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# A Complete geometric classification of spectral configurations for two-particle Schrödinger operators on $\mathbb{Z}$ with a rank-three interaction

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**ABSTRACT** We study a family of lattice Schrödinger operators  $H_{\mu}(K)$ , describing two identical bosons on the one-dimensional lattice  $\mathbb{Z}$ , where  $K \in \mathbb{T}$  is the quasi-momentum. The interaction is described by the coupling vector  $\mu = (\mu_1, \mu_2, \mu_3)$ , where  $\mu_1$  acts at the origin and  $\mu_2, \mu_3$  at the sites  $|x| = 1, 2$ . In this paper, we focus on the zero quasi-momentum fiber  $H_{\mu}(0)$ , whose essential spectrum is the interval  $[0, 8]$ , while discrete eigenvalues may occur both below 0 and above 8.

Using the Fredholm determinant, we derive explicit threshold polynomials whose zero sets:

$$\Gamma^{\pm} := \{\mu \in \mathbb{R}^3 : C^{\pm}(\mu) = 0\}$$

define three critical surfaces in  $\mathbb{R}^3$ . These surfaces partition the parameter space into regions with constant eigenvalue counts and identify exactly the parameter values at which eigenvalues emerge from, or are absorbed into, the thresholds 0 and 8.

A central result of this work is the complete geometric classification of the spectral configuration sets  $\mathcal{S} = (n_-, n_+)$ . We show that the  $(\mu_2, \mu_3)$ -plane is partitioned into domains  $D_j^{\pm}$ , which strictly govern the range of the spectral counting functions. We prove that the parameter  $\mu_3$  acts as a global phase controller: the critical values  $\mu_3 = \pm 2$  separate qualitatively different spectral regimes, determining the set of all attainable configurations under the global rank-three constraint.

Finally, we extend our analysis to  $K \neq 0$  and demonstrate that the discrete spectrum is preserved for all quasi-momenta whenever  $|\mu_3| > 2$ .

**KEYWORDS** Two-particle lattice Schrödinger operator, discrete spectrum, rank-three perturbation, Fredholm determinant, threshold asymptotics, critical surfaces, spectral classification.

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## 1. Introduction

Discrete Schrödinger operators on lattices constitute an important class of models in mathematical physics, providing a natural framework for the study of quantum systems in periodic media such as crystalline solids and optical lattices [1–10]. In contrast to continuous models, lattice Hamiltonians are characterized by bounded dispersion relations, and therefore their essential spectrum forms a compact interval. This feature gives rise to specific spectral effects absent in the continuous case, including the possibility of discrete eigenvalues both below and above the spectral band [11–22].

Recent experimental developments in optical lattice systems have confirmed the existence of lattice-induced bound states, including repulsively bound atom pairs, which have no direct analogue in continuous models [20, 23–25]. These phenomena have stimulated intensive studies of the spectral properties of few-particle lattice Hamiltonians and their threshold behaviour.

A fundamental aspect of lattice systems is the analysis of threshold effects, where eigenvalues emerge from or disappear into the edges of the essential spectrum. Such phenomena play a crucial role in the description of bound states and have been extensively studied in the framework of discrete Schrödinger operators [21, 22].

A standard method for analyzing translation-invariant lattice Hamiltonians is the Floquet–Bloch decomposition, which reduces the full operator to a direct integral of fiber operators parametrized by the total quasi-momentum  $K \in \mathbb{T}^d$  [2, 3, 26]. The spectral analysis of these fiber operators provides a complete description of bound states and their dependence on the quasi-momentum.

In the present paper, we consider a two-particle Schrödinger operator on the one-dimensional lattice  $\mathbb{Z}$  with a symmetric finite-range interaction and focus on the zero quasi-momentum fiber  $K = 0$ , whose essential spectrum is the interval

[0, 8]. Our main goal is to establish a complete geometric classification of all possible discrete spectrum configurations in terms of the interaction parameters.

### 1.1. Model and main results

We consider a system of two identical spinless bosons on  $\mathbb{Z}$  interacting through a symmetric finite-range potential

$$\hat{v}_\mu(x) = \mu_1 \delta_{|x|,0} + \mu_2 \delta_{|x|,1} + \mu_3 \delta_{|x|,2}, \quad \mu = (\mu_1, \mu_2, \mu_3) \in \mathbb{R}^3, \quad (1)$$

which generates a rank-three perturbation of the free discrete Laplacian. After Fourier transform and Floquet–Bloch reduction, the corresponding fiber Hamiltonian  $H_\mu(0)$  acts in the even-function subspace  $L^{2,e}(\mathbb{T})$  and has essential spectrum [0, 8]. Since the perturbation is of rank three, the total number of discrete eigenvalues outside the essential spectrum is finite and does not exceed three.

The spectral problem is reduced to the analysis of an explicit Fredholm determinant  $\Delta_\mu(z)$  associated with the Lippmann–Schwinger operator. Its threshold asymptotics at the band edges 0 and 8 are governed by two explicit polynomials  $C^\pm(\mu)$ , whose zero sets define critical surfaces

$$\Gamma^\pm = \{\mu \in \mathbb{R}^3 : C^\pm(\mu) = 0\}.$$

These surfaces describe precisely the parameter values at which eigenvalues emerge from or disappear into the essential spectrum.

The main result of the paper is a complete geometric classification of all admissible discrete spectrum configurations of  $H_\mu(0)$ . We prove that the  $(\mu_2, \mu_3)$ -plane is partitioned into three disjoint domains  $D_j^\pm$  ( $j = 0, 1, 2$ ), which determine the possible values of the eigenvalue counting functions  $n_\pm$ . By analyzing the intersections of these domains and combining them with the global rank-three constraint, we obtain an explicit classification of all realizable spectral pairs  $(n_-, n_+)$ .

A distinguished role is played by the parameter  $\mu_3$ : the critical values  $\mu_3 = \pm 2$  separate different global spectral regimes. In particular, for  $\mu_3 < -2$  the operator always possesses at least one eigenvalue below the essential spectrum, while for  $\mu_3 > 2$  it always possesses at least one eigenvalue above it. This yields a complete partition of the parameter space into spectral phase regions characterized by the exact numbers of bound states below and above the essential spectrum.

By deriving comparison estimates, we extend the results obtained for  $K = 0$  to arbitrary quasi-momenta  $K \in \mathbb{T}$ . These estimates show that the number of eigenvalues  $n_\pm(H_\mu(K))$  is controlled by its corresponding value at the origin. In particular, when  $|\mu_3| > 2$ , they guarantee that the discrete spectrum is non-empty for every  $K \in \mathbb{T}$ , yielding uniform lower bounds on the number of eigenvalues across the Brillouin zone.

The distribution of the discrete spectrum for two-particle Hamiltonians has been investigated in several recent works, such as [27, 29–33]. While these studies identified various spectral regimes for specific interaction models, a comprehensive global description of the parameter space was not provided. Our approach fills this gap by rigorously partitioning the interaction manifold into disjoint regions where the exact number and location of discrete eigenvalues  $n_\pm$  remain invariant. This geometric classification provides a complete characterization of the eigenvalue birth and annihilation mechanisms across the entire range of parameters.

### 1.2. Outline of the paper

In Section 2, we introduce the model and perform the Floquet–Bloch decomposition. Section 3 establishes the Fredholm determinant representation and derives its threshold asymptotics. Section 4 is devoted to the geometric analysis of the critical surfaces and the partition of the parameter space. In Section 5, we classify all realizable spectral configurations and describe their global dependence on the interaction parameters. Finally, Section 6 summarizes the results and outlines possible generalizations.

## 2. The Two-Particle Hamiltonian

### 2.1. Position-space representation

Let  $\mathbb{Z}$  be the one-dimensional integer lattice, and denote by

$$\ell^2(\mathbb{Z} \times \mathbb{Z}), \quad \ell^{2,s}(\mathbb{Z} \times \mathbb{Z}) := \{\hat{f} \in \ell^2(\mathbb{Z} \times \mathbb{Z}) : \hat{f}(x_1, x_2) = \hat{f}(x_2, x_1)\}$$

the Hilbert space of square-summable functions and its symmetric subspace, respectively. The total Hamiltonian

$$\hat{\mathbb{H}}_\mu = \hat{\mathbb{H}}_0 + \hat{\mathbb{V}}_\mu, \quad \mu = (\mu_1, \mu_2, \mu_3) \in \mathbb{R}^3,$$

is a bounded self-adjoint operator on  $\ell^{2,s}(\mathbb{Z} \times \mathbb{Z})$ . The free Hamiltonian  $\hat{\mathbb{H}}_0$  is the two-particle discrete Laplacian on  $\mathbb{Z}^2$ :

$$\begin{aligned} (\hat{\mathbb{H}}_0 \hat{f})(x_1, x_2) = & [2\hat{f}(x_1, x_2) - \hat{f}(x_1 + 1, x_2) - \hat{f}(x_1 - 1, x_2)] \\ & + [2\hat{f}(x_1, x_2) - \hat{f}(x_1, x_2 + 1) - \hat{f}(x_1, x_2 - 1)]. \end{aligned}$$

The interaction operator  $\hat{V}_\mu$  acts as a multiplication operator:

$$(\hat{V}_\mu \hat{f})(x_1, x_2) = \hat{v}_\mu(x_1 - x_2) \hat{f}(x_1, x_2),$$

where the finite-range interaction potential  $\hat{v}_\mu$  is defined by (1).

## 2.2. Momentum-space representation

Let  $\mathbb{T} := \mathbb{R}/2\pi\mathbb{Z} \equiv (-\pi, \pi]$  denote the one-dimensional torus. Applying the Fourier transform  $\mathcal{F} : \ell^2(\mathbb{Z}) \rightarrow L^2(\mathbb{T})$  to both particle coordinates, we obtain the momentum-space representation

$$H_\mu := (\mathcal{F} \otimes \mathcal{F}) \hat{\mathbb{H}}_\mu (\mathcal{F}^* \otimes \mathcal{F}^*) = H_0 + V_\mu, \quad \mu \in \mathbb{R}^3,$$

acting on the Hilbert space  $L^{2,s}(\mathbb{T} \times \mathbb{T})$  of symmetric square-integrable functions on  $\mathbb{T}^2$ . The free operator  $H_0$  acts as multiplication by the two-particle dispersion relation,

$$(H_0 f)(p, q) = [\varepsilon(p) + \varepsilon(q)] f(p, q),$$

with

$$\varepsilon(p) = 2(1 - \cos p), \quad p \in \mathbb{T}.$$

The interaction operator  $V_\mu$  becomes an integral operator,

$$(V_\mu f)(p, q) = \frac{1}{2\pi} \int_{\mathbb{T}} v_\mu(p - u) f(u, p + q - u) du,$$

where the kernel is  $v_\mu(p) = \mu_1 + 2\mu_2 \cos p + 2\mu_3 \cos 2p$ .

## 2.3. Floquet–Bloch decomposition and fiber Hamiltonians

Since  $H_\mu$  is translation invariant, we apply the Floquet–Bloch decomposition with respect to the total quasi-momentum  $K \in \mathbb{T}$ :

$$L^{2,s}(\mathbb{T} \times \mathbb{T}) \simeq \int_{\mathbb{T}}^{\oplus} L^{2,e}(\mathbb{T}) d\nu(K), \quad H_\mu \simeq \int_{\mathbb{T}}^{\oplus} H_\mu(K) d\nu(K),$$

where  $d\nu$  is the normalized Lebesgue measure and  $L^{2,e}(\mathbb{T}) \subset L^2(\mathbb{T})$  is the subspace of even functions. For each  $K \in \mathbb{T}$ , the fiber Hamiltonian

$$H_\mu(K) = H_0(K) + V_\mu$$

acts as

$$(H_0(K)f)(p) = \mathcal{E}_K(p) f(p), \quad \mathcal{E}_K(p) = 4\left(1 - \cos \frac{K}{2} \cos p\right),$$

and

$$(V_\mu f)(p) = \sum_{i=1}^3 \mu_i \langle \phi_i, f \rangle \phi_i(p),$$

where we introduce the orthonormal form factors

$$\phi_1(t) = 1, \quad \phi_2(t) = \sqrt{2} \cos t, \quad \phi_3(t) = \sqrt{2} \cos 2t, \quad t \in \mathbb{T}.$$

**Remark 1.** The Floquet–Bloch decomposition reduces the translation-invariant Hamiltonian  $H_\mu$  to a direct integral of fiber operators  $H_\mu(K)$ ,  $K \in \mathbb{T}$ . The essential spectrum of  $H_\mu$  is the union over  $K$  of the essential spectra of the fibers, while discrete eigenvalues of the fibers correspond to bound states with total quasi-momentum  $K$ . Because  $V_\mu$  is of finite rank (at most three), each fiber  $H_\mu(K)$  is a finite-rank perturbation of a multiplication operator, which greatly simplifies the spectral analysis.

## 2.4. Essential spectrum

The free fiber Hamiltonian  $H_0(K)$  has purely absolutely continuous spectrum consisting of a single band:

$$\sigma(H_0(K)) = [\mathcal{E}_{\min}(K), \mathcal{E}_{\max}(K)],$$

where

$$\mathcal{E}_{\min}(K) = 4\left(1 - \cos \frac{K}{2}\right) \geq \mathcal{E}_{\min}(0) = 0,$$

$$\mathcal{E}_{\max}(K) = 4\left(1 + \cos \frac{K}{2}\right) \leq \mathcal{E}_{\max}(0) = 8.$$

Since  $V_\mu$  is a finite-rank operator, Weyl's theorem on the invariance of the essential spectrum (see [26]) under compact perturbations (and, in particular, under finite-rank perturbations) implies

$$\sigma_{\text{ess}}(H_\mu(K)) = [\mathcal{E}_{\min}(K), \mathcal{E}_{\max}(K)].$$

Consequently, any discrete eigenvalue of  $H_\mu(K)$  must lie in the spectral gaps:

$$\sigma_{\text{disc}}(H_\mu(K)) \subset (-\infty, \mathcal{E}_{\min}(K)) \cup (\mathcal{E}_{\max}(K), \infty).$$

Let  $n_-(H_\mu(K))$  and  $n_+(H_\mu(K))$  denote the number of discrete eigenvalues (counting multiplicities) below and above the essential spectrum, respectively. Because  $V_\mu$  has rank at most three, we obtain the universal bound

$$n(H_\mu(K)) := n_-(H_\mu(K)) + n_+(H_\mu(K)) \leq 3, \quad \forall K \in \mathbb{T}. \quad (2)$$

**Remark 2.** The bound (2) is a direct consequence of the finite-rank nature of the perturbation: a finite-rank perturbation can create at most as many eigenvalues (outside the essential spectrum) as its rank, counting multiplicities. This observation will be crucial later when we classify the discrete spectrum, as it restricts the possible pairs  $(n_-, n_+)$  that can occur.

### 3. Fredholm determinant and threshold asymptotics

In this section, we restrict our attention to the specific case  $K = 0$ , representing zero total quasi-momentum. In this regime, the essential spectrum of  $H_0(0)$  is significantly reduced to the interval  $[0, 8]$ .

#### 3.1. The transposed Lippmann–Schwinger operator

For  $z \in \mathbb{R} \setminus [0, 8]$ , the resolvent of the free operator

$$R_0(0, z) := (H_0(0) - zI)^{-1}$$

is well-defined as a bounded operator.

**Definition 1.** For  $z \in \mathbb{R} \setminus [0, 8]$ , the transposed Lippmann–Schwinger operator associated with  $H_\mu(0)$  is defined by

$$L_\mu(0, z) := -V_\mu R_0(0, z).$$

**Remark 3.** Since  $V_\mu$  is of finite rank,  $L_\mu(0, z)$  acts non-trivially only on the finite-dimensional space spanned by the form factors  $\phi_1, \phi_2, \phi_3$ . Consequently, the eigenvalue problem reduces to a  $3 \times 3$  matrix equation, and the Fredholm determinant admits an explicit algebraic representation.

The following lemma establishes the spectral correspondence between  $H_\mu(0)$  and its Lippmann–Schwinger operator.

**Lemma 1.** A point  $z \in \mathbb{R} \setminus [0, 8]$  is an eigenvalue of  $H_\mu(0)$  with multiplicity  $m$  if and only if 1 is an eigenvalue of  $L_\mu(0, z)$  with the same multiplicity.

*Proof.* The eigenvalue equation  $H_\mu(0)\psi = z\psi$  is equivalent to

$$(H_0(0) - z)\psi = -V_\mu\psi.$$

Applying the resolvent  $R_0(0, z)$  yields

$$\psi = -V_\mu R_0(0, z)\psi,$$

which means that  $\psi$  is an eigenvector of  $L_\mu(0, z)$  corresponding to the eigenvalue 1. The converse follows analogously.  $\square$

**Lemma 2.** A point  $z \in \mathbb{R} \setminus [0, 8]$  is an eigenvalue of  $H_\mu(0)$  if and only if

$$\Delta_\mu(z) = 0,$$

where

$$\Delta_\mu(z) := \det(I - L_\mu(0, z)) = \det\left(\delta_{ij} + \mu_j a_{ij}(z)\right)_{i,j=1}^3. \quad (3)$$

The matrix elements are given by

$$a_{ij}(z) := \langle R_0(0, z)\phi_j, \phi_i \rangle = \int_{\mathbb{T}} \frac{\phi_i(t)\phi_j(t)}{\mathcal{E}_0(t) - z} d\nu(t), \quad i, j = 1, 2, 3. \quad (4)$$

Moreover, the function  $\Delta_\mu(\cdot)$  has at most three zeros in  $\mathbb{R} \setminus [0, 8]$ .

*Proof.* By Lemma 1,  $z \in \mathbb{R} \setminus [0, 8]$  is an eigenvalue of  $H_\mu(0)$  if and only if 1 is an eigenvalue of  $L_\mu(0, z)$ . Since  $L_\mu(0, z)$  is a finite-rank operator, this is equivalent to  $\det(I - L_\mu(0, z)) = 0$ . Hence

$$z \in \sigma_{\text{disc}}(H_\mu(0)) \iff \Delta_\mu(z) = 0.$$

Finally, since  $V_\mu$  has rank at most three, the operator  $H_\mu(0)$  has at most three discrete eigenvalues in  $\mathbb{R} \setminus [0, 8]$ . Therefore,  $\Delta_\mu(\cdot)$  has at most three zeros in  $\mathbb{R} \setminus [0, 8]$ .  $\square$

**Lemma 3.** The functions  $a_{ij}(z)$ ,  $i, j = 1, 2, 3$ , satisfy the following symmetry and asymptotic properties.

(i) **Parity relation:**

$$a_{ij}(8 - z) = (-1)^{i+j+1} a_{ij}(z), \quad i, j \in \{1, 2, 3\}.$$

(ii) **Asymptotic expansions at the band edges:**

$$a_{ij}(z) = \begin{cases} \frac{\phi_i(0)\phi_j(0)}{2\sqrt{2}\zeta_0(z)} + A_{ij} + O(\zeta_0(z)), & z \nearrow 0, \\ -\frac{\phi_i(\pi)\phi_j(\pi)}{2\sqrt{2}\zeta_8(z)} - A_{ij} + O(\zeta_8(z)), & z \searrow 8, \end{cases} \quad (5)$$

where  $\zeta_0(z) = \sqrt{-z}$  (for  $z < 0$ ),  $\zeta_8(z) = \sqrt{z-8}$  (for  $z > 8$ ), and the constant matrix  $A$  is given by

$$A = \begin{pmatrix} 0 & -\frac{\sqrt{2}}{4} & -\frac{\sqrt{2}}{2} \\ -\frac{\sqrt{2}}{4} & -\frac{1}{2} & -1 \\ -\frac{\sqrt{2}}{2} & -1 & -1 \end{pmatrix}.$$

*Proof.* (i) By definition (4),

$$a_{ij}(8 - z) = \int_{\mathbb{T}} \frac{\phi_i(t)\phi_j(t)}{\mathcal{E}_0(t) - (8 - z)} d\nu(t).$$

Using the identities

$$\mathcal{E}_0(t + \pi) = 8 - \mathcal{E}_0(t), \quad \phi_k(t + \pi) = (-1)^{k+1} \phi_k(t),$$

and performing the change of variables  $t \mapsto t + \pi$ , we obtain

$$a_{ij}(8 - z) = (-1)^{i+j+1} a_{ij}(z).$$

(ii) To derive the asymptotics as  $z \nearrow 0$ , we write

$$a_{ij}(z) = \int_{\mathbb{T}} \frac{\phi_i(t)\phi_j(t) - \phi_i(0)\phi_j(0)}{\mathcal{E}_0(t) - z} d\nu(t) + \phi_i(0)\phi_j(0) \int_{\mathbb{T}} \frac{d\nu(t)}{\mathcal{E}_0(t) - z}.$$

The first integral is regular at  $z = 0$  and therefore admits the expansion  $A_{ij} + O(\zeta_0(z))$ . For the second integral, using the local expansion  $\mathcal{E}_0(t) = 2t^2 + O(t^4)$ ,  $t \rightarrow 0$ , we obtain

$$\int_{\mathbb{T}} \frac{d\nu(t)}{\mathcal{E}_0(t) - z} = \frac{1}{2\sqrt{2}\zeta_0(z)} + O(1), \quad z \nearrow 0.$$

Combining these relations, we obtain the asymptotic expansion (5) as  $z \nearrow 0$ .

