается для графеновых материалов. Предлагаемый механизм адсорбции основан на гидрофобном взаимодействии между адсорбентом и адсорбатом с образованием связей Н– π и π – π .

Ключевые слова: малослойный графен, графен, СВС-синтез, адсорбция, родамин 6G, метиленовый синий.

Fe-Mo/Al₂O₃ катализатор разложения метана, синтезированный методом горения раствора с использованием щавелевой кислоты

Курмашов П.Б., Шишин А.А., Головахин В., Даниленко М.А., Шпакова С. А., Белов Н.А., Гудыма Т. С., Ухина А. В., Ищенко А. В., Баннов А. Г.

В данной работе сообщается о синтезе катализаторов 80 % Fe–10 % Mo/10 % Al₂O₃ методом растворного горения с использованием щавелевой кислоты в качестве топлива. Катализаторы были испытаны в реакции разложения метана при 850 °С и 1 атм в течение 6 ч. Синтезированные образцы были охарактеризованы методами рентгеновской дифракции, просвечивающей электронной микроскопии, фотоседиментационного анализа и др. Удельный выход углерода составил от 5,8 до 8,4 г/г_{кат}, а выход водорода – от 1,0 до 1,4 моль/г_{кат} соответственно. Каталитическое разложение метана на Fe-Mo/Al₂O₃ приводило к образованию смеси бамбукоподобных и многостенных углеродных нанотрубок. Было установлено, что наивысший выход МУНТ достигался при соотношении топливо/окислитель, равном 0,022.

Ключевые слова: катализ, растворное горение, метан, катализатор, Fe-Mo-катализатор.

Ni/CeO₂ катализаторы, синтезированные методом растворного горения с использованием пористого носителя γ -Al₂O₃, для эффективного производства H₂ путем водяного риформинга глицерина

Матвеева А.Н., Омаров Ш.О., Теневич М.И.

Проведена оценка водяного риформинга глицерина (APR) для получения H₂ на Ni/CeO₂ (CeNi) катализаторе, полученном путем введения пористого носителя γ -Al₂O₃ в реакционную смесь в процессе синтеза методом растворного горения. Такой подход позволяет получить катализатор с улучшенным объёмом и средним размером пор, что имеет решающее значение для облегчения диффузии реагентов. В отличие от массивной CeNi системы, присутствие оксида алюминия увеличивает доступность активных наночастиц никеля и улучшает дисперсность оксида церия и никеля. Результаты APR глицерина показывают, что CeNi/ γ -Al₂O₃ обеспечивает большую степень превращения глицерина и выход водорода по сравнению с массивной системой. Примечательно, что уменьшение содержания активного компонента вдвое приводит к 2,3-кратному увеличению активности, которое не зависит от скорости потока исходного сырья и, следовательно, от степени диффузионных ограничений. Полученный в данном исследовании катализатор превзошел известные аналоги по скорости образования H₂, сохраняя при этом высокую степень превращения глицерина и селективность по H₂.

Ключевые слова: никель, оксид церия, оксид алюминия, синтез растворного горения, водяной риформинг, глицерин, водород.



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Научный журнал
ISSN 2220-8054
DOI: 10.17586/2220-8054

2026. Том 17. № 3

Свидетельство о регистрации средства массовой информации ПИ № ФС 77–49048
выдано 22.03.2012 г. Федеральной службой по надзору в сфере
связи, информационных технологий и массовых коммуникаций (Роскомнадзор)

Учредитель и издатель:

федеральное государственное автономное образовательное учреждение высшего
образования «Национальный исследовательский университет ИТМО»
197101, Российская Федерация, Санкт-Петербург, Кронверкский пр., 49, литер А

Адрес редакции:

191002, Санкт-Петербург г., ул. Ломоносова, д. 9, литер А
телефон: (812) 607-02-54, e-mail: nanojournal@itmo.ru
<http://nanojournal.ifmo.ru/>

Главный редактор: д.ф.-м.н., проф. Попов Игорь Юрьевич, iypopov@itmo.ru

Подписано в печать 30.06.2026 Дата выхода в свет 01.07.2026

Тираж 100 экз. 1 завод – 16 экз. Заказ № 17. Подписная цена.

Отпечатано: в ООО «Университетские телекоммуникации» Типография на Биржевой
Адрес: 199034, Санкт-Петербург, В.О., Биржевая линия, д. 16
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