The asymptotics as  $z \searrow 8$  follows immediately from part (i) by replacing  $z$  with  $8 - z$  and using

$$\phi_k(\pi) = (-1)^{k+1} \phi_k(0).$$

□

**Lemma 4** (Determinant asymptotics). For any  $\mu \in \mathbb{R}^3$ ,

$$\Delta_{\mu}(z) = \begin{cases} C^{-}(\mu) \frac{1}{2\sqrt{2}\zeta_0(z)} + D^{-}(\mu) + O(\zeta_0(z)), & z \nearrow 0, \\ C^{+}(\mu) \frac{1}{2\sqrt{2}\zeta_8(z)} + D^{+}(\mu) + O(\zeta_8(z)), & z \searrow 8, \end{cases}$$

where  $\zeta_0(z) = \sqrt{-z}$  ( $z < 0$ ),  $\zeta_8(z) = \sqrt{z-8}$  ( $z > 8$ ), and the coefficients are

$$\begin{aligned} C^{\pm}(\mu) &= \mp(\mu_1 + 2\mu_2 + 2\mu_3 + \tfrac{1}{4}\mu_1\mu_2\mu_3) + \tfrac{1}{2}\mu_1\mu_2 + \mu_1\mu_3 + \mu_2\mu_3, \\ D^{\pm}(\mu) &= 1 \pm (\tfrac{1}{2}\mu_2 + \mu_3 + \tfrac{1}{8}\mu_1\mu_2\mu_3) - \tfrac{1}{2}\mu_2\mu_3 - \tfrac{1}{8}\mu_1\mu_2 - \tfrac{1}{2}\mu_1\mu_3. \end{aligned} \quad (6)$$

*Proof sketch.* The asymptotic formulas follow directly from the determinant representation (3) and the expansions (5) by collecting the leading singular and constant terms. □

#### 4. Geometric Classification of Critical Parameters

In this section, we investigate the geometric structure of the critical parameters where spectral transitions occur. The zeros of the threshold polynomials  $C^\pm(\mu)$ , introduced in Lemma 4, correspond to the emergence or disappearance of discrete eigenvalues at the band edges. Therefore, we focus on the characterization of the critical surfaces

$$\Gamma^\pm = \{\mu \in \mathbb{R}^3 : C^\pm(\mu) = 0\}. \quad (7)$$

**Remark 4.** The polynomials  $C^\pm(\mu)$  satisfy the symmetry relation

$$C^+(\mu_1, \mu_2, \mu_3) = C^-(-\mu_1, -\mu_2, -\mu_3),$$

which reflects the invariance of the model under the transformation  $\mu \mapsto -\mu$ . This symmetry allows one to deduce the geometric structure of  $\Gamma^+$  from that of  $\Gamma^-$ .

##### 4.1. Threshold polynomials and affine structure

A key property that simplifies the analysis of  $\Gamma^\pm$  is the affine (linear) dependence of  $C^\pm$  on the parameter  $\mu_1$ . This allows us to represent the critical surfaces as graphs of functions over the  $(\mu_2, \mu_3)$ -plane.

**Lemma 5** (Affine structure). *For each sign  $\pm$ , the threshold polynomial  $C^\pm(\cdot)$  can be uniquely decomposed as*

$$C^\pm(\mu) = Q_0^\pm(\mu_2, \mu_3) + \mu_1 Q_1^\pm(\mu_2, \mu_3), \quad (8)$$

where the coefficients are given by

$$\begin{aligned} Q_0^\pm(\mu_2, \mu_3) &= \mu_2 \mu_3 \mp 2(\mu_2 + \mu_3), \\ Q_1^\pm(\mu_2, \mu_3) &= \mu_3 + \frac{1}{2}\mu_2 \mp (1 + \frac{1}{4}\mu_2 \mu_3). \end{aligned}$$

*Proof.* The affine linearity in  $\mu_1$  (given in (8)) follows directly from the explicit formula for  $C^\pm(\mu)$  given in (6). The coefficients are obtained by evaluating  $C^\pm$  and its partial derivative at  $\mu_1 = 0$ :

$$Q_0^\pm(\mu_2, \mu_3) = C^\pm(0, \mu_2, \mu_3), \quad Q_1^\pm(\mu_2, \mu_3) = \left. \frac{\partial C^\pm}{\partial \mu_1} \right|_{\mu_1=0}.$$

A straightforward computation yields the expressions stated above.  $\square$

##### 4.2. Partition of the parameter plane

The geometry of the surface  $\Gamma^\pm$  is governed by the zero set of the coefficient  $Q_1^\pm$ . We now partition the  $(\mu_2, \mu_3)$ -plane according to the sign of this polynomial.

**Lemma 6.** *The zero set of the polynomial  $Q_1^\pm(\cdot, \cdot)$  coincides with the graph of the rational function*

$$\mu_2^\pm(\mu_3) = \frac{4(\mu_3 \mp 1)}{\mu_3 \mp 2}, \quad \mu_3 \in \mathbb{R} \setminus \{\pm 2\}. \quad (9)$$

The domain of the function  $\mu_2^\pm(\cdot)$  consists of two disjoint intervals:

$$I_0^- = (-2, \infty), \quad I_1^- = (-\infty, -2); \quad I_0^+ = (-\infty, 2), \quad I_1^+ = (2, \infty).$$

Consequently, the graph splits into two disjoint, smooth, unbounded curves

$$\tau_i^\pm := \{(\mu_2, \mu_3) : \mu_2 = \mu_2^\pm(\mu_3), \mu_3 \in I_i^\pm\}, \quad i = 0, 1.$$

These curves partition the  $(\mu_2, \mu_3)$ -plane into three disjoint, open, connected, unbounded components  $D_j^\pm$  ( $j = 0, 1, 2$ ) where  $Q_1^\pm$  has a constant sign. Explicitly,

$$\begin{aligned} D_0^\pm &:= \{(\mu_2, \mu_3) : \mu_3 \in I_0^\pm, \pm\mu_2 < \pm\mu_2^\pm(\mu_3)\}, \\ D_1^\pm &:= \{(\mu_2, \mu_3) : \mu_3 \in I_0^\pm, \pm\mu_2 > \pm\mu_2^\pm(\mu_3)\} \cup \{(\mu_2, \mu_3) : \mu_3 = \pm 2\} \\ &\quad \cup \{(\mu_2, \mu_3) : \mu_3 \in I_1^\pm, \pm\mu_2 < \pm\mu_2^\pm(\mu_3)\}, \\ D_2^\pm &:= \{(\mu_2, \mu_3) : \mu_3 \in I_1^\pm, \pm\mu_2 > \pm\mu_2^\pm(\mu_3)\}. \end{aligned} \quad (10)$$

*Proof.* By solving the linear equation  $Q_1^\pm(\mu_2, \mu_3) = 0$  for  $\mu_2$ , we directly obtain the expression for  $\mu_2^\pm(\mu_3)$  in (9). The singularity at  $\mu_3 = \pm 2$  generates a vertical asymptote that naturally splits the curve into two continuous branches  $\tau_0^\pm$  and  $\tau_1^\pm$ . The domains  $D_j^\pm$  are constructed such that their boundaries are formed by these branches and the line of singularity. Within each domain, the sign of  $Q_1^\pm$  is invariant by continuity, as  $Q_1^\pm$  is continuous and non-vanishing on  $D_j^\pm$ .  $\square$

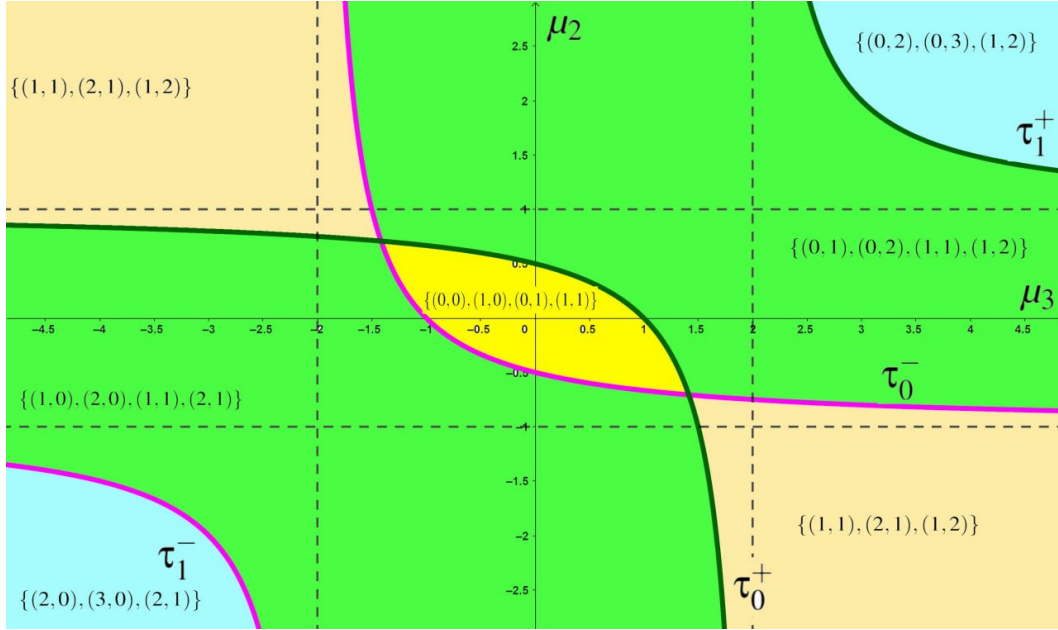


FIG. 1. Geometric structure of the domains  $D_j^-$  and  $D_j^+$  in the  $(\mu_2, \mu_3)$ -plane, separated by the critical curves  $\tau_i^-$  and  $\tau_i^+$ ,  $i = 0, 1$

**Remark 5.** The components  $D_j^\pm$ ,  $j = 0, 1, 2$  are shown schematically in Figure 1. For the minus sign (lower threshold),  $D_0^-$  lies to the left of the left branch,  $D_1^-$  is the region between the two branches (including the vertical line  $\mu_3 = -2$ ), and  $D_2^-$  lies to the right of the right branch. For the plus sign (upper threshold), the roles of left/right are reversed due to the sign conventions in the inequalities.

### 4.3. Geometry of the critical surfaces

We now characterise the critical surfaces  $\Gamma^\pm$  as a union of smooth sheets and describe the resulting partition of the parameter space  $\mathbb{R}^3$ .

**Lemma 7** (Structure of  $\Gamma^\pm$ ). The zero set  $\Gamma^\pm$  defined in (7) consists of three disjoint, smooth, unbounded sheets:

$$\Gamma^\pm = \Gamma_0^\pm \cup \Gamma_1^\pm \cup \Gamma_2^\pm, \quad (11)$$

where each sheet  $\Gamma_j^\pm$  is the graph of the rational function

$$\mu_1^\pm(\mu_2, \mu_3) = -\frac{Q_0^\pm(\mu_2, \mu_3)}{Q_1^\pm(\mu_2, \mu_3)} \quad (12)$$

over the domain  $D_j^\pm$ :

$$\Gamma_j^\pm := \{(\mu_1, \mu_2, \mu_3) : \mu_1 = \mu_1^\pm(\mu_2, \mu_3), (\mu_2, \mu_3) \in D_j^\pm\}, \quad j = 0, 1, 2.$$

These sheets partition  $\mathbb{R}^3$  into four disjoint, open, connected, unbounded components  $\mathcal{C}_k^\pm$  ( $k = 0, 1, 2, 3$ ) defined as follows:

$$\begin{aligned} \mathcal{C}_0^\pm &:= \{\mu : (\mu_2, \mu_3) \in D_0^\pm, \pm\mu_1 < \pm\mu_1^\pm(\mu_2, \mu_3)\}, \\ \mathcal{C}_1^\pm &:= \{\mu : (\mu_2, \mu_3) \in D_0^\pm, \pm\mu_1 > \pm\mu_1^\pm(\mu_2, \mu_3)\} \cup \{\mu : (\mu_2, \mu_3) \in \tau_0^\pm\} \\ &\quad \cup \{\mu : (\mu_2, \mu_3) \in D_1^\pm, \pm\mu_1 < \pm\mu_1^\pm(\mu_2, \mu_3)\}, \\ \mathcal{C}_2^\pm &:= \{\mu : (\mu_2, \mu_3) \in D_1^\pm, \pm\mu_1 > \pm\mu_1^\pm(\mu_2, \mu_3)\} \cup \{\mu : (\mu_2, \mu_3) \in \tau_1^\pm\} \\ &\quad \cup \{\mu : (\mu_2, \mu_3) \in D_2^\pm, \pm\mu_1 < \pm\mu_1^\pm(\mu_2, \mu_3)\}, \\ \mathcal{C}_3^\pm &:= \{\mu : (\mu_2, \mu_3) \in D_2^\pm, \pm\mu_1 > \pm\mu_1^\pm(\mu_2, \mu_3)\}. \end{aligned} \quad (13)$$

Within each region  $\mathcal{C}_k^\pm$ , the threshold polynomial  $C^\pm$  has a constant sign (alternating as  $k$  increases).

*Proof.* The threshold equation  $C^\pm(\mu) = 0$  is affine in  $\mu_1$  and can be expressed as  $\mu_1 Q_1^\pm(\mu_2, \mu_3) = -Q_0^\pm(\mu_2, \mu_3)$ . Since the system of equations  $Q_0^\pm(\mu_2, \mu_3) = Q_1^\pm(\mu_2, \mu_3) = 0$  has no real solutions, it follows that  $Q_1^\pm$  is non-vanishing on the critical surface  $\Gamma^\pm$ . Thus,  $\Gamma^\pm$  is uniquely represented as the graph of the rational function  $\mu_1^\pm(\mu_2, \mu_3) = -Q_0^\pm/Q_1^\pm$  over the domain  $\mathbb{R}^2 \setminus (\tau_0^\pm \cup \tau_1^\pm)$ .

By Lemma 6, the domain of  $\mu_1^\pm$  is the union of three disjoint, open components  $D_0^\pm$ ,  $D_1^\pm$ , and  $D_2^\pm$  (see Figure 1). Since  $\mu_1^\pm$  is continuous on each  $D_i^\pm$ , its graph  $\Gamma^\pm$  naturally inherits this topological structure, consisting of three disjoint, smooth sheets  $\Gamma_i^\pm$ .

The sign of  $C^\pm(\mu)$  is governed by the factorization  $C^\pm(\mu) = Q_1^\pm \cdot [\mu_1 - \mu_1^\pm(\mu_2, \mu_3)]$ . Within each region  $\mathcal{C}_k^\pm$ , the continuity of  $Q_1^\pm$  and  $\mu_1^\pm$  ensures that  $C^\pm$  remains non-vanishing. A sign change occurs only when crossing a sheet  $\Gamma_i^\pm$  or passing through the singular boundaries  $\tau_k^\pm$ , which precisely defines the transitions between the four spectral regions.  $\square$

#### 4.4. Discrete spectrum classification

We now characterise the dependence of the number of discrete eigenvalues on the interaction parameter vector  $\mu = (\mu_1, \mu_2, \mu_3) \in \mathbb{R}^3$ . The discrete spectrum phases are determined by the sign of the threshold polynomials  $C^\pm(\mu)$ , which in turn depends on the position of  $\mu$  relative to the critical surfaces  $\Gamma^\pm$  (see (11)).

**Theorem 1.** *The numbers of discrete eigenvalues  $n_\pm(H_\mu(0))$  are determined by the interaction parameters as follows:*

(i) *Within each open connected component  $\mathcal{C}_k^\pm$ , where  $C^\pm(\mu) \neq 0$ , the count is constant:*

$$n_\pm(H_\mu(0)) = k \quad \text{if } \mu \in \mathcal{C}_k^\pm, \quad k \in \{0, 1, 2, 3\}.$$

(ii) *On the critical surfaces  $\Gamma_j^\pm$ , where  $C^\pm(\mu) = 0$ , the count is given by*

$$n_\pm(H_\mu(0)) = j \quad \text{if } \mu \in \Gamma_j^\pm, \quad j \in \{0, 1, 2\}.$$

*Proof.* The proof is based on the analytic properties of the Fredholm determinant  $\Delta_\mu(z)$  and the continuity of discrete eigenvalues.

(i) For any  $\mu \in \mathcal{C}_k^\pm$ , the condition  $C^\pm(\mu) \neq 0$  ensures that the threshold  $z = 0$  (resp.  $z = 8$ ) is not a zero of the determinant. Since  $\Delta_\mu(z)$  is analytic outside the essential spectrum and depends continuously on  $\mu$ , the number of its zeros in  $(-\infty, 0)$  (resp.  $(8, \infty)$ ) is locally constant by the argument principle. The connectivity of each component  $\mathcal{C}_k^\pm$  then implies that this count remains globally constant within the region. The specific values of  $k$  are determined by evaluating  $\Delta_\mu(z)$  at representative points in each domain or by considering the asymptotic behavior as  $|\mu_1| \rightarrow \infty$ . A detailed proof can be obtained by referring to the proofs of a similar theorem presented in [27].

(ii) On the critical surface  $\Gamma_j^\pm$ , the leading singular coefficient  $C^\pm$  vanishes, so the corresponding eigenvalue lies exactly at the threshold and is not counted as a discrete eigenvalue. The remaining eigenvalues are those that have already crossed the threshold, giving the count  $j$ .  $\square$

**Remark 6.** *The components  $\mathcal{C}_k^\pm$ ,  $k = 0, 1, 2, 3$  are ordered by the number of discrete eigenvalues they host: as  $k$  increases, the sign of  $C^\pm$  changes, and one additional eigenvalue appears at the corresponding threshold. The boundaries  $\Gamma_j^\pm$  correspond to the moment when the  $j$ -th eigenvalue (counting from the threshold) is exactly at the band edge. The singular curves  $\tau_i^\pm$  (where  $Q_1^\pm = 0$ ) correspond to vertical asymptotes of  $\mu_1^\pm$ ; they separate regions where the graph  $\Gamma^\pm$  has different asymptotic behaviour.*

Since the collection of regions  $\{\mathcal{C}_k^\pm\}_{k=0}^3$  together with their boundaries  $\{\Gamma_j^\pm\}_{j=0}^2$  covers  $\mathbb{R}^3$ , we define the combined spectral sets

$$\mathcal{R}_\alpha^\pm := \mathcal{C}_\alpha^\pm \cup \Gamma_\alpha^\pm, \quad \alpha \in \{0, 1, 2, 3\},$$

where we set  $\Gamma_3^\pm = \emptyset$  for consistency.

**Corollary 1.** *For any  $\mu \in \mathbb{R}^3$ , the operator  $H_\mu(0)$  has exactly  $\alpha$  discrete eigenvalues below (resp. above) the essential spectrum if and only if  $\mu \in \mathcal{R}_\alpha^-$  (resp.  $\mu \in \mathcal{R}_\alpha^+$ ):*

$$n_\pm(H_\mu(0)) = \alpha \iff \mu \in \mathcal{R}_\alpha^\pm, \quad \alpha \in \{0, 1, 2, 3\}.$$

*Proof.* The equivalence follows directly from Theorem 1: on  $\mathcal{C}_\alpha^\pm$  we have  $n_\pm = \alpha$ ; on  $\Gamma_\alpha^\pm$  (for  $\alpha = 0, 1, 2$ ) we also have  $n_\pm = \alpha$ ; and for  $\alpha = 3$ ,  $\Gamma_3^\pm = \emptyset$  and  $\mathcal{C}_3^\pm$  gives  $n_\pm = 3$ . The sets  $\mathcal{R}_\alpha^\pm$  are disjoint for different  $\alpha$  and cover  $\mathbb{R}^3$ .  $\square$

The intersection regions  $\mathcal{G}_{\alpha\beta}$ , representing the sets of parameters where the spectral indices  $\alpha$  and  $\beta$  are simultaneously realised, are defined by

$$\mathcal{G}_{\alpha\beta} := \mathcal{R}_\alpha^- \cap \mathcal{R}_\beta^+, \quad \alpha, \beta \in \{0, 1, 2, 3\}.$$

The collection of these intersections forms a partition of the parameter space:

$$\mathbb{R}^3 = \bigcup_{\alpha, \beta=0}^3 \mathcal{G}_{\alpha\beta}, \quad \mathcal{G}_{\alpha\beta} \cap \mathcal{G}_{\alpha'\beta'} = \emptyset \text{ for } (\alpha, \beta) \neq (\alpha', \beta'). \quad (14)$$

**Theorem 2.** *The operator  $H_\mu(0)$  has exactly  $\alpha$  discrete eigenvalues below the essential spectrum and  $\beta$  discrete eigenvalues above it if and only if  $\mu \in \mathcal{G}_{\alpha\beta}$ . Moreover,  $\mathcal{G}_{\alpha\beta}$  is non-empty precisely when  $\alpha + \beta \leq 3$ .*



*Proof.* The first statement follows from Corollary 1 and the definition of  $\mathcal{G}_{\alpha\beta}$ . The partition property (14) ensures that each  $\mu$  gives a unique pair  $(\alpha, \beta)$ . The condition  $\alpha + \beta \leq 3$  is a consequence of the rank-three nature of the perturbation (see (2)), which limits the total number of discrete eigenvalues. Conversely, for any pair  $(\alpha, \beta)$  with  $\alpha + \beta \leq 3$ , one can construct parameters achieving this configuration (e.g., by choosing  $\mu_1$  appropriately in the corresponding region), so the intersection is non-empty.  $\square$

**Remark 7.** The geometric classification provided in this section is exhaustive. The sets  $\mathcal{G}_{\alpha\beta}$  are either open (when both  $\alpha$  and  $\beta$  come from open regions) or include boundary parts (when one or both indices correspond to critical surfaces). Their explicit description can be obtained by intersecting the corresponding  $\mathcal{R}_{\alpha}^{\pm}$  and  $\mathcal{R}_{\beta}^{\pm}$ ; the resulting regions are semi-algebraic sets.

## 5. Spectral configurations in the $(\mu_2, \mu_3)$ plane and their classification

In this section, we provide a geometric classification of the spectral regimes for the operator  $H_{\mu}(0)$ . The partition of the  $(\mu_2, \mu_3)$ -plane into the domains  $D_k^{\pm}$ ,  $k = 0, 1, 2$  (see (10)) plays a crucial role in determining the range of the spectral configuration mapping. Before establishing the main spectral counts, we characterize the fundamental geometric properties and symmetries of these regions in the following lemma.

**Lemma 8** (Geometric structure of  $D_k^{\pm}$ ). *The domains  $D_k^{\pm}$ ,  $k = 0, 1, 2$ , satisfy the following properties:*

- (i) *Origin symmetry:*  $D_k^{\pm} = \{(\mu_2, \mu_3) \in \mathbb{R}^2 : (-\mu_2, -\mu_3) \in D_k^{\mp}\}$ ;
- (ii) *Sub-domain inclusion:*  $D_2^{+} \subset D_0^{-}$  and  $D_2^{-} \subset D_0^{+}$ ;
- (iii) *Maximal index disjointness:*  $D_2^{-} \cap D_2^{+} = \emptyset$ .

Figure 2 illustrates the intersections and relative positions of these domains.

*Sketch of Proof.* The symmetry (i) follows directly from the parity of the threshold polynomials and the definitions of  $\mu_2^{\pm}(\mu_3)$ . The inclusion (ii) and disjointness (iii) are established by analyzing the boundaries  $\mu_2^{\pm}(\mu_3)$  and the intervals  $I_k^{\pm}$ , which ensure that the growth conditions for  $D_2^{\pm}$  do not overlap and are strictly bounded by the conditions defining  $D_0^{\mp}$ .  $\square$

Following the geometric characterization of the domains  $D_k^{\pm}$ , we now determine the admissible spectral configurations  $(n_-, n_+)$  within their various intersections. While the parameter  $\mu_1$  shifts the eigenvalues within the gaps, the set of all possible values for the pair  $(n_-, n_+)$  is strictly governed by the location of  $(\mu_2, \mu_3)$  in the parameter plane.

For any fixed  $j, k \in \{0, 1, 2\}$ , let us consider a fixed pair of interaction parameters  $(\mu_2, \mu_3) \in D_j^{-} \cap D_k^{+}$ . For a given  $\mu_1 \in \mathbb{R}$ , we denote by  $n_-(\mu_1)$  and  $n_+(\mu_1)$  the number of discrete eigenvalues of the operator  $H_{\mu}(0)$  lying below and above the essential spectrum, respectively:

$$n_-(\mu_1) := n_-(H_{\mu}(0)), \quad n_+(\mu_1) := n_+(H_{\mu}(0)).$$

The pair  $(n_-(\mu_1), n_+(\mu_1))$  characterizes the spectral configuration of the operator for a specific intensity  $\mu_1$ . To analyze the evolution of the spectrum, we define the spectral configuration mapping  $n : \mathbb{R} \rightarrow \mathbb{Z}_{\geq 0}^2$  as follows:

$$n(\mu_1) = (n_-(\mu_1), n_+(\mu_1)), \quad \mu_1 \in \mathbb{R}.$$

The central object of our analysis is the range of this mapping, which represents the set of all spectral configurations attainable for the given geometry  $(\mu_2, \mu_3)$ . We denote this set by  $\mathcal{S}_{jk}$  and define it as the image of the function  $n$  over the entire real line:

$$\mathcal{S}_{jk} := \text{Im}(n) = \{n(\mu_1) : \mu_1 \in \mathbb{R}\}. \quad (15)$$

By identifying the elements of  $\mathcal{S}_{jk}$ , we effectively determine all possible spectral phases that the operator  $H_{\mu}(0)$  can exhibit as the interaction  $\mu_1$  varies over  $\mathbb{R}$ .

The following theorem provides a complete classification of the spectral configuration sets  $\mathcal{S}_{jk}$ . This result is based on two fundamental constraints: the independent component-wise bounds established in Lemma 9 (and further refined in Remark 8), and the global rank-three condition, which limits the total number of discrete eigenvalues.

**Lemma 9** (Independent bounds). *Let  $j, k \in \{0, 1, 2\}$ . For the fixed  $(\mu_2, \mu_3) \in D_j^{-} \cap D_k^{+}$  and for every  $\mu_1 \in \mathbb{R}$ , the followings are true:*

- (i)  $n_-(\mu_1) \in \{j, j+1\}$ ;
- (ii)  $n_+(\mu_1) \in \{k, k+1\}$ ;

*Proof.* We prove the assertion for  $n_-$ ; the case for  $n_+$  follows by symmetry. Fix  $(\mu_2, \mu_3) \in D_j^{-}$ . According to the definition of the disjoint components  $\mathcal{C}_k^{-}$  in (13), the parameter vector  $\mu = (\mu_1, \mu_2, \mu_3)$  must belong to one of the following sets as  $\mu_1$  varies over  $\mathbb{R}$ :

- (1) The region where  $\mu_1 > \mu_1^{-}(\mu_2, \mu_3)$ , which corresponds to  $\mu \in \mathcal{C}_j^{-}$ ;
- (2) The threshold hypersurface  $\Gamma_j^{-} := \{\mu : \mu_1 = \mu_1^{-}(\mu_2, \mu_3)\}$ ;

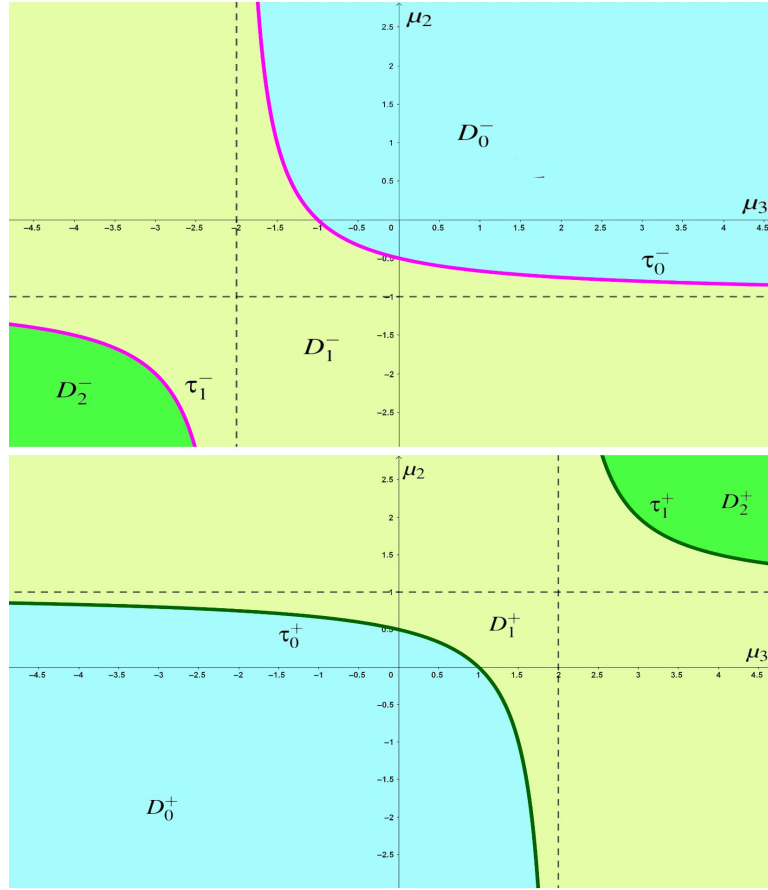


FIG. 2. Geometric structure of the intersections  $D_j^- \cap D_k^+$  in the  $(\mu_2, \mu_3)$ -plane. Each overlapping region  $D_j^- \cap D_k^+$  corresponds to a specific set of attainable spectral configurations  $\mathcal{S}_{jk}$ , as characterized in Theorem 3

(3) The region where  $\mu_1 < \mu_1^-(\mu_2, \mu_3)$ , which corresponds to  $\mu \in \mathcal{C}_{j+1}^-$ .

Thus, for any  $\mu_1 \in \mathbb{R}$ , we have the inclusion  $\mu \in \mathcal{C}_j^- \cup \Gamma_j^- \cup \mathcal{C}_{j+1}^-$ . By Theorem 1, the eigenvalue count  $n_-$  is exactly  $j$  in  $\mathcal{C}_j^- \cup \Gamma_j^-$  and  $j+1$  in  $\mathcal{C}_{j+1}^-$ . This implies that  $n_-(\mu_1) \in \{j, j+1\}$ .  $\square$

**Remark 8.** For fixed  $(\mu_2, \mu_3) \in D_k^-$ , let  $\mu_1^-(\mu_2, \mu_3)$  be the threshold function defined in (12). By Lemma 9, the count  $n_-$  depends on the position of  $\mu_1$  relative to the threshold graph  $\mu_1^-(\mu_2, \mu_3)$ :

$$n_- = \begin{cases} k, & \mu_1 \geq \mu_1^-(\mu_2, \mu_3), \\ k+1, & \mu_1 < \mu_1^-(\mu_2, \mu_3). \end{cases}$$

Similarly, for fixed  $(\mu_2, \mu_3) \in D_k^+$ , let  $\mu_1^+(\mu_2, \mu_3)$  be defined in (12). Then

$$n_+ = \begin{cases} k, & \mu_1 \leq \mu_1^+(\mu_2, \mu_3), \\ k+1, & \mu_1 > \mu_1^+(\mu_2, \mu_3). \end{cases}$$

**Theorem 3** (Classification of configurations on domain intersections). Let  $(\mu_2, \mu_3) \in D_j^- \cap D_k^+$  with  $j, k \in \{0, 1, 2\}$ , and let  $\mathcal{S}_{jk}$  be the spectral configuration set defined by (15). Then

$$\mathcal{S}_{jk} = (\{j, j+1\} \times \{k, k+1\}) \cap \{(a, b) \in \mathbb{N}_0^2 : a + b \leq 3\}. \quad (16)$$

More explicitly,

$$\begin{aligned}\mathcal{S}_{00} &= \{(0, 0), (1, 0), (0, 1), (1, 1)\}, \\ \mathcal{S}_{10} &= \{(1, 0), (2, 0), (1, 1), (2, 1)\}, \\ \mathcal{S}_{11} &= \{(1, 1), (2, 1), (1, 2)\}, \\ \mathcal{S}_{20} &= \{(2, 0), (3, 0), (2, 1)\}, \\ \mathcal{S}_{01} &= \{(0, 1), (0, 2), (1, 1), (1, 2)\}, \\ \mathcal{S}_{02} &= \{(0, 2), (0, 3), (1, 2)\}.\end{aligned}$$

*Proof.* Let  $(\mu_2, \mu_3) \in D_j^- \cap D_k^+$ . From Lemma 9, any spectral configuration  $(n_-, n_+) \in \mathcal{S}_{jk}$  must satisfy  $n_- \in \{j, j+1\}$  and  $n_+ \in \{k, k+1\}$ . Additionally, the global rank-three constraint  $n_- + n_+ \leq 3$  must hold (see (2)). This implies the inclusion:

$$\mathcal{S}_{jk} \subseteq (\{j, j+1\} \times \{k, k+1\}) \cap \{(a, b) : a + b \leq 3\}.$$

To prove that  $\mathcal{S}_{jk}$  coincides with the intersection of these two conditions, we analyze the configuration as a function of  $\mu_1$  by comparing it to the threshold values of the functions  $\mu_1^- := \mu_1^-(\mu_2, \mu_3)$  and  $\mu_1^+ := \mu_1^+(\mu_2, \mu_3)$ . According to the Remark 8, for a fixed  $(\mu_2, \mu_3) \in \mathbb{R}^2$ , the spectral counts are step functions of  $\mu_1$ :

$$n_-(\mu_1) = \begin{cases} j, & \mu_1 \geq \mu_1^- \\ j+1, & \mu_1 < \mu_1^- \end{cases} \quad \text{and} \quad n_+(\mu_1) = \begin{cases} k, & \mu_1 \leq \mu_1^+ \\ k+1, & \mu_1 > \mu_1^+ \end{cases}$$

The set of realized configurations  $\mathcal{S}_{jk}$  is thus determined by the relative order of  $\mu_1^-$  and  $\mu_1^+$ . Specifically:

- If  $\mu_1 \in [\mu_1^-, \mu_1^+]$  (assuming  $\mu_1^- \leq \mu_1^+$ ), the configuration is  $(j, k)$ .
- If  $\mu_1 > \max\{\mu_1^-, \mu_1^+\}$ , the configuration is  $(j, k+1)$ .
- If  $\mu_1 < \min\{\mu_1^-, \mu_1^+\}$ , the configuration is  $(j+1, k)$ .
- If  $\mu_1$  lies between  $\mu_1^-$  and  $\mu_1^+$  in the case where  $\mu_1^+ < \mu_1 < \mu_1^-$ , the configuration is  $(j+1, k+1)$ , provided that  $(j+1) + (k+1) \leq 3$ .

Since  $\mu_1$  can take any real value, all four combinations  $\{(j, k), (j, k+1), (j+1, k), (j+1, k+1)\}$  are attainable if and only if they satisfy the total rank constraint  $n_- + n_+ \leq 3$ . If a pair violates this constraint, the corresponding interval for  $\mu_1$  becomes empty. Therefore the inclusion above is actually an equality.

It remains to compute the finite intersection for each pair  $(j, k)$ . For example, when  $j = 1, k = 1$ :

$$\{1, 2\} \times \{1, 2\} = \{(1, 1), (1, 2), (2, 1), (2, 2)\}.$$

The condition  $a + b \leq 3$  excludes  $(2, 2)$ , giving  $\mathcal{S}_{11} = \{(1, 1), (2, 1), (1, 2)\}$ . Similarly,

$$\mathcal{S}_{20} = \{2, 3\} \times \{0, 1\} \cap \{a + b \leq 3\} = \{(2, 0), (3, 0), (2, 1)\}.$$

The other cases are computed in the same way, yielding the explicit lists stated in the theorem.  $\square$

### 5.1. An algebraic criterion for domain intersections

For the rank-three case the intersections  $D_j^- \cap D_k^+$ ,  $j, k \in \{0, 1, 2\}$  can be visualized directly (see Figure 2), but such a geometric approach becomes impractical as the rank of the perturbation increases. To provide a robust analytical framework that transcends low-dimensional geometry, we establish an algebraic criterion for the non-emptiness of domain intersections. This criterion is a first step toward extending the analysis to higher-rank perturbations (rank- $N$ ), where spectral regimes must be identified through the consistency of reachable state sets rather than graphical overlaps.

**Theorem 4.** Let  $j, k \in \{0, 1, 2\}$  be arbitrary integers, and let  $D_j^-$  and  $D_k^+$  be the domains in the  $(\mu_2, \mu_3)$  plane defined in (10). The intersection  $D_j^- \cap D_k^+$  is non-empty if and only if the set of reachable spectral configurations  $\mathcal{S}_{jk}$ , defined in (16), is non-empty:

$$D_j^- \cap D_k^+ \neq \emptyset \iff \mathcal{S}_{jk} \neq \emptyset.$$

*Proof.* ( $\Rightarrow$ ) Suppose that  $D_j^- \cap D_k^+ \neq \emptyset$  and fix a point  $(\mu_2, \mu_3) \in D_j^- \cap D_k^+$ . Then, for any  $\mu_1 \in \mathbb{R}$ , the parameter vector  $\boldsymbol{\mu} = (\mu_1, \mu_2, \mu_3)$  corresponds to a spectral configuration  $(n_-(\mu_1), n_+(\mu_1))$  which, by definition, belongs to  $\mathcal{S}_{jk}$ . Thus,  $\mathcal{S}_{jk} \neq \emptyset$ .

( $\Leftarrow$ ) Conversely, suppose that  $\mathcal{S}_{jk} \neq \emptyset$ . This implies there exists at least one configuration  $(n_-, n_+) \in \mathcal{S}_{jk}$  that is reachable for some parameter vector  $\boldsymbol{\mu} = (\mu_1, \mu_2, \mu_3)$ . According to the definition of  $\mathcal{S}_{jk}$  in (16), the existence of such a configuration requires  $(\mu_2, \mu_3) \in D_j^- \cap D_k^+$ . Consequently,

$$D_j^- \cap D_k^+ \neq \emptyset.$$

$\square$

**Example 1** (Non-existence of specific regimes). *The power of the algebraic criterion is best illustrated by considering the case  $j = 2$  and  $k = 2$ . Geometrically, it is established in Lemma 1 that  $D_2^- \cap D_2^+ = \emptyset$ , meaning there is no point in the parameter plane that simultaneously supports the indices  $j = 2$  and  $k = 2$ .*

*Algebraically, this is reflected in the emptiness of the set  $\mathcal{S}_{22}$ . Indeed, according to (16):*

$$\mathcal{S}_{22} = (\{2, 3\} \times \{2, 3\}) \cap \{(a, b) \in \mathbb{N}_0^2 : a + b \leq 3\}.$$

*The Cartesian product  $\{2, 3\} \times \{2, 3\}$  contains the configurations*

$$\{(2, 2), (2, 3), (3, 2), (3, 3)\}.$$

*For all these pairs, the sum  $a + b \geq 4$ , which violates the rank-three constraint  $a + b \leq 3$ . Consequently,  $\mathcal{S}_{22} = \emptyset$ , which is in perfect agreement with the geometric fact that  $D_2^- \cap D_2^+ = \emptyset$ .*

**Remark 9.** *The algebraic criterion is particularly useful when the domains  $D_j^\pm, j = 0, 1, 2$  are defined by polynomial inequalities; one can then check feasibility of the combined system without explicit geometric construction. This idea generalises naturally to higher-rank perturbations.*

## 5.2. Global spectral classifications

After characterizing the local configurations in the  $(\mu_2, \mu_3)$ -plane, we now establish a global classification of the discrete spectrum. In this context, we treat  $\mu_3$  as a fixed structural parameter and analyze the attainable spectral states as the remaining coupling intensities  $(\mu_1, \mu_2)$  vary over the entire real plane.

To formalize this, for a fixed  $\mu_3 \in \mathbb{R}$ , we define the global spectral configuration mapping  $N_{\mu_3} : \mathbb{R}^2 \rightarrow \mathbb{Z}_{\geq 0}^2$  as follows:

$$N_{\mu_3} : (\mu_1, \mu_2) \rightarrow (n_-(H_{\mu}(0)), n_+(H_{\mu}(0))), \mu = (\mu_1, \mu_2, \mu_3), (\mu_1, \mu_2) \in \mathbb{R}^2.$$

The main object of interest is the set of all reachable configurations for a given  $\mu_3$ , which corresponds to the image (range) of this mapping:

$$\mathcal{S}_{\mu_3} := \text{Im}(N_{\mu_3}) = \{N_{\mu_3}(\mu_1, \mu_2) : (\mu_1, \mu_2) \in \mathbb{R}^2\}.$$

The following theorem demonstrates that the topology of the parameter space and the resulting range  $\mathcal{S}_{\mu_3}$  undergo qualitative shifts at the critical thresholds  $\mu_3 = \pm 2$ .

**Theorem 5** (Global Classification of Spectral Configurations). *The set of reachable spectral configurations  $\mathcal{S}_{\mu_3}$  is uniquely determined by the value of  $\mu_3$  as follows:*

- (i) *If  $\mu_3 < -2$ , then  $\mathcal{S}_{\mu_3} = \{(1, 0), (1, 1), (1, 2), (2, 0), (2, 1), (3, 0)\}$ ;*
- (ii) *If  $|\mu_3| \leq 2$ , then  $\mathcal{S}_{\mu_3} = \{(0, 0), (0, 1), (0, 2), (1, 0), (1, 1), (1, 2), (2, 0), (2, 1)\}$ ;*
- (iii) *If  $\mu_3 > 2$ , then  $\mathcal{S}_{\mu_3} = \{(0, 1), (0, 2), (0, 3), (1, 1), (1, 2), (2, 1)\}$ .*

*Proof.* By construction, the global set  $\mathcal{S}_{\mu_3}$  can be expressed as the union of the local configuration sets  $\mathcal{S}_{jk}$  over all indices  $j, k$  for which the parameter pair  $(\mu_2, \mu_3)$  can actually reside in the intersection  $D_j^- \cap D_k^+$ . Thus, for a fixed  $\mu_3$ , we have:

$$\mathcal{S}_{\mu_3} = \bigcup \{ \mathcal{S}_{jk} : \exists \mu_2 \in \mathbb{R} \text{ such that } (\mu_2, \mu_3) \in D_j^- \cap D_k^+ \}.$$

The proof then proceeds by analyzing the non-emptiness of the domains  $D_j^\pm$  relative to the value of  $\mu_3$ :

*Case (i):  $\mu_3 < -2$ .* In this regime, the domain  $D_0^-$  is empty for all  $\mu_2 \in \mathbb{R}$ . This implies that  $j \geq 1$  must hold, ensuring at least one eigenvalue exists below the spectrum ( $n_- \geq 1$ ). Combining the local sets  $\mathcal{S}_{jk}$  for  $j \in \{1, 2\}$  and  $k \in \{0, 1\}$  from Theorem 3, and filtering by the global rank-three condition  $n_- + n_+ \leq 3$ , we obtain the set specified in (i).

*Case (ii):  $|\mu_3| \leq 2$ .* In this central strip, the intersection  $D_0^- \cap D_0^+$  is non-empty, which allows for the vacuum configuration  $(0, 0)$ . All local sets  $\mathcal{S}_{jk}$  contribute to the union, and the exhaustive search over  $j, k \in \{0, 1, 2\}$  under the constraint  $a + b \leq 3$  yields the collection in (ii).

*Case (iii):  $\mu_3 > 2$ .* Due to the origin symmetry established in Lemma 1, the domain  $D_0^+$  is empty in this region. This forces  $n_+ \geq 1$  for any choice of  $(\mu_1, \mu_2)$ . The union of  $\mathcal{S}_{jk}$  for  $k \in \{1, 2\}$  and  $j \in \{0, 1\}$  leads directly to the set listed in (iii).  $\square$

**Remark 10.** *The critical values  $\mu_3 = \pm 2$  act as bifurcation points for the spectral template. At  $\mu_3 = -2$ , the domain  $D_0^-$  collapses, leading to a "spectral jump" where the zero-eigenvalue state  $(0, n_+)$  is no longer attainable. A symmetric transition occurs at  $\mu_3 = 2$  for the upper eigenvalues.*

### 5.3. Comparison with nonzero quasimomentum

**Theorem 6.** For any  $\mu \in \mathbb{R}^3$  and  $K \in \mathbb{T} \setminus \{0\}$ ,

$$n_{\pm}(H_{\mu}(K)) \geq n_{\pm}(H_{\mu}(0)).$$

Moreover, if  $H_{\mu}(0)$  possesses a threshold resonance at  $z = 0$  (resp.  $z = 8$ ), then for any  $K \neq 0$ ,

$$n_{-}(H_{\mu}(K)) > n_{-}(H_{\mu}(0)) \quad (\text{resp. } n_{+}(H_{\mu}(K)) > n_{+}(H_{\mu}(0))).$$

*Sketch of proof.* The proof of Theorem 6 is established by analyzing the displacement of the essential spectrum and the monotonicity of the discrete eigenvalues with respect to the total momentum  $K$ . The core argument relies on the comparison of the Lippman-Schwinger operators associated with  $H_{\mu}(K)$  and  $H_{\mu}(0)$ . Specifically, the inequality follows from the fact that the minimum of the two-particle energy band is attained at  $K = 0$ . A detailed rigorous derivation is provided in [27, Theorem 3.1].  $\square$

**Corollary 2.** If  $\mu \in \mathcal{G}_{\alpha\beta}$  for  $\alpha, \beta \in \{0, 1, 2\}$ , then the following lower bounds hold:

$$n_{-}(H_{\mu}(K)) \geq \alpha \quad \text{and} \quad n_{+}(H_{\mu}(K)) \geq \beta$$

for all  $K \in \mathbb{T}$ . Moreover, if  $\alpha + \beta = 3$ , then these inequalities become equalities for all  $K \in \mathbb{T}$ .

*Proof.* The result follows directly from Theorem 6 and Theorem 2.  $\square$

A key observation from the above classification is the persistence of the discrete spectrum in the extreme regimes. Specifically, for any quasi-momentum  $K$ , the existence of at least one eigenvalue is guaranteed when  $|\mu_3|$  is sufficiently large. This is summarized in the following corollary.

**Corollary 3.** For any  $K \in \mathbb{T}$ , the following lower bounds on the number of eigenvalues hold:

- If  $\mu_3 < -2$ , then  $n_{-}(H_{\mu}(K)) \geq 1$ .
- If  $\mu_3 > 2$ , then  $n_{+}(H_{\mu}(K)) \geq 1$ .

In these regimes, the discrete spectrum is non-empty for all values of the total momentum  $K$ .

*Proof.* The proof follows directly from the global classification established in Theorem 5 and the monotonicity properties with respect to the total momentum  $K$  provided in Theorem 6.  $\square$

## 6. Conclusion

In this study we have provided a complete global classification of the discrete spectrum configurations  $(n_{-}, n_{+})$  for the fiber Hamiltonian  $H_{\mu}(0)$  with a symmetric rank-three potential. By exploiting the affine dependence of the Fredholm determinant on  $\mu_1$ , we have systematically mapped the transitions between different spectral phases.

The main conclusions are as follows:

- **Necessary and sufficient conditions:** We have established a partition of  $\mathbb{R}^3$  into disjoint sets  $\mathcal{G}_{\alpha\beta}$  ( $\alpha, \beta = 0, 1, 2, 3, \alpha + \beta \leq 3$ ) that provide necessary and sufficient conditions for the realisation of any spectral state  $(\alpha, \beta)$ . These conditions are consistent with the rank-three nature of the perturbation, which imposes the fundamental bound  $n_{-} + n_{+} \leq 3$ .
- **Spectral phase determination:** The  $(\mu_2, \mu_3)$  plane is divided into domains  $D_j^{\pm}$  ( $j = 0, 1, 2$ ) that act as “spectral templates”. For any  $\mu_1$ , the possible numbers of eigenvalues  $n_{\pm}$  are restricted to a specific set determined solely by the  $(\mu_2, \mu_3)$  region. Thus the interaction range (governed by  $\mu_2, \mu_3$ ) defines the potential’s capacity to support bound states, while the central intensity  $\mu_1$  acts as a secondary trigger for eigenvalue emergence within those bounds.
- **Global role of  $\mu_3$ :** The parameter  $\mu_3$  controls the global topological structure of the spectrum. Transitions at the critical values  $\mu_3 = \pm 2$  fundamentally alter the admissible configurations, e.g., forcing at least one eigenvalue below the lower threshold when  $\mu_3 < -2$  or above the upper threshold when  $\mu_3 > 2$ .

These findings offer a robust framework for predicting the multiplicity and configuration of the discrete spectrum in lattice systems with multi-site interactions. The methods developed here can be extended to analyse spectral properties in higher dimensions or in systems with more complex interaction geometries.

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## On eigenvalues of the discrete Schrödinger operator on a ladder of a $d$ -dimensional square lattice

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**ABSTRACT** We consider a discrete Schrödinger operator  $H$  on a ladder of  $d$ -dimensional square lattices with a self-adjoint matrix-valued potential whose entries are the scalars  $\lambda$  and  $\mu$ . We investigate conditions for the existence of eigenvalues and describe their exact locations in terms of the parameters  $\lambda$  and  $\mu$  for the cases  $d = 1$  and  $d = 2$ .

**KEYWORDS** discrete Schrödinger operator; eigenvalue; discrete spectrum.

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### 1. Introduction

In paper [1], the authors studied finite graphene nanostructures—graphene nanoflakes and graphene quantum dots—from a quantum-mechanical perspective. They showed that when graphene is reduced to nanoscale dimensions, its electronic properties differ significantly from those of bulk graphene because of finite-size effects, quantum confinement, edge geometry (zigzag versus armchair), and the shape of the nanostructure. This observation is directly relevant to discrete Schrödinger models, since finite lattice Hamiltonians naturally reproduce the size-dependent discrete energy levels arising in such nanosystems. Paper [2] focuses on recent experimental progress in graphene quantum dots. It emphasizes that graphene quantum dots are model nanosystems for studying quantum confinement of Dirac fermions, quasi-bound states, Berry phase effects, edge-induced confinement, and single-electron phenomena. Moreover, this work shows that graphene quantum dots are experimentally realizable nanosystems whose energy levels and localization properties can be naturally described by discrete lattice Hamiltonians.

The existence conditions for eigenvalues of the discrete Schrödinger operator with a  $\delta$  potential were studied in [3]. The same operator was considered in [4], where the authors investigated the behavior of the spectral edges (embedded eigenvalues and resonances) at the two ends of the continuous spectrum, in particular it is shown that an embedded eigenvalue does appear for  $d \geq 5$  but does not for  $1 \leq d \leq 4$ . An exact expression for the number of discrete eigenvalues of discrete Laplacian with finitely supported potential is described in [7]. K. Ando et al. [10] described the spectral properties of the Schrödinger operators with compactly supported potentials on square, triangular, hexagonal, Kagome, diamond, subdivision lattices. The inverse scattering for discrete Schrödinger operators with compactly supported potentials on  $\mathbb{Z}^d$  and on the hexagonal lattice were studied in [5] and [6] only for special cases, in these papers, the discreteness of embedded eigenvalues of these operators was proved.

The absence of embedded eigenvalues for Schrödinger operators with exponentially decaying potentials was proved in [9] using the unique continuation property. Using basic tools from several complex variables and algebraic geometry, in particular Hilbert's Nullstellensatz, Isozaki and Morioka [8] established a Rellich–Vekua type theorem for Schrödinger operators on the square lattice in the case of finitely supported potentials. The Rellich–Vekua type uniqueness theorem, the unique continuation theorem, and the non-existence of eigenvalues embedded in the continuous spectrum for discrete Schrödinger operators with compactly supported potentials on periodic lattices including the square, triangular, and hexagonal lattices were studied in [10], where Kagome lattice and the subdivision of the square lattice, there are examples of Hamiltonians with compactly supported potentials having embedded eigenvalues. Paper [11] extended the results of [10] for Schrödinger operators with exponentially decreasing potentials on a class of lattices including square, triangular, hexagonal lattices and their ladders. The authors discussed the unique continuation property and provided a

counterexample for Hamiltonians on a ladder of a  $d$ -dimensional square lattice with a diagonal matrix potential whose entries are identical scalars, exhibiting an embedded eigenvalue.

Note that the Schrödinger operators with compactly supported potentials acting on the diagonal entries of ladder graphs were also studied in [10] and [12] as simple examples of a general class of perturbed periodic operators possessing embedded eigenvalues. In particular, in [10], the compactly supported potentials were taken to be  $\delta$ -potentials acting on the diagonal entries. In [12], a broad class of operators obtained by coupling  $m$  (possibly different) operators defined on identical graphs was investigated. The resulting operator decouples into  $m$  independent subsystems with different spectral bands. Consequently, a non-embedded eigenvalue of one subsystem may become an embedded eigenvalue of the full coupled system if it lies inside a spectral band of another subsystem. Ladder graphs belong exactly to this class. In particular, Example 2 of [12] considers a non-compact perturbation acting on the off-diagonal entries.

In the present paper, we investigate spectral properties of the discrete Schrödinger operator  $H$  on a ladder of  $d$ -dimensional square lattices with a self-adjoint matrix-valued potential whose entries are the scalars  $\lambda$  and  $\mu$ . The main aim of this paper is to determine conditions for the existence of eigenvalues and to describe their exact locations in terms of the parameters  $\lambda$  and  $\mu$  for the cases  $d = 1$  and  $d = 2$ . In particular, we clarify the existence of eigenvalues embedded in the essential spectrum of  $H$ . Due to the symmetry of the ladder graph, the investigated problem reduces to the study of the Schrödinger type operators  $H_1$  and  $H_2$  on the lattice  $\mathbb{Z}^d$ , with delta potentials whose coupling constants are  $\lambda \pm \mu$ . Moreover, a non-embedded eigenvalue of  $H_1$  may become an embedded eigenvalue of the operator  $H$  if it lies within a spectral band of  $H_2$ , and conversely. Remark that this reduced problem is similar to that considered in [3], where the eigenvalues of a Schrödinger operator with a delta potential depending on a coupling constant parameter were investigated. Although the Schrödinger operator with a  $\delta$ -potential has been studied previously, the reduced operators considered in the present paper depends on the parameters  $\lambda \pm \mu$ . Therefore, it is of particular interest to provide a precise description of the eigenvalues in terms of the parameters  $\lambda$  and  $\mu$ .

## 2. Basic statements and the main results

### 2.1. Ladder of $d$ -dimensional square lattice in $\mathbb{R}^{d+1}$

The ladder of  $d$ -dimensional square lattice is realized in  $\mathbb{R}^{d+1}$ . (See [10]) Let  $\mathcal{L}_0 = \{(n_1, \dots, n_d, 0) : n_j \in \mathbb{Z}\}$ . Letting  $p_1 = (0, \dots, 0, 0)$  and  $p_2 = (0, \dots, 0, 1)$ , we put

$$\mathcal{V} = \mathcal{V}_1 \cup \mathcal{V}_2,$$

where

$$\mathcal{V}_j = p_j + \mathcal{L}_0.$$

For  $v \in \mathcal{V}$ , we put

$$N_v = \{\omega \in \mathcal{V} : |\omega - v| = 1\}, \quad j = 1, 2.$$

The degree of a vertex  $v \in \mathcal{V}$  is the number of vertices adjacent to  $v$ . For all  $v \in \mathcal{V}$ ,  $\deg(v) = \#N_v = 2d + 1$ .

There exists a bijection  $\mathcal{V} \ni a \leftrightarrow (j(a), n(a)) \in \{1, 2\} \times \mathbb{Z}^d$  such that  $a = p_{j(a)} + v(n(a))$ . Then  $\ell_2(\mathcal{V})$  is isomorphic to  $\ell_2^{(2)}(\mathbb{Z}^d)$ , where  $\ell_2^{(2)}(\mathbb{Z}^d)$  is the Cartesian product Hilbert space of two copies of  $\ell_2(\mathbb{Z}^d)$ .

Any function  $\hat{f}$  on  $\mathcal{V}$  is written as  $\hat{f}(n) = (\hat{f}_1(n), \hat{f}_2(n)), n \in \mathbb{Z}^d$ , where  $\hat{f}_j(n)$  is identified with a function on  $p_j + \mathcal{L}_0$ . Hence  $\ell_2(\mathcal{V})$  is the Hilbert space equipped with the inner product

$$(\hat{f}, \hat{g})_{\ell_2(\mathcal{V})} = \sum_{j=1}^2 (\hat{f}_j, \hat{g}_j)_{deg},$$

where  $(f, g)_{deg}$  denotes the weighted inner product in  $\ell_2(\mathbb{Z}^d)$  defined as  $(f, g)_{deg} = \sum_{v \in \mathcal{V}} \deg(v) f(v) \overline{g(v)}$ .

Let  $L_2(\mathbb{T}^d)$  be the Hilbert space of square-integrable functions defined on  $\mathbb{T}^d$ ,  $\mathbb{T} = (-\pi, \pi]$ , and let  $L_2^{(2)}(\mathbb{T}^d)$  denote the Cartesian product Hilbert space of two copies of  $L_2(\mathbb{T}^d)$ , where  $L_2^{(2)}(\mathbb{T}^d)$  is equipped with the inner product

$$(f, g)_{L_2^{(2)}(\mathbb{T}^d)} = \sum_{j=1}^2 \int_{\mathbb{T}^d} f_j(x) \overline{g_j(x)} dx.$$

We then define a unitary operator  $\mathcal{F} : \ell_2(\mathcal{V}) \rightarrow L_2^{(2)}(\mathbb{T}^d)$ ,

$$(\mathcal{F}\hat{f})_j = (2\pi)^{-d/2} \sqrt{2d+1} \sum_{n \in \mathbb{Z}^d} \hat{f}_j(n) e^{i(n,x)},$$

where the inverse  $\mathcal{F}^{-1} : L_2^{(2)}(\mathbb{T}^d) \rightarrow \ell_2(\mathcal{V})$  of  $\mathcal{F}$  is defined as

$$(\mathcal{F}^{-1} f_j)(n) = \frac{(2\pi)^{-d/2}}{\sqrt{2d+1}} \int_{\mathbb{T}^d} e^{-i(n,x)} f_j(x) dx.$$



Recall that the shift operator  $S_k$  acts on a sequence  $(a(n))_{n \in \mathbb{Z}^d}$  as follows:

$$(S_k(a))(n) = a(n + e_k),$$

where  $e_1 = (1, 0, \dots, 0), \dots, e_d = (0, \dots, 0, 1)$ ,  $k = \overline{1, d}$ . Then we have

$$\mathcal{F}\hat{S}_k = e^{-ix_k} \mathcal{F}.$$

The Laplacian  $\hat{\Delta}$  on the ladder  $\mathcal{V}$  is defined by the following formula

$$(\hat{\Delta}f)(n) = \frac{1}{2d+1} \begin{pmatrix} f_2(n) + \sum_{k=1}^d (f_1(n + e_k) + f_1(n - e_k)) \\ f_1(n) + \sum_{k=1}^d (f_2(n + e_k) + f_2(n - e_k)) \end{pmatrix},$$

Consider the discrete Schrödinger operator on the  $d$ -dimensional ladder  $\mathcal{V}$  defined in the form

$$\hat{H} = -\hat{\Delta} - \hat{V},$$

where  $\hat{V}$  is a potential defined on  $\ell_2^{(2)}(\mathbb{Z}^d)$  as a multiplication operator by real-valued,  $2 \times 2$  matrices:

$$V(n) = \begin{pmatrix} \lambda \hat{v}(n) & \mu \hat{v}(n) \\ \mu \hat{v}(n) & \lambda \hat{v}(n) \end{pmatrix}, \quad \hat{v}(n) = \begin{cases} (2\pi)^d, & \text{for } n = \theta, \\ 0, & \text{for } n \neq \theta, \end{cases}$$

where  $\lambda$  and  $\mu$  are real numbers with  $(\lambda, \mu) \neq (0, 0)$ ,  $\theta$  is zero element in  $\mathbb{Z}^d$ .

To study spectral properties of  $\hat{H}$ , we consider  $H = \mathcal{F}\hat{H}\mathcal{F}^{-1}$ , where  $H$  acts in the Hilbert space  $L_2^{(2)}(\mathbb{T}^d)$  as

$$H = H_0 - V,$$

$H_0$  is a multiplication operator by matrix

$$H_0(x) = \frac{-1}{2d+1} \begin{pmatrix} 2 \sum_{i=1}^d \cos x_i & 1 \\ 1 & 2 \sum_{i=1}^d \cos x_i \end{pmatrix}$$

and  $V$  is an operator matrix

$$V = \begin{pmatrix} \lambda \mathbf{v} & \mu \mathbf{v} \\ \mu \mathbf{v} & \lambda \mathbf{v} \end{pmatrix}$$

with the integral operator  $\mathbf{v}f = \int_{\mathbb{T}^d} f(s)ds$ . Under these consideration,  $H$  is a self-adjoint operator.

We denote by  $\sigma(A)$ ,  $\sigma_p(A)$  and  $\sigma_{ess}(A)$ , respectively, the spectrum, the point spectrum and the essential spectrum of the operator  $A$ .

The operator  $H_0$  was previously analyzed in [6], where it was shown that

$$\sigma(H_0) = [-1, 1].$$

Because  $V$  is a compact operator, Weyl's theorem for the essential spectrum [14] yields

$$\sigma_{ess}(H) = \sigma(H_0).$$

Let

$$\tilde{H} = \begin{pmatrix} H_1 & 0 \\ 0 & H_2 \end{pmatrix},$$

where

$$H_1 = H_{10} - (\lambda + \mu)\mathbf{v}, \quad H_2 = H_{20} - (\lambda - \mu)\mathbf{v},$$

$H_{10}$  and  $H_{20}$  are multiplication operators on  $L_2(\mathbb{T}^d)$  by functions

$$E_{10}(x) = -\frac{2}{2d+1} \sum_{i=1}^d \cos x_i - \frac{1}{2d+1} \quad \text{and} \quad E_{20}(x) = -\frac{2}{2d+1} \sum_{i=1}^d \cos x_i + \frac{1}{2d+1},$$

respectively.

**Lemma 1.** *The operator  $\tilde{H}$  is unitarily equivalent to the operator  $H$ .*

Since the operators  $H$  and  $\tilde{H}$  are unitarily equivalent, they have the same spectrum:

$$\sigma_p(H) = \sigma_p(\tilde{H}), \quad \sigma_{ess}(H) = \sigma_{ess}(\tilde{H}).$$

Therefore, an investigation eigenvalue problem for  $H$  reduces to study eigenvalue problems for  $H_1$  and  $H_2$ , since

$$\sigma(H) = \sigma(H_1) \cup \sigma(H_2).$$

We note that the Weyl theorem for the essential spectrum [14] implies that the essential spectrum  $\sigma_{ess}(H_\alpha)$ ,  $\alpha = 1, 2$  of the operator  $H_\alpha$  coincides with the spectrum of the unperturbed operator  $H_{\alpha 0}$ , since  $\mathbf{v}$  is the one rank operator. In this case,  $\sigma_{ess}(H_1)$  and  $\sigma_{ess}(H_2)$  coincide with the range of the functions  $E_{10}$  and  $E_{20}$ , respectively, i.e.,

$$\sigma_{ess}(H_1) = [-1, \frac{2d-1}{2d+1}] \quad \text{and} \quad \sigma_{ess}(H_2) = [\frac{-2d+1}{2d+1}, 1].$$

In particular cases for  $d$  we have

$$\begin{aligned} \sigma_{ess}(H_1) &= [-1, \frac{1}{3}] \quad \text{and} \quad \sigma_{ess}(H_2) = [-\frac{1}{3}, 1] \quad \text{for} \quad d = 1, \\ \sigma_{ess}(H_1) &= [-1, \frac{3}{5}] \quad \text{and} \quad \sigma_{ess}(H_2) = [-\frac{3}{5}, 1] \quad \text{for} \quad d = 2. \end{aligned}$$

Let

$$\begin{aligned} \Delta_1(z) &= 1 - (\lambda + \mu) \int_{\mathbb{T}^d} \frac{dx}{E_{10}(x) - z}, \quad z \notin \sigma_{ess}(H_1), \\ \Delta_2(z) &= 1 - (\lambda - \mu) \int_{\mathbb{T}^d} \frac{dx}{E_{20}(x) - z}, \quad z \notin \sigma_{ess}(H_2). \end{aligned}$$

**Lemma 2.** *The number  $z \in \mathbb{R} \setminus \sigma_{ess}(H_\alpha)$ ,  $\alpha = 1, 2$ , is an eigenvalue of the operator  $H_\alpha$  if and only if  $\Delta_\alpha(z) = 0$ .*

## 2.2. The main results for the case $d = 1$

The following lemmas describe the location of the eigenvalue  $z_\alpha$  of the operator  $H_\alpha$  with respect to the constants  $\lambda$  and  $\mu$ .

**Lemma 3.** *For any  $\lambda + \mu \neq 0$ , the operator  $H_1$  has a unique eigenvalue  $z_1$  lying on  $\mathbb{R} \setminus [-1, \frac{1}{3}]$  and  $H_1$  has no any eigenvalue for  $\lambda = -\mu$ . More precisely,*

- (1)  $z_1 \in (-\infty, -1)$ ,  $z_1 = \frac{-1 - 2\sqrt{1 + 9\pi^2(\lambda + \mu)^2}}{3}$  for  $\lambda + \mu > 0$ ;
- (2)  $z_1 \in (\frac{1}{3}, 1)$ ,  $z_1 = \frac{-1 + 2\sqrt{1 + 9\pi^2(\lambda + \mu)^2}}{3}$  for  $-\frac{1}{\sqrt{3}\pi} < \lambda + \mu < 0$ . Moreover, in this case  $z_1$  lies in the essential spectrum  $\sigma_{ess}(H_2)$ ;
- (3)  $z_1 = 1$  for  $\lambda + \mu = -\frac{1}{\sqrt{3}\pi}$ , i.e.  $z_1 = 1$  is the threshold of  $\sigma_{ess}(H_2)$ ;
- (4)  $z_1 \in (1, \infty)$ ,  $z_1 = \frac{-1 + 2\sqrt{1 + 9\pi^2(\lambda + \mu)^2}}{3}$  for  $\lambda + \mu < -\frac{1}{\sqrt{3}\pi}$ .

**Lemma 4.** *For any  $\lambda - \mu \neq 0$ , the operator  $H_2$  has a unique eigenvalue  $z_2$  lying on  $\mathbb{R} \setminus [-\frac{1}{3}, 1]$  and  $H_2$  has no any eigenvalue for  $\lambda = \mu$ . More precisely,*

- (1)  $z_2 \in (1, \infty)$ ,  $z_2 = \frac{1 + 2\sqrt{1 + 9\pi^2(\lambda - \mu)^2}}{3}$  for  $\lambda - \mu < 0$ ;
- (2)  $z_2 \in (-1, -\frac{1}{3})$ ,  $z_2 = \frac{1 - 2\sqrt{1 + 9\pi^2(\lambda - \mu)^2}}{3}$  for  $0 < \lambda - \mu < \frac{1}{\sqrt{3}\pi}$ . Moreover, in this case,  $z_2$  lies in the essential spectrum  $\sigma_{ess}(H_1)$ ;
- (3)  $z_2 = -1$  for  $\lambda - \mu = \frac{1}{\sqrt{3}\pi}$ , i.e.  $z_2 = -1$  is the threshold of  $\sigma_{ess}(H_1)$ ;
- (4)  $z_2 \in (-\infty, -1)$ ,  $z_2 = \frac{1 - 2\sqrt{1 + 9\pi^2(\lambda - \mu)^2}}{3}$  for  $\lambda - \mu > \frac{1}{\sqrt{3}\pi}$ .

We introduce the following sets:

$$l_1 = \{(\lambda, \mu) : \lambda + \mu = 0\}, \quad l_2 = \{(\lambda, \mu) : \lambda - \mu = 0\},$$

$$D_1 = \{(\lambda, \mu) : -\frac{1}{\sqrt{3}\pi} \leq \lambda + \mu < 0\}, \quad D_2 = \{(\lambda, \mu) : 0 < \lambda - \mu \leq \frac{1}{\sqrt{3}\pi}\}.$$

Combining Lemma 3 and Lemma 4, we immediately obtain the following theorem.

TABLE 1. Locations of the eigenvalues of the operator  $H$  for all  $(\lambda, \mu) \in \mathbb{R}$ 

| $\lambda - \mu$                   | $\lambda + \mu$                           |                                           |                                                            |                                                |                                            |
|-----------------------------------|-------------------------------------------|-------------------------------------------|------------------------------------------------------------|------------------------------------------------|--------------------------------------------|
|                                   | $(-\infty, -\frac{1}{\sqrt{3\pi}})$       | $(-\frac{1}{\sqrt{3\pi}})$                | $(-\frac{1}{\sqrt{3\pi}}, 0)$                              | 0                                              | $(0, \infty)$                              |
| $(-\infty, 0)$                    | $z_1 > 1$<br>$z_2 > 1$                    | $z_1 = 1$<br>$z_2 > 1$                    | $z_1 \in (\frac{1}{3}, 1)$<br>$z_2 > 1$                    | $\nexists z_1$<br>$z_2 > 1$                    | $z_1 < -1$<br>$z_2 > 1$                    |
| 0                                 | $z_1 > 1$ ,<br>$\nexists z_2$             | $z_1 = 1$ ,<br>$\nexists z_2$             | $z_1 \in (\frac{1}{3}, 1)$ ,<br>$\nexists z_2$             | —                                              | $z_1 < -1$<br>$\nexists z_2$               |
| $(0, \frac{1}{\sqrt{3\pi}})$      | $z_1 > 1$<br>$z_2 \in (-1, -\frac{1}{3})$ | $z_1 = 1$<br>$z_2 \in (-1, -\frac{1}{3})$ | $z_1 \in (\frac{1}{3}, 1)$<br>$z_2 \in (-1, -\frac{1}{3})$ | $\nexists z_1$<br>$z_2 \in (-1, -\frac{1}{3})$ | $z_1 < -1$<br>$z_2 \in (-1, -\frac{1}{3})$ |
| $\frac{1}{\sqrt{3\pi}}$           | $z_1 > 1$<br>$z_2 = -1$                   | $z_1 = 1$<br>$z_2 = -1$                   | $z \in (\frac{1}{3}, 1)$<br>$z_2 = -1$                     | $\nexists z_1$<br>$z_2 = -1$                   | $z_1 < -1$<br>$z_2 = -1$                   |
| $(\frac{1}{\sqrt{3\pi}}, \infty)$ | $z_1 > 1$<br>$z_2 < -1$                   | $z_1 = 1$<br>$z_2 < -1$                   | $z_1 \in (\frac{1}{3}, 1)$ ,<br>$z_2 = -1$                 | $\nexists z_1$<br>$z_2 < -1$                   | $z_1 < -1$<br>$z_2 < -1$                   |

**Theorem 2.1.** (1) For  $(\lambda, \mu) \in \mathbb{R}^2 \setminus (l_1 \cup l_2)$  the operator  $H$  has two eigenvalues  $z_1$  and  $z_2$ . Moreover, if  $(\lambda, \mu) \in D_1 \cap D_2$ , then  $z_1, z_2 \in \sigma_{ess}(H)$  and if  $(\lambda, \mu) \in D_\alpha \setminus (D_1 \cap D_2)$ , then  $z_\alpha \in \sigma_{ess}(H)$ ,  $\alpha = 1, 2$ ;

(2) For  $(\lambda, \mu) \in (l_1 \cup l_2) \setminus (0, 0)$  the operator  $H$  has a unique eigenvalue. Moreover, if  $(\lambda, \mu) \in D_1 \cap l_2$  then  $z_1 \in \sigma_{ess}(H)$  and if  $(\lambda, \mu) \in D_2 \cap l_1$  then  $z_2 \in \sigma_{ess}(H)$ .

Table 1 presents the precise locations of the eigenvalues of the operator  $H$  for all  $(\lambda, \mu) \in \mathbb{R}$ , where in some cases the eigenvalues lie in  $\sigma_{ess}(H)$ .

### 2.3. The main results for the case $d = 2$

The following lemmas describe the location of the eigenvalue  $z_\alpha$  of  $H_\alpha$  with respect to constants  $\lambda$  and  $\mu$ .

Let  $K(\cdot)$  be the first-kind Elliptic function then  $K(\frac{2}{3}) \approx 1, 8096675$ .

**Lemma 5.** For any  $\lambda + \mu \neq 0$ , the operator  $H_1$  has a unique eigenvalue  $z_1$  lying on  $\mathbb{R} \setminus [-1, \frac{3}{5}]$  and  $H_1$  has no any eigenvalue for  $\lambda = -\mu$ . More precisely,

- (1)  $z_1 \in (-\infty, -1)$  for  $\lambda + \mu > 0$ ;
- (2)  $z_1 \in (\frac{3}{5}, 1)$  for  $-\frac{3}{20\pi K(\frac{2}{3})} < \lambda + \mu < 0$ . Moreover, in this case,  $z_1$  lies in the essential spectrum  $\sigma_{ess}(H_2)$ ;
- (3)  $z_1 = 1$  for  $\lambda + \mu = -\frac{3}{20\pi K(\frac{2}{3})}$ , i.e.  $z_1 = 1$  is the threshold of  $\sigma_{ess}(H_2)$ ;
- (4)  $z_1 \in (1, \infty)$  for  $\lambda + \mu < -\frac{3}{20\pi K(\frac{2}{3})}$ .

**Lemma 6.** For any  $\lambda - \mu \neq 0$ , the operator  $H_2$  has a unique eigenvalue  $z_2$  lying on  $\mathbb{R} \setminus [-\frac{3}{5}, 1]$  and  $H_2$  has no any eigenvalue for  $\lambda = \mu$ . More precisely,

- (1)  $z_2 \in (1, \infty)$  for  $\lambda - \mu < 0$ ;
- (2)  $z_2 \in (-1, -\frac{3}{5})$  for  $0 < \lambda - \mu < \frac{3}{20\pi K(\frac{2}{3})}$ . Moreover, in this case  $z_2$  lies in the essential spectrum  $\sigma_{ess}(H_1)$ ;
- (3)  $z_2 = -1$  for  $\lambda - \mu = \frac{3}{20\pi K(\frac{2}{3})}$ , i.e.  $z_2 = -1$  is the threshold of  $\sigma_{ess}(H_1)$ ;
- (4)  $z_2 \in (-\infty, -1)$  for  $\lambda - \mu > \frac{3}{20\pi K(\frac{2}{3})}$ .

To describe locations of eigenvalues of the operator  $H$ , we introduce the following sets:

$$l_1 = \{(\lambda, \mu) : \lambda + \mu = 0\} \quad \text{and} \quad l_2 = \{(\lambda, \mu) : \lambda - \mu = 0\},$$

$$D_1 = \{(\lambda, \mu) : -\frac{3}{20\pi K(\frac{2}{3})} \leq \lambda + \mu < 0\} \quad \text{and} \quad D_2 = \{(\lambda, \mu) : 0 < \lambda - \mu \leq \frac{3}{20\pi K(\frac{2}{3})}\}.$$

The following Theorem 2.2 is established by combining the results obtained in Lemma 5 and Lemma 6.

**Theorem 2.2.** (1) For  $(\lambda, \mu) \in \mathbb{R}^2 \setminus (l_1 \cup l_2)$  the operator  $H$  has two eigenvalues. Moreover, if  $(\lambda, \mu) \in D_1 \cap D_2$  then  $z_1, z_2 \in \sigma_{ess}(H)$  and if  $(\lambda, \mu) \in D_\alpha \setminus (D_1 \cap D_2)$  then  $z_\alpha \in \sigma_{ess}(H)$ ,  $\alpha = 1, 2$ ;

(2) For  $(\lambda, \mu) \in (l_1 \cup l_2) \setminus (0, 0)$ , the operator  $H$  has exactly one eigenvalue. Moreover, if  $(\lambda, \mu) \in D_1 \cap l_2$  then  $z_1 \in \sigma_{ess}(H)$  and if  $(\lambda, \mu) \in D_2 \cap l_1$  then  $z_2 \in \sigma_{ess}(H)$ .

### 3. Proof of the main theorems and lemmas

*Proof of the Lemma 1.* Consider a unitary operator  $U$  acting in  $L_2^{(2)}(\mathbb{T}^d)$  as

$$U = \frac{1}{\sqrt{2}} \begin{pmatrix} I & I \\ I & -I \end{pmatrix},$$

where  $I$  is a unit operator on  $L_2(\mathbb{T}^d)$ . Then, we verify the following equality

$$HU^* = (H_0 - V)U^* = \frac{1}{\sqrt{2}} \begin{pmatrix} H_{10} - \lambda \mathbf{v} - \mu \mathbf{v} & H_{20} - \lambda \mathbf{v} + \mu \mathbf{v} \\ H_{10} - \lambda \mathbf{v} - \mu \mathbf{v} & -H_{20} + \lambda \mathbf{v} - \mu \mathbf{v} \end{pmatrix}.$$

Therefore,

$$UHU^* = \begin{pmatrix} H_1 & 0 \\ 0 & H_2 \end{pmatrix} = \tilde{H}.$$

□

*Proof of Lemma 2. Necessity.* Let a number  $z$  be an eigenvalue of the operator  $H_1$  corresponding to the eigenfunction  $\varphi \in L_2(\mathbb{T}^d)$ , i.e

$$H_1 \varphi = z \varphi, \quad \varphi \neq 0.$$

Then

$$(H_{10} - zI)\varphi = (\lambda + \mu)V\varphi$$

or

$$\varphi(x) = (\lambda + \mu) \frac{C_\varphi}{E_{10}(x) - z}, \quad (1)$$

since  $E_{10}(x) \neq z$  for  $z \in \mathbb{R} \setminus \sigma_{ess}(H_1)$ , where

$$C_\varphi = \int_{\mathbb{T}^d} \varphi(x) dx. \quad (2)$$

Substituting (1) to (2), we obtain

$$C_\varphi \Delta_1(z) = 0, \quad \Delta_1(z) = 1 - (\lambda + \mu) \int_{\mathbb{T}^d} \frac{dx}{E_{10}(x) - z}.$$

Since  $\varphi \neq 0$ , so  $C_\varphi \neq 0$ . Hence  $\Delta_1(z) = 0$ .

**Sufficiency.** Let  $\Delta_1(z) = 0$  for  $z \in \mathbb{R} \setminus \sigma_{ess}(H_1)$ . Then, the function  $\varphi(x) = \frac{\lambda + \mu}{E_{10}(x) - z}$  belongs to  $L_2(\mathbb{T}^d)$  and satisfies the equation  $H_1 \varphi = x \varphi$ , i.e.  $\varphi$  is an eigenfunction of the operator  $H_1$  corresponding to the eigenvalue  $z$ .

The theorem for the case  $\alpha = 2$  can be proved similarly. □

*Proof of Lemma 3.* To prove lemma, according to the Lemma 2, we investigate zeros of the function

$$\Delta_1(z) = 1 - (\lambda + \mu) \int_{-\pi}^{\pi} \frac{dx}{-\frac{2}{3} \cos x - \frac{1}{3} - z}.$$

We need the classical identity

$$\int_{-\pi}^{\pi} \frac{dx}{A + B \cos x} = \frac{2\pi \operatorname{sgn}(A)}{\sqrt{A^2 - B^2}}, \quad |A| > |B| > 0. \quad (3)$$

Choosing  $A = -\frac{1}{3} - z$  and  $B = -\frac{2}{3}$  for  $z \in \mathbb{R} \setminus (-1, \frac{1}{3})$ , from (3) we have

$$\int_{-\pi}^{\pi} \frac{dx}{-\frac{2}{3} \cos x - \frac{1}{3} - z} = \frac{2\pi \operatorname{sgn}(-\frac{1}{3} - z)}{\sqrt{(-\frac{1}{3} - z)^2 - (-\frac{2}{3})^2}} = \frac{2\pi \operatorname{sgn}(-\frac{1}{3} - z)}{\sqrt{z^2 + \frac{2}{3}z - \frac{1}{3}}}.$$

Hence, the function  $\Delta_1(z)$  represents as

$$\Delta_1(z) = 1 - (\lambda + \mu) \frac{2\pi \operatorname{sgn}(-\frac{1}{3} - z)}{\sqrt{z^2 + \frac{2}{3}z - \frac{1}{3}}}. \quad (4)$$

(1) Let  $\lambda + \mu > 0$ . Then according to (4)  $\Delta_1(z) > 0$  for  $z > \frac{1}{3}$ . For  $z < -1$ , the equation  $\Delta_1(z) = 0$  is

$$\sqrt{z^2 + \frac{2}{3}z - \frac{1}{3}} = 2\pi(\lambda + \mu).$$

Squaring both sides yields

$$z^2 + \frac{2}{3}z - \frac{1}{3} = 4\pi^2(\lambda + \mu)^2.$$

The roots of this quadratic equation are

$$z_{\pm} = \frac{-1 \pm 2\sqrt{1 + 9\pi^2(\lambda + \mu)^2}}{3}.$$

Due to  $z_+ > -1$ , we identify that  $z_- = \frac{-1 - 2\sqrt{1 + 9\pi^2((\lambda + \mu)^2)}}{3}$  as a unique root of  $\Delta_1(z) = 0$ . Hence by the Lemma 2, the number  $z_-$  is the unique eigenvalue lying in  $(-\infty, -1)$ .

Let  $\lambda + \mu < 0$ . Then  $\Delta_1(z) > 0$  for  $z < -1$ . For  $z > \frac{1}{3}$  the equation  $\Delta_1(z) = 0$  is equivalent to

$$\sqrt{z^2 + \frac{2}{3}z - \frac{1}{3}} = -2\pi(\lambda + \mu).$$

Then, the number  $z_+ = \frac{-1 + 2\sqrt{1 + 9\pi^2(\lambda + \mu)^2}}{3}$  is a unique root of the equation  $\Delta_1(z) = 0$  for  $z > \frac{1}{3}$ . So, by Lemma 2, the number  $z_+$  is the unique eigenvalue lying in  $(\frac{1}{3}, \infty)$ .

(2) Let  $-\frac{1}{\sqrt{3}\pi} < \lambda + \mu < 0$ . Then  $z_+ = \frac{-1 + 2\sqrt{1 + 9\pi^2(\lambda + \mu)^2}}{3} < 1$ , i.e.  $z_+ \in (\frac{1}{3}, 1)$ .

One can see that

(3)  $z_+ = 1$  for  $\lambda + \mu = -\frac{1}{\sqrt{3}\pi}$

and

(4)  $z_+ = \frac{-1 + 2\sqrt{1 + 9\pi^2((\lambda + \mu)^2)}}{3} > 1$  for  $\lambda + \mu < -\frac{1}{\sqrt{3}\pi}$ . □

We omit the proof of Lemma 4, since it proceeds analogously to the proof of Lemma 3.

*Proof of Lemma 5.* We investigate zeros of the function

$$\Delta_1(z) = 1 - (\lambda + \mu)I(z),$$

where

$$I(z) = \int_{\mathbb{T}^2} \frac{dx}{E_{10}(x) - z}.$$

(1) Let  $\lambda + \mu > 0$ . Then the function  $I(z)$  is positive on  $(-\infty, -1)$  and strictly increasing, with range  $(0, \infty)$ . Hence, from the continuity  $I(z)$ , the equation

$$1 - (\lambda + \mu)I(z) = 0$$

has unique solution in  $(-\infty, -1)$ . Since  $I(z) < 0$  for  $z \in (\frac{3}{5}, \infty)$ ,  $\Delta_1(z) > 1$ . Therefore, according to the Lemma 2 the operator  $H_1$  has unique eigenvalue  $z$  and it lies on  $(-\infty, -1)$ .

(3) Let  $\lambda + \mu = \frac{-3}{20\pi K(\frac{2}{3})}$ . We show that  $\Delta_1(1) = 0$ , i.e.  $I(1) = \frac{-20\pi}{3}K(\frac{2}{3})$ . In the calculation of the integral

$$I(1) = \int_{\mathbb{T}^2} \frac{dx}{\frac{-2}{5}(\cos x_1 + \cos x_2) - \frac{6}{5}},$$

using (3), we obtain

$$I(1) = \int_{-\pi}^{\pi} \frac{-10\pi dx_1}{\sqrt{(2\cos x_1 + 6)^2 - 4}}.$$

By applying the substitution  $\tan x_1 = t$ , we arrive at the first-kind elliptic integral in the form

$$I(1) = \int_{-\infty}^{\infty} \frac{-20\pi dt}{\sqrt{(6t^2 + 10)(2t^2 + 6)}}.$$

To compute  $I(1)$ , we use the following identity (See formula 3.147.5 in [13])

$$\int_{-\infty}^{\infty} \frac{dt}{\sqrt{(At^2 + C)(Bt^2 + D)}} = \frac{1}{\sqrt{CD}} \frac{2}{\sqrt{a}} K(k)$$

with

$$k = \sqrt{1 - \frac{b}{a}}, \quad a > b > 0, \quad a = \frac{A}{C}, \quad b = \frac{B}{D},$$

where  $K(k) = \frac{\pi}{2} \left[ 1 + \left(\frac{1}{2}\right)^2 k^2 + \left(\frac{1 \cdot 3}{2 \cdot 4}\right)^2 k^4 + \left(\frac{1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6}\right)^2 k^6 + \dots \right]$ . Then we have  $I(1) = \frac{-20\pi}{3} K(\frac{2}{3})$ ,  $K(\frac{2}{3}) \approx 1,8096675$ . Thus,  $\Delta_1(1) = 0$ , hence the number  $z = 1$  is the unique eigenvalue of  $H_1$ .

(2) Let  $\frac{-3}{20\pi K(\frac{2}{3})} < \lambda + \mu < 0$ . Then for  $z \in (\frac{3}{5}, 1)$ , we have

$$1 - (\lambda + \mu)I(z) < 1 + \frac{3}{20\pi K(\frac{2}{3})} I(z) < 1 + \frac{3}{20\pi K(\frac{2}{3})} I(1) = 0.$$

The function  $I(z)$  is continuous and strictly increasing on  $(\frac{3}{5}, 1)$ . Then from the equality

$$\lim_{z \rightarrow \frac{3}{5} + 0} I(z) = -\infty,$$

the equation

$$\Delta_1(z) = 1 - (\lambda + \mu)I(z) = 0$$

has exactly one solution in  $(\frac{3}{5}, 1)$ .

For  $(1, \infty)$  the relation  $I(z) \in (\frac{-20\pi}{3} K(\frac{2}{3}), 0)$  holds. Then  $\Delta_1(z) = 1 - (\lambda + \mu)I(z) < 0$  for  $z \in (1, \infty)$ . So, according to Lemma 2, the operator  $H_1$  has a unique eigenvalue  $z_1 \in (\frac{3}{5}, 1)$  for  $\lambda + \mu \in (\frac{-3}{20\pi K(\frac{2}{3})}, 0)$ .

(4) Let  $\lambda + \mu < \frac{-3}{20\pi K(\frac{2}{3})}$ . Since  $\Delta_1(z) = 1 - (\lambda + \mu)I(z) < 0$ ,

$$\lim_{z \rightarrow \infty} I(z) = 1$$

and  $I(z)$  increases on  $(1, \infty)$ , the function  $\Delta_1(z)$  has a unique zero in  $(1, \infty)$ . □

The proof of Lemma 6 is similar to the proof of Lemma 5.

#### 4. Conclusion

In the present paper, we investigate the spectral properties of the discrete Schrödinger operator  $H$  on a ladder graph of  $d$ -dimensional square lattices with a self-adjoint matrix-valued potential whose entries are real parameters  $\lambda$  and  $\mu$ . The considered operator  $H$  can be regarded as a perturbation of the operator studied in [10] by a matrix operator with off-diagonal  $\delta$ -potentials having coupling constant  $\lambda$ . Due to the symmetry of the ladder graph, the investigated problem is reduced to the study of the Schrödinger-type operators  $H_1$  and  $H_2$  on the lattice  $\mathbb{Z}^d$  with  $\delta$ -potentials whose coupling constants are  $\lambda \pm \mu$ . Moreover, a non-embedded eigenvalue of  $H_1$  may become an embedded eigenvalue of the operator  $H$  if it lies within a spectral band of  $H_2$ , and conversely. This reduced problem is similar to that considered in [3], where the eigenvalues of the Schrödinger operator with  $\delta$ -potential depending on coupling constant parameter were investigated. Furthermore, by applying methods similar to those used in [3], we obtained a complete description of the eigenvalues in terms of the parameters  $\lambda$  and  $\mu$ .

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## Two-phase core-shell nanoparticle model

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**ABSTRACT** A two-phase core-shell model for nanoparticle melting is proposed, in which a solid core is surrounded by a quasi-liquid shell. The model provides self-consistent analytical expressions for the size-dependent melting temperature and effective surface tension, along with kinetic equations describing the temporal evolution of the shrinking solid core under external heating. The analysis identifies distinct melting regimes, including a pronounced acceleration in the final stage caused by curvature-induced melting-point depression. Numerical estimates for silver and copper nanoparticles demonstrate that size effects can significantly reduce melting time. The results offer simple and physically transparent relations that clarify nanoscale melting behavior, provide an intuitive interpretation of the Tolman length, and explain the overheating observed in molecular dynamics simulations.

**KEYWORDS** core-shell nanoparticles, two-phase model, melting kinetics, thermodynamic equilibrium, surface effects, size-dependent properties, phase transition

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### 1. Introduction

The design of nanomaterials with tailored physicochemical properties remains a central challenge in modern materials science and nanotechnology [1, 2]. At the nanoscale, material properties undergo profound changes due to the dominant influence of surface effects [3–12]. Unlike bulk materials, where the fraction of surface atoms is negligible, in nanoparticles, it can reach 50 % or more. Therefore, the heterogeneous structure and size-dependent effects must be explicitly considered when describing both thermodynamic and kinetic behavior.

Classical thermodynamics, particularly Gibbs' theory, provides a powerful framework for describing equilibrium in macroscopic systems, but its direct application to nanoparticles is limited. The Laplace equation, which relates the pressure difference across a curved interface to the surface tension, depends on the choice of the dividing surface, such as the equimolar surface or the surface of tension, complicating the description of interfacial phenomena [13, 14]. In this classical picture, the interface is usually treated as infinitely thin, neglecting its finite thickness and the detailed molecular structure. As a result, several key quantities in the theory, including the Tolman length [15], which measures the offset between the surface of tension and the equimolar surface, are not uniquely defined and remain difficult to determine both theoretically and experimentally. These ambiguities often lead to discrepancies between macroscopic thermodynamic predictions and molecular dynamics simulations, particularly for very small nanoparticles where surface effects and molecular-scale fluctuations are significant [16–19]. Most previous studies have focused on the size dependence of melting temperature and surface tension, while the kinetics of the melting process has remained largely unexplored. This gap highlights the need for analytical models capable of describing both equilibrium properties and the time-dependent behavior of melting in nanoscale systems.

In this work, we develop a two-phase core-shell model of nanoparticles, in which the solid core is surrounded by a shell treated as a melted or quasi-liquid layer, consistent with the concept of surface premelting [20–25]. This approach reflects the enhanced mobility of surface atoms even below the bulk melting temperature. The core and shell are treated as coupled thermodynamic subsystems, enabling the description of both equilibrium conditions and melting kinetics, specifically the temporal evolution of the core radius under external heating.

In developing the present model, we focus on the thermodynamically controlled regime of nanoparticle melting, where the characteristic timescale of heat transfer through the shell is much shorter than that of atomic diffusion. Under such conditions, typical for nanoparticles with radii below several tens of nanometers, mass transport can be neglected, and the melting dynamics are governed primarily by interfacial curvature and heat conduction. This assumption enables a consistent analytical description of the melting process without introducing additional kinetic coefficients or diffusion terms.

Analytical expressions are derived for the radius-dependent melting temperature and the effective surface tension. In the limiting cases of large particle radius or vanishing shell thickness, the model reproduces the classical Laplace and



Gibbs–Thomson relations, ensuring consistency with macroscopic thermodynamics. This integrated framework thus provides a versatile theoretical tool for analyzing both equilibrium properties and dynamic melting behavior of nanoparticles, emphasizing the decisive role of the surface layer.

## 2. Thermodynamic analysis of a core-shell nanoparticle

We consider a single nanoparticle represented as a two-phase system, consisting of a solid core surrounded by a liquid shell. The core and shell are treated as coupled phases capable of mass exchange, with the shell having a finite thickness  $\delta$  comparable to the particle radius  $R$ . This formulation assumes that each phase maintains a uniform, bulk-like density (or molar volume) despite the nanoscale confinement, so that the solid and liquid can be characterized by constant material parameters. The surface layer is modeled as a melted or quasi-liquid phase, consistent with the concept of surface premelting, reflecting the enhanced mobility of surface atoms compared to the bulk.

Subscripts  $c$  and  $s$  denote the core and shell phases, respectively. For thermodynamic stability, the chemical potentials in both phases must be equal

$$\mu_c = \mu_s, \quad (1)$$

which implies that there is no net transfer of atoms or molecules between the core and the shell. It should be noted that strictly speaking, the chemical potential of a solid component is tensorial due to mechanical stress anisotropy [26]. For a spherical nanoparticle under isotropic surface stress and absent external shear fields, the stress tensor in the core reduces to a hydrostatic pressure. In this specific symmetric case, the tensorial chemical potential condition simplifies to the scalar equality of Eq. (1), which is widely used in nanothermodynamics of spherical particles [26]. We emphasize that this is a simplification: strictly speaking, in a crystalline solid core the chemical potential is a tensor and may vary with distance from the center. However, for the present model we adopt the hydrostatic (fluid-like) approximation for the solid core. This simplification is justified for spherical particles whose radius is much larger than the interatomic spacing, and is sufficient for the analytical description of the melting kinetics. We employ this approximation to maintain the transparency of the model. Within this fluid-like description, the distinction between thermodynamic surface energy and mechanical surface stress is neglected as a higher-order correction, consistent with standard treatments of isotropic solid–liquid interfaces [26, 27].

Expanding the chemical potentials linearly in pressure around the bulk phases at zero pressure within this hydrostatic approximation gives the equilibrium relation

$$\mu_{0c} + v_c p_c = \mu_{0s} + v_s p_s. \quad (2)$$

Here,  $p_c$  and  $p_s$  are the pressures in the core and shell;  $v_c$  and  $v_s$  denote the molar volumes of the core (solid) and shell (liquid) phases;  $\mu_{0c}$  and  $\mu_{0s}$  are the chemical potentials of the bulk phases at the same temperature  $T$  and zero pressure. At the core-shell interface, the Laplace equation describes the pressure difference due to surface curvature:

$$p_s = p_c - \frac{2\sigma_i}{R_c}, \quad (3)$$

where  $\sigma_i$  is the solid-liquid interfacial tension ( $\sigma_{SL}$ ),  $R_c = R - \delta$  is the core radius. This relation shows that the pressure in the core is always higher than in the shell. The quantity  $\sigma_i$  in Eq. (3) denotes the interfacial tension defined at the surface of tension, for which the Laplace relation holds exactly without terms involving  $\partial\sigma/\partial R$  [13, 14]. Substituting (3) into (2) gives one

$$\Delta\mu + p_c \Delta v + \frac{2\sigma_i v_s}{R_c} = 0. \quad (4)$$

where  $\Delta\mu = \mu_{0c} - \mu_{0s}$  and  $\Delta v = v_c - v_s$ . Eq. (4) is the fundamental equilibrium condition, relating the properties of the core and shell, their molar volumes, pressures, and the core radius.

The model predicts a decrease in the melting point for the nanoparticle. Near the bulk melting temperature  $T_{m0}$ , the difference between the chemical potentials of the bulk solid and liquid phases can be expressed as

$$\Delta\mu \approx T\Delta S_m - \Delta H_m \approx -\Delta H_m \left(1 - \frac{T}{T_{m0}}\right), \quad (5)$$

where  $\Delta S_m$  and  $\Delta H_m$  are the bulk molar entropy and enthalpy of fusion, respectively. Here,  $\Delta S_m = \Delta H_m/T_{m0}$  represents the increase in disorder per mole as the solid melts into the liquid phase in the bulk material. Substituting (5) into (4) and solving for the equilibrium melting temperature  $T_m(R_c)$  leads to the formula

$$T_m(R_c) = T_{m0} \left[1 - \frac{1}{\Delta H_m} \left(p_c \Delta v + \frac{2\sigma_i v_s}{R_c}\right)\right]. \quad (6)$$

Equation (6) shows that the melting temperature decreases with decreasing core radius  $R_c$ , primarily due to the surface curvature term proportional to  $R_c^{-1}$ . When the volume change  $\Delta v$  between the solid and liquid phases is negligible, Eq. (6) reduces to the classical Gibbs–Thomson relation. This expression quantitatively describes the melting-point depression in small particles. In such particles, the enhanced surface-to-volume ratio and interfacial curvature promote surface premelting and increase the thermodynamic instability of the solid phase.

Equation (6) contains two contributions that control the shift of the nanoparticle melting temperature relative to the bulk value: the curvature term  $2\sigma_i v_s / R_c$  and the volumetric term  $p_c \Delta v$ . Here we adopt the notation  $\Delta v = v_c - v_s$  (solid minus liquid). For most metals, melting is accompanied by an increase of the molar volume of the substance, so that  $v_c < v_s$  and therefore  $\Delta v < 0$ . Under compressive internal pressure ( $p_c > 0$ ), the product  $p_c \Delta v$  is negative, which reduces the quantity subtracted in Eq. (6) and thus produces an *effective elevation* of the apparent bulk melting temperature. Defining

$$T_\infty = T_{m0} \left( 1 - \frac{p_c \Delta v}{\Delta H_m} \right), \quad (7)$$

one recovers the conventional Gibbs–Thomson form

$$T_m(R_c) \approx T_\infty \left( 1 - \frac{2\sigma_i v_s}{\Delta H_m R_c} \right). \quad (8)$$

Strict substitution of Eq. (7) into Eq. (6) yields  $T_m = T_\infty - 2\sigma_i v_s T_{m0} / (\Delta H_m R_c)$ . Since  $|T_\infty - T_{m0}| / T_{m0} \ll 1$  ( $\sim 3 - 6\%$  for Ag, Cu), replacing  $T_{m0} \rightarrow T_\infty$  in the curvature term introduces a second-order correction ( $\lesssim 1\%$ ). The compact form (8) is therefore retained without affecting quantitative results. Because  $\Delta v < 0$  in the usual solid  $\rightarrow$  liquid volume-increase case,  $T_\infty > T_{m0}$ , which provides a simple and physically transparent explanation for the systematic overestimation of the “bulk” melting point often reported in molecular-dynamics studies carried out at (effectively) fixed volume. For example, fitting the Gibbs–Thomson relation to the silver nanoparticle data [23] yields an extrapolated bulk temperature  $T_\infty = 1303 \pm 12$  K (cf. the experimental value  $T_{m0} = 1234$  K), i.e. an apparent overheating of about 70 K that can be attributed to the volumetric contribution  $p_c \Delta v$ . From the fitted curvature parameter  $K = 1.07 \pm 0.06$  K nm and  $\sigma_i = K \Delta H_m / (2v_s)$ , we estimate the solid-liquid interfacial energy  $\sigma_i = 0.55 \pm 0.03$  N/m. These results therefore indicate that both the observed overheating and the high effective interfacial energy are consistent with the volume-change contribution ( $\Delta v < 0$ ) inherent to the melting of silver. This effect is illustrated in Fig. 1.

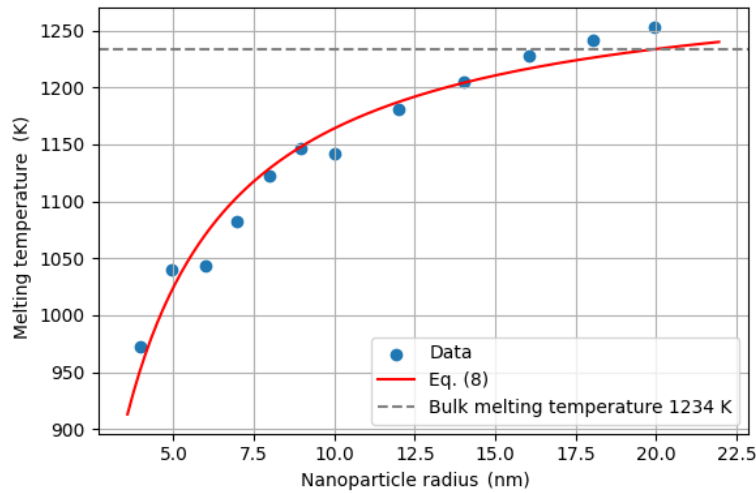


FIG. 1. Size dependence of the melting temperature of silver nanoparticles. Symbols – MD simulation data from Ref. [23]; solid line – fit to the Gibbs–Thomson relation, Eq. (8). The extrapolated bulk value  $T_\infty = 1303$  K exceeds the experimental melting temperature  $T_{m0} = 1234$  K, indicating an apparent overheating due to the negative volume change ( $\Delta v < 0$ ) upon melting

For a core-shell particle, the total excess free energy associated with interfaces can be expressed as the sum of the inner and outer surface contributions

$$F_{\text{surf}} = 4\pi R^2 \sigma_s + 4\pi R_c^2 \sigma_i, \quad (9)$$

where  $\sigma_s$  is the liquid-vapor surface tension ( $\sigma_{LV}$ ). To describe the overall thermodynamic behavior of the nanoparticle, it is convenient to introduce an effective surface tension  $\sigma$  that gives the same total excess energy as if the entire particle were homogeneous

$$F_{\text{surf}} = 4\pi R^2 \sigma. \quad (10)$$

Equating (9) and (10) yields

$$\sigma(R) = \sigma_s + \sigma_i \left( 1 - \frac{\delta}{R} \right)^2 \approx \sigma_s + \sigma_i \left( 1 - \frac{2\delta}{R} \right), \quad (11)$$

where the linear approximation is valid for thin shells, i.e., when  $\delta \ll R$ .

Equations (9)–(11) treat the liquid shell as a macroscopic phase with bulk-like properties and additive interfacial contributions. For ultrathin shells ( $\delta \sim 1$  nm), one might in principle need to consider corrections such as the distinction between mechanical surface stress and thermodynamic surface energy [26, 27], or the difference between the Helmholtz

free energy and the grand thermodynamic potential that arises in open systems [28], as well as effects specific to confined liquid films [29]. However, in our model the system is closed (total number of particles  $N = \text{const}$ ) and the Helmholtz free energy  $F(T, V, N)$  is the natural thermodynamic potential. The surface tensions  $\sigma_s$  and  $\sigma_i$  are defined as the excess Helmholtz free energy per unit area of the corresponding interfaces at fixed  $T$ ,  $V$ ,  $N$ . Since our system is closed, no transition to the grand canonical ensemble or to the grand thermodynamic potential  $\Omega$  is required. Moreover, our system consists of a solid core and a liquid shell in direct contact, with no thin film confined between two surfaces; therefore, disjoining pressure effects are not present. The additive approximation, Eq. (9), is adopted for all shell thicknesses considered in this work, while noting that for  $\delta \sim 1$  nm additional molecular-scale effects may become relevant.

Although the model explicitly describes a two-phase solid-liquid system, it can equally be interpreted as an effective solid-vapor interface, with the liquid layer serving as the intrinsic transition region between the solid core and the vapor environment. In this interpretation, the effective surface tension defined by Eqs. (9)–(11) must be identified with the curvature-dependent surface tension in the Tolman formula [13–15]:

$$\sigma(R) \approx \sigma_\infty \left( 1 - \frac{2\delta_T}{R} \right), \quad (12)$$

where  $\sigma_\infty$  is the surface tension of the corresponding flat interface and  $\delta_T$  is the Tolman length. For a pure substance, the flat-limit interfacial energy of the effective solid-vapor boundary satisfies  $\sigma_\infty = \sigma_{SV} = \sigma_{LV} + \sigma_{SL} = \sigma_s + \sigma_i$  by Young's equation with zero contact angle [29]. Matching the curvature-dependent term in Eq. (11) with the Tolman expansion (12) yields

$$\delta_T = \delta \frac{\sigma_i}{\sigma_s + \sigma_i} = \delta \frac{\sigma_{SL}}{\sigma_{SV}}, \quad (13)$$

which provides a direct physical meaning to the Tolman length: it is proportional to the equilibrium thickness of the premelted liquid layer, with a dimensionless factor determined by the relative interfacial tensions. According to thermodynamic models and experimental estimates for typical metals, the ratio  $\sigma_{SL}/\sigma_{SV}$  lies within  $0.15 \pm 0.03$  [30]; consequently, the Tolman length is approximately one-seventh of the premelted layer thickness. Within this framework,  $\delta_T$  is necessarily positive for the solid-core/liquid-shell morphology; a sign reversal would require an inverted structure (e.g., a liquid core surrounded by a solid shell), which lies outside the present scope.

Thus, the effective surface tension (11) provides a unified description that incorporates both geometric confinement and interfacial curvature effects across the full size range from bulk to nanoscale.

While the classical Gibbs phase rule ( $F = C - P + 2$ ) predicts a unique melting temperature for bulk systems, its application to nanoparticles requires modification due to the significant contribution of curved interfaces. The generalized form  $F = C - P + 3$ , which includes curvature as an additional parameter, explains the continuous dependence  $T_m(R_c)$  derived in our model. This extended thermodynamic framework naturally accommodates the size-induced melting point depression and validates the physical consistency of our core-shell approach.

### 3. Melting kinetics of core-shell nanoparticle

Building on the thermodynamic framework established above, we now turn to the kinetics of nanoparticle melting. In the core-shell model, melting is treated as a dynamic process in which the solid core gradually transforms into the surrounding liquid shell. The temporal evolution of the core radius  $R_c(t)$  is governed by the rate of mass transfer across the core-shell interface, which depends on the local thermodynamic driving force, i.e., the difference in chemical potentials between the solid and liquid phases.

The heat balance at the core-shell interface can be expressed as

$$L_v \frac{dV_c}{dt} = -(Q - P), \quad (14)$$

where  $V_c = 4\pi R_c^3/3$  is the core volume,  $L_v = \Delta H_m/v_c$  is the volumetric latent heat of fusion (energy per unit volume),  $Q$  is the heat flux through the shell to the core, and  $P$  represents the power dissipated in the liquid shell due to convective mixing and viscous effects.

Equation for the heat flux is obtained from the steady-state heat conduction equation in a spherical shell. For radial symmetry, the temperature profile satisfies

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dT}{dr} \right) = 0, \quad (15)$$

with boundary conditions  $T(R_c) = T_m(R_c)$  and  $T(R) = T_p$ . The solution gives

$$T(r) = T_m + (T_p - T_m) \frac{1/R_c - 1/r}{1/R_c - 1/R}, \quad (16)$$

and the total heat flux through the shell is

$$Q = -4\pi r^2 \lambda_s \frac{dT}{dr}, \quad (17)$$

which yields

$$Q = 4\pi\lambda_s \frac{T_p - T_m(R_c)}{R_c^{-1} - R^{-1}} = 4\pi\lambda_s \Delta T(R_c) \frac{RR_c}{R - R_c}, \quad (18)$$

where  $\Delta T(R_c) = T_p - T_m(R_c)$  is the overheating,  $T_p$  is the temperature of the external heat source,  $\lambda_s$  is the thermal conductivity of the liquid shell.

To complete the energy balance, we must account for dissipative losses in the liquid shell. Within the framework of nonequilibrium thermodynamics, the rate of energy dissipation  $P$  is defined as the product of a generalized flux and its conjugate thermodynamic force. For the moving core-shell interface, the generalized flux is identified with the interface velocity  $J = |dR_c/dt|$ , which characterizes the rate of the phase transformation. The conjugate thermodynamic force represents the total resistive force exerted by the liquid shell against the interface motion. Since the hydrodynamic flow and mixing effects induced by the boundary displacement occupy the entire liquid region, the total resistance scales proportionally with the volume of the shell. Thus, we model the generalized force as  $F_{\text{diss}} = \gamma(R^3 - R_c^3)$ , where  $\gamma$  is an effective coefficient characterizing the specific resistance per unit volume due to fluid motion and viscous losses. The product of this force and the flux yields the dissipative power:

$$P = \gamma(R^3 - R_c^3) \left| \frac{dR_c}{dt} \right|, \quad (19)$$

The use of the absolute value for the velocity ensures that the dissipation power remains positive definite ( $P \geq 0$ ) regardless of the direction of the interface motion (melting or solidification), thereby satisfying the Second Law of Thermodynamics. This phenomenological relation captures the essential scaling of energy losses with both the active fluid volume and the kinetics of the phase boundary.

Combining (14), (18) and (19), and noting that  $dV_c/dt = 4\pi R_c^2(dR_c/dt)$ , we obtain the governing differential equation for the core radius evolution:

$$\frac{dR_c}{dt} = -\frac{R\lambda_s}{L_v} \frac{T_p - T_m(R_c)}{(R - R_c) \left[ R_c + \frac{\gamma}{4\pi L_v R_c} (R^3 - R_c^3) \right]}. \quad (20)$$

The kinetic equation (20) describes the evolution of the solid core radius down to the nanoscale. However, the continuum thermodynamics framework underlying Eq. (8) breaks down when the core radius becomes comparable to the characteristic length  $l_c = 2\sigma_i v_s / \Delta H_m$ . For copper this gives  $l_c \approx 0.15$  nm, i.e., of the order of the interatomic distance. This scale marks the natural lower limit of the present continuum model.

Formally, Eq. (8) predicts  $T_m \rightarrow 0$  at  $R_c = l_c$ , and the dissipation term in Eq. (20) diverges as  $R_c \rightarrow 0$ . To ensure physical consistency, we integrate the kinetic equation from the initial radius  $R_c(0) = R$  down to a final cutoff radius  $R_c \sim l_c$ . Below this size, the distinction between solid and liquid phases becomes ambiguous due to strong finite-size effects and thermal fluctuations. Since the volume of the remaining core scales as  $l_c^3$ , the contribution of the final stage to the total melting time is negligible for  $R \gg l_c$ . Thus, the melting time is defined as the time required to reduce the core to the  $l_c$ . Under the assumptions  $R \gg R_c, l_c$  and constant overheating  $\Delta T$ , equation (20) can be simplified by approximating  $(R - R_c) \approx R$  and  $(R^3 - R_c^3) \approx R^3$ . This yields:

$$t_m \approx \frac{L_v R^2}{2\lambda_s \Delta T} + \frac{\gamma R^3}{4\pi L_v} \log \left( \frac{R}{l_c} \right). \quad (21)$$

The first term represents the conventional diffusion-limited melting time, while the second term accounts for the additional delay due to viscous dissipation in the liquid shell. The cutoff at  $R \sim l_c$  ensures the physical consistency of the solution by avoiding the divergence of the dissipation term at vanishing core radius.

Let us now proceed to the exact solution of equation (20) taking into account (8). We introduce the following notations

$$x = \frac{R_c}{R}, \quad \tau = \frac{\lambda_s T_{m0}}{L_v R^2} t, \quad x_0 = \frac{2\sigma_i v_s}{R \Delta H_m}, \quad \theta = \frac{T_p}{T_\infty} - 1, \quad \Gamma = \frac{\gamma R}{4\pi L_v}.$$

Taking this into account, we obtain an ordinary differential equation with separable variables

$$\frac{dx}{d\tau} = -\frac{x_0 + \theta x}{(1 - x)[x^2 + \Gamma(1 - x^3)]}, \quad x \in [1, x_0]. \quad (22)$$

The melting time  $\tau_m$  for  $\Gamma = 0$  is given by

$$\tau_m = \frac{x_0^3 - 1}{3\theta} - \frac{(x_0 + \theta)(x_0^2 - 1)}{2\theta^2} + \frac{x_0(x_0 + \theta)(x_0 - 1)}{\theta^3} + \frac{x_0^2(x_0 + \theta)}{\theta^4} \log \left[ \frac{x_0 + \theta}{x_0(1 + \theta)} \right]. \quad (23)$$

Taking the limit  $x_0 \rightarrow 0$  in equation (23) yields  $\tau_m = 1/(6\theta)$ .

For a copper nanoparticle [31–34] with  $R = 10$  nm,  $\Delta T = 10$  K, and material parameters  $L_v = 2 \cdot 10^9$  J/m<sup>3</sup>,  $\lambda_s = 150$  W/(m·K),  $\sigma_i = 0.13$  N/m,  $\Delta H_m = 13.2$  kJ/mol, and  $T_\infty = 1356$  K, Eq. (23) yields  $t_m \approx 4$  ps. This result is significantly smaller than the estimate from Eq. (21), confirming the extremely rapid melting in nanoscale particles and highlighting the critical importance of self-consistently accounting for the size-dependent melting temperature when

modeling ultrafast phase transitions. Accounting for energy dissipation in the liquid shell allows, through the adjustment of the parameter  $\Gamma > 0$ , for achieving complete agreement with molecular dynamics simulation results for the melting time (tens to hundreds of ps [31–34]).

An explicit solution  $x = x(\tau)$  of eq. (22) is not available, making numerical methods the preferred approach. Numerical solution of eq. (22) is conveniently implemented in block-diagram simulation tools (e.g., Simulink, Scilab Xcos, SimInTech, or similar environments). The integral formulation allows building intuitive graphical models that visually represent the melting kinetics and enable efficient parameter variation studies. Eq. (22) can be rewritten in integral form as

$$x(\tau) = 1 - \int_0^\tau \frac{(x_0 + \theta x(s)) ds}{(1 - x(s)) [x^2(s) + \Gamma(1 - x^3(s))]} \quad (24)$$

The integration is performed until  $x(\tau) = x_0$ , indicating complete melting. The numerical implementation utilizes basic arithmetic blocks, a single integrator, and feedback based on  $x(\tau)$ . In addition, a PL software block is employed to stop the calculation when the core reaches complete melting.

Figure 2 presents the block diagram and the resulting numerical solution. The parameters for the calculation were chosen as representative values typical for metallic nanoparticles. The numerical integration was carried out using the RK45 method (Dormand–Prince adaptive step-size control). The temporal evolution of the core radius reveals three well-defined kinetic stages, each governed by distinct physical mechanisms. The process initiates with a rapid, nearly exponential decrease in radius, driven by the large initial core size and the applied overheating, which promote fast interface propagation. This initial transient gradually transitions into a quasi-linear regime, where the melting rate remains approximately constant as heat conduction through the growing liquid shell becomes rate-limiting. The final stage exhibits marked acceleration, characterized by a progressively increasing melting rate. This terminal acceleration arises directly from the size-dependent melting temperature depression described by the Gibbs–Thomson relation: as the core radius diminishes, the thermodynamic driving force  $T_p - T_m(R_c)$  intensifies nonlinearly, creating an autocatalytic effect that rapidly completes the phase transformation.

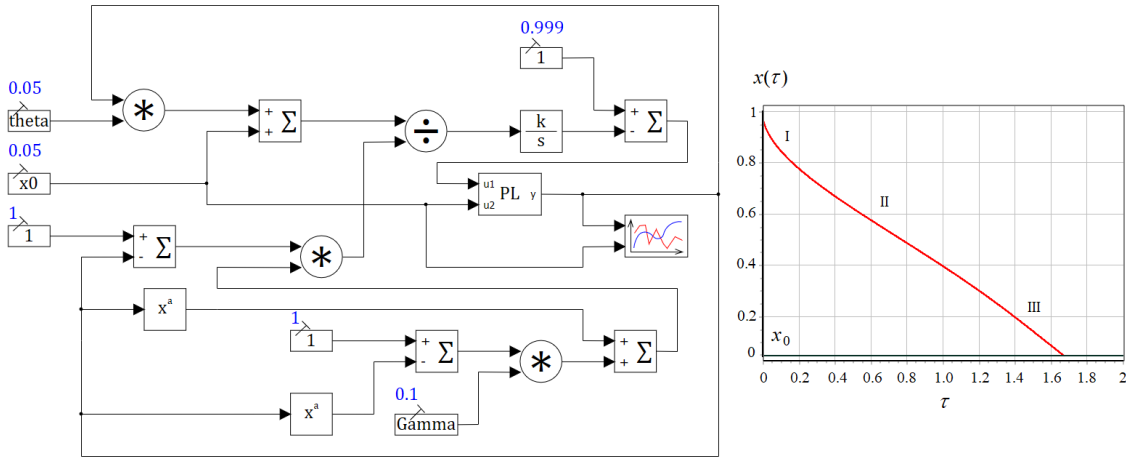


FIG. 2. Melting kinetics of a nanoparticle ( $x_0 = 0.05$ ,  $\theta = 0.05 > 0$ ,  $\Gamma = 0.1$ ): block diagram of the SimInTech simulation model and temporal evolution of the normalized core radius showing distinct melting regimes

The influence of the size dependence of the melting temperature can be quantitatively assessed by comparing two melting kinetics: one assuming a constant melting temperature and the other accounting for the size-dependent decrease of  $T_m$  with decreasing core radius. This comparison is most clearly demonstrated within the  $\Gamma = 0$  approximation. For the constant-temperature case, the evolution of the core radius is described by

$$\frac{dx}{d\tau} = -\frac{\theta}{x(1-x)}, \quad x \in [1, 0], \quad (25)$$

with the analytical solution

$$\tau = \frac{1 - 3x^2 + 2x^3}{6\theta}, \quad \tau_m = \frac{1}{6\theta}, \quad (26)$$

which corresponds to the classical description with a fixed driving force for phase transformation.

Figure 3 shows the calculated  $x(\tau)$  curves for both cases, highlighting the fundamental differences in process dynamics. The model with a constant melting temperature (red dashed line) exhibits a smooth deceleration of the melting rate as the core radius decreases, and the linear melting stage is noticeably prolonged. In contrast, the model accounting for size

dependence (blue solid line) reveals a pronounced acceleration in the final stage, which is associated with the decrease in  $T_m(R_c)$  during core melting. This acceleration significantly reduces the total melting time, underscoring the critical importance of considering surface curvature when modeling phase transitions in nanoparticles. A comparison of the calculations in Figs. 2 and 3 further reveals that viscous dissipation significantly retards the melting process, particularly during its final stage, thereby partially counteracting the curvature-induced acceleration.

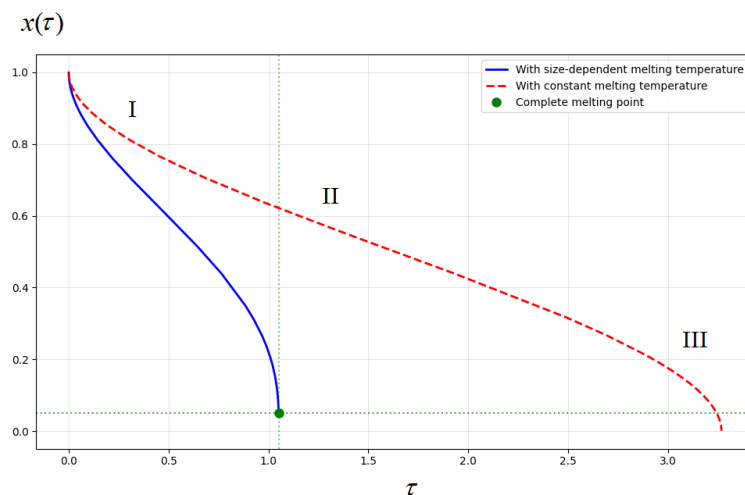


FIG. 3. Quantitative comparison of melting models: size-dependent versus constant melting temperature ( $x_0 = 0.05$ ,  $\theta = 0.05 > 0$ ,  $\Gamma = 0$ ). The more than threefold reduction in melting time demonstrates the significant impact of curvature-induced melting point depression on nanoscale phase transformation kinetics

#### 4. Conclusion

A consistent thermodynamic–kinetic framework for nanoparticle melting has been developed based on a two-phase core-shell model. The theory explicitly incorporates the finite thickness and physical properties of the quasi-liquid surface layer, providing a natural extension of classical thermodynamics to nanoscale systems. Analytical expressions for the size-dependent melting temperature and effective surface tension clarify the physical meaning of the Tolman correction, linking it directly to the structural thickness of the liquid shell.

The kinetic formulation demonstrates that melting proceeds through distinct stages governed by the interplay between interfacial curvature and heat conduction. The model predicts a pronounced size dependence of the melting time, with characteristic acceleration at the final stage due to curvature-enhanced overheating. These predictions quantitatively account for the fast melting observed in molecular dynamics simulations and pump-probe experiments.

The proposed framework unifies equilibrium and dynamic descriptions of phase transitions in nanoparticles, yielding compact analytical relations and transparent physical insight. It provides a basis for predicting the thermal stability of nanostructured materials and for guiding the design of thermally robust nanodevices.

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## Structure, mechanical and filtration properties of graphyne compounds of the self-intercalated type

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**ABSTRACT** We performed a study of the structure and properties of hybrid carbon compounds based on graphyne layers with a self-intercalated type of crystal lattice using ab initio calculations. It is found that only compounds based on  $\alpha$ -graphyne-1 and  $\beta$ 1-graphyne-2 can have an ordered crystal structure. Calculations have shown that the most stable  $\alpha$ -type phase is tetragonal ( $I/4mcm$ ) self-intercalated  $\alpha$ -graphyne-1 with a density of 1.28 g/cm<sup>3</sup>, a bulk modulus of 31 GPa, a Young's modulus from 3 to 107 GPa, which is characterized by a minimum negative linear compressibility of  $-11.7 \text{ TPa}^{-1}$  along the [001] axis. This makes it a promising material for use in pressure sensors. Additionally, the  $I/4mcm$  phase can be used as a selective filter for hydrogen molecules, the permeability of which can be increased by uniaxial compression or stretching perpendicular to [001]. The studied nanostructured phases can be unambiguously identified from the calculated powder X-ray diffraction patterns.

**KEYWORDS** nanostructured materials, graphyne, mechanical characteristics, filtration properties, powder X-ray diffraction patterns, density functional theory calculations

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### 1. Introduction

Carbon materials constitute a distinctive class of materials due to the wide variety of physical properties, enabling their efficient application in electronics, energetics, optics, and medical science [1]. The capacity of carbon materials to manifest distinct properties while maintaining an identical chemical composition stems from the abundance of polymorphic and polytypic variants exhibited by the three main carbon allotropes: diamond, graphite, and carbyne [2–7]. In particular, the polymorphs and polytypes of diamond exhibit outstanding mechanical characteristics, which determine their applications as wear-resistant and protective coatings [8, 9], along with high thermal conductivity, which is a key property for materials used in energy conversion systems [10]. In turn, polymorphic varieties of graphene exhibit a high specific surface area and are widely used, in particular, in the production of ionistors [1]. An even greater change in the properties of carbon materials is observed when nanostructured compounds contain carbon atoms with different hybridization types [11]. Such carbon compounds are called hybrid. Hybrid phases and nanostructures can be divided into four groups, each distinguished by the hybridization (coordination) of atoms. The first group includes graphyne and carbynoid compounds consisting of  $sp^2$  and  $sp$  hybridized atoms [12]. The second group of compounds from  $sp^2+sp^3$  hybridized atoms is represented by experimentally observed graphite-diamond nanocomposites [13, 14], polymerized fullerenes [15, 16], as well as numerous hypothetical nanostructures and phases [17, 18]. Carbynodiamonds, carbynocubanes, and carbynoid crystals with a lonsdaleite-like structure [19] belong to the class of compounds composed of  $sp^3$ - and  $sp$ -hybridized carbon atoms. The final group of hybrids, which consist of atoms with all three types of hybridization (coordination) in their structure, is represented by graphene layers or tetrahedral carbon frameworks, connected by carbyne chains [20, 21], as well as by polymerized carbynofullerenes [22]. The most promising group for the search for nanostructured materials with potential use as molecular filters with unique mechanical properties is the group of carbynoid hybrids ( $sp^2+sp$ ), as it features a wide range of structural varieties of compounds with high porosity resulting from the presence of linear segments of  $sp$ -atoms.

Based on the classification scheme presented in [12], hybrid  $sp^2+sp$  nanostructured compounds are categorized into four structural groups, exhibiting crystallographic dimensionality from 0D to 3D (Fig. 1). The first group of quasi-zero-dimensional compounds, labeled [0D, 2-3], includes spherical-shaped molecules known as carbynofullerenes [23]. The



second group [1D, 2-3] contains graphyne nanotubes, which were first predicted theoretically [2,24] and later successfully synthesized experimentally [25]. The third group of layered [2D, 2-3] compounds is represented by graphyne layers, the study of which also followed the path from theoretical prediction [26] to successful synthesis [27] through the development of numerous methods for producing graphyne compounds with varying morphologies and degrees of structural ordering [28]. Three-dimensional phases with hinged and chiral structures belong to the fourth group of [3D, 2-3] hybrid compounds [29]. Among these structural groups, the last two are particularly notable because graphyne layers show the greatest potential as selective filters and electrodes in ion batteries [30], while three-dimensional carbynoid phases with a hinged structural type demonstrate unusual mechanical properties, namely, an increase in their linear dimensions or cross-sectional areas under hydrostatic compression [31]. The filtration applications of conventional nanostructures and carbynoid crystals are severely constrained because external mechanical stresses induce only minor changes in pore size in covalently bonded materials. The development of novel carbon materials with self-intercalated crystal lattices [32] exemplified by yne-diamonds (diamondynes) that combine covalent and van der Waals interactions [33,34], represents a viable pathway forward. Hybrid interpenetrating nanostructures featuring this mixed type of interatomic bonding could enable the development of carbon compounds that exhibit significant structural changes under external stress, thereby allowing control over the filtration properties of the porous material. Thus, the aim of the present work is to conduct an *ab initio* investigation of the structure, stability, mechanical properties, and filtration characteristics of self-intercalated hybrid compounds.

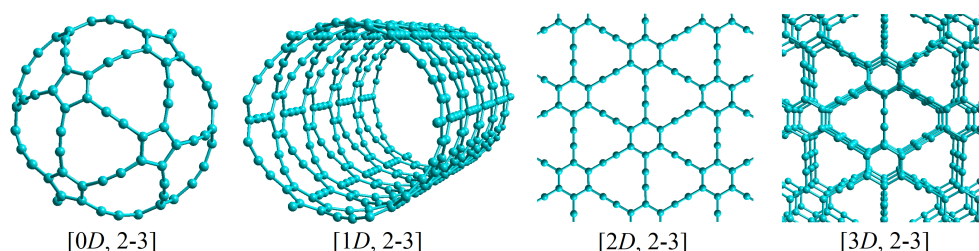


FIG. 1. Hybrid carbon nanostructures and three-dimensional phases

## 2. Models and computational methods

The structure of self-intercalated phases was obtained by interlocking of crystal lattices of two types of structural precursors. The first type of precursors is graphyne layers, while in addition to “graphyne-1” (G1) layers, graphyne layers with four-atom carbyne chain fragments (G2) were examined as structural precursors for self-intercalated phase formation, and their variants are shown in Fig. 2. Formation of self-intercalated phases was carried out on the basis of graphyne layers of one structural type using the method described in [35] in the range of angles from 60 to 90°. The second type of precursors are three-dimensional  $sp^2+sp$  carbon phases constructed by implantation of chain carbon units into the structure of three-dimensional graphites. Implantation of chains into the structure of three-dimensional graphites in this work was carried out by analogy with the formation of  $\alpha$ -graphyne layers based on hexagonal graphene, therefore the compounds obtained in this way are three-dimensional hybrid phases of the  $\alpha$ -type. In this work, three phases named *bct*-C<sub>16</sub>, *sh*-C<sub>24</sub>-I and *sh*-C<sub>24</sub>-II (Fig. 2), were considered as precursors of the second type, which were formed on the basis of three-dimensional graphites *bct*-4, 6(3)-I-06a and *H*-6, respectively [36–38]. The choice of these phases was due to the presence of flat units with low internal stresses in their structure. The mutual penetration of three-dimensional hybrid phases was carried out in such a way that the closest distances between atoms of adjacent sublattices were maximized.

The calculation of structural parameters and properties of crystalline phases and nanostructures was performed using the density functional theory (DFT) method implemented in the Quantum ESPRESSO software package [39]. The initial structures of the layered and three-dimensional precursors were calculated using the generalized gradient approximation (GGA) in the PBE formulation [40], using parameters from references [41,42]. Further calculations of three-dimensional phases comprising interlocked sublattices were carried out using the vdW-DF exchange-correlation functional, which correctly accounts van der Waals interactions [43]. Standard ultrasoft pseudopotential was used to account for the influence of nuclei and core electrons. For calculations in the Brillouin zone, a kinetic energy cutoff of 46 Ry was used, along with  $k$ -grids of  $6 \times 6 \times 6$  or  $4 \times 4 \times 4$  (if the number of atoms is at least 120). Relaxation of the structure of the phases was performed until the force acting on each atom fell below 1.5 meV/Å and the pressure fell below 0.3 kbar. As a result of the relaxation of the 2H graphite structure with this set of parameters, the calculated interplanar distances  $d_{002}$  are equal to 3.51 Å, which is less than 5 % higher than the experimentally determined value [1], suggesting that the vdW-DF method is capable of adequately calculating the structures of hybrid carbon compounds with covalent-van der Waals bonding. In addition, the calculated parameters of the crystal lattices of 3C diamond (3.582 Å) and hexagonal graphene (2.463 Å) differ by less than 0.5 % from the experimental values [1] and practically coincide with the values calculated within

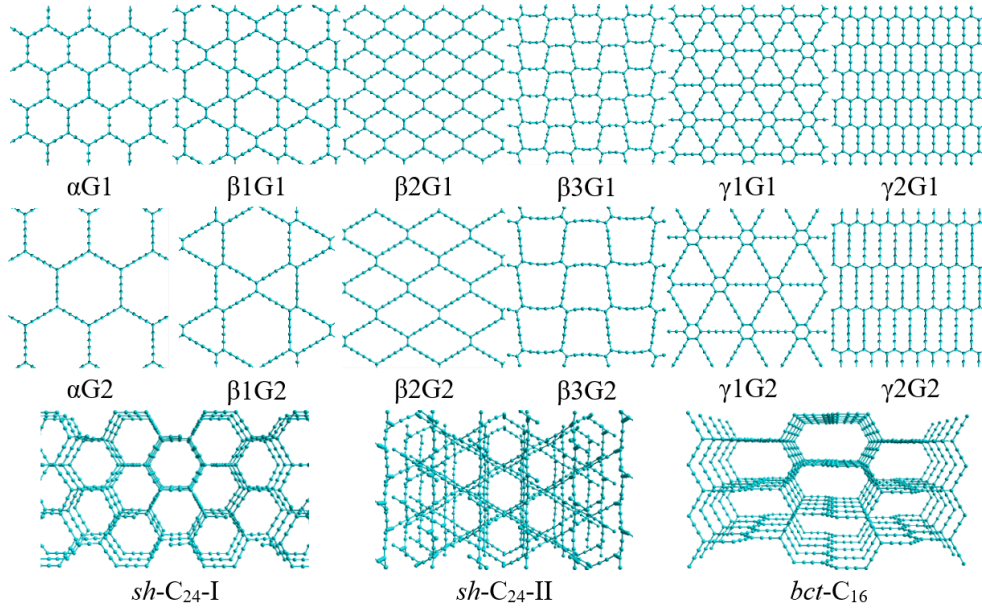


FIG. 2. Structural precursors of self-intercalated phases

the DFT-GGA method in [44]. Structural data of the most stable self-intercalated phases is provided in Supplementary materials file.

The effect of temperature on the structural stability of the three-dimensional phase with the lowest specific energy was investigated using the molecular dynamics method at temperatures up to 550 K over a period of 7 ps with a timestep of  $\Delta t = 1$  fs. The calculations were performed using a doubled unit cell along with a  $3 \times 3 \times 3$   $k$ -point grid. Molecular dynamics modeling using a  $1 \times 1 \times 2$  supercell was also used to investigate the motion of  $H_2$  molecules within the crystal lattice of the most stable self-intercalated phase.

To investigate the mechanical properties of the most stable self-intercalated phase, simulations of hydrostatic compression and uniaxial mechanical stimulus along the principal crystallographic directions were performed. The bulk modulus  $B_0$  and its derivative  $B'_0$  were calculated using the Vinet equation [45]:

$$P = 3 \left( 1 - \left( \frac{V}{V_0} \right)^{1/3} \right) B_0 \left( \exp \frac{3(B'_0 - 1)}{2} \left( 1 - \left( \frac{V}{V_0} \right)^{1/3} \right) \right) \left( \frac{V_0}{V} \right)^2, \quad (1)$$

where  $P$  is the pressure;  $V_0$  and  $V$  are the volume of the phase at zero pressure and under hydrostatic pressure  $P$ , respectively. The bulk modulus of 2H-graphite, calculated using equation (1), is 48.8 GPa, which exceeds the experimentally determined value (34 GPa [1]) by 43.5 %. The calculated value of the bulk modulus of graphite exhibits a significant discrepancy with respect to the experimental value, but demonstrates closer agreement with experimental data compared to the value of  $\sim 285$  GPa obtained by the authors of paper [46]. For 3C diamond, the Vinet equation yields a bulk modulus of 438.4 GPa, which is in excellent agreement with the experimental value of 446.1 GPa [47].

The Young's modulus ( $Y$ ) was calculated using the following formula:

$$Y = \frac{F/S}{\Delta l/l}, \quad (2)$$

where  $F$  is the tensile force magnitude;  $S$  is the cross-sectional area whose normal vector is aligned with force application direction;  $\Delta l/l$  is the relative change in crystal length along the force axis. The calculated Young's modulus values for 2H-graphite under uniaxial tension along the zigzag and armchair directions demonstrate close agreement, with an average value of 0.88 TPa. This value is in good agreement with the experimental data reported in references [48, 49], which lie within the range from 0.92 to 1.1 TPa. Under uniaxial tension along the [001] direction, the calculated Young's modulus is 23.9 GPa, which is 34 % lower than the experimental value (36.5 GPa [50]), as a result of the elevated calculated value  $d_{002}$  (3.51 Å) in comparison with the experimental measurement [1].

Linear compressibility ( $K$ ) can be determined as

$$K_l = -\frac{1}{l} \left( \frac{\partial l}{\partial P} \right)_T, \quad (3)$$

where  $l$  is the value of the unit cell parameter ( $l = a, b, c$ );  $T$  is the temperature.

The possibility of experimental identification of three-dimensional nanostructured carbon phases was investigated using the powder X-ray diffraction pattern simulation for characteristic chromium  $K_\alpha$ -radiation ( $\lambda_{Cr-K\alpha} = 2.2909$  Å).

### 3. Results and discussion

Calculations using the density functional theory method showed that the most stable are the self-intercalated (SI), phases from the  $\alpha$ G1 and  $\beta$ 1G2 layers, the total energies of which are lower than the total energies of the isolated layers by 0.043 and 0.029 eV/atom, respectively. The structure of the three-dimensional self-intercalated phase 3D-SI- $\alpha$ G1 consists of flat  $\alpha$ G1 layers (Fig. S1) and is characterized by a tetragonal unit cell (symmetry spacegroup  $I/4mcm$ ) containing 32 atoms (Fig. 3a). The lattice parameters of 3D-SI- $\alpha$ G1 are  $a = 8.460$ ,  $c = 6.980$  Å. The density of this phase is 40.8 % lower than the calculated density of 2H-graphite and amounts to 1.28 g/cm<sup>3</sup>. The crystal structure of 3D-SI- $\alpha$ G1 contains three nonequivalent atomic positions (Table S1). The SI phase based on  $\beta$ 1G2, in which the layers are wave-like curved (Fig. S2), also has an ordered crystalline structure (Fig. 3b). The body-centered crystal lattice of the 3D-SI- $\beta$ 1G2 phase belongs to the  $Ibam$  space group, which features a rhombic unit cell with a basis of 120 atoms. The lattice parameters are  $a = 14.33$ ,  $b = 24.16$ ,  $c = 7.426$  Å. The density of 3D-SI- $\beta$ 1G2 is 0.93 g/cm<sup>3</sup>, which is 56.9 % lower than the calculated density of 2H-graphite. The atomic positions in the 3D-SI- $\beta$ 1G2 lattice correspond to eight nonequivalent crystallographic positions (Table S2). Three-dimensional self-intercalated phases based on other structural types of graphyne layers may be unstable, since interlocking of two such layers leads to an increase in total energy of 0.12 eV/Å (for one-dimensional nanostructures).

To determine the stability of the studied SI phases based on graphyne layers, sublimation energies ( $E_{\text{sub}}$ ) were calculated as the difference between the total energy of atoms in a particular phase and the energy of isolated carbon atoms. The calculated  $E_{\text{sub}}$  values for the SI phases based on  $\alpha$ G1 and  $\beta$ 1G2 layers are 7.855 and 7.859 eV/atom, respectively. The  $E_{\text{sub}}$  of the self-intercalated phases based on  $\alpha$ G1 and  $\beta$ 1G2 are higher than those for the graphite-like phases based on layers of the same structural types by 3 and -11 meV/atom, respectively. This indicates an increased stability of the SI phase based on  $\alpha$ G1 with respect to the graphite-like phase from graphyne layers of the same structural type. However, in addition to phases consisting of covalently unbonded  $\alpha$ G1 layers, three-dimensional hybrid  $\alpha$ -type phases are likely candidates for formation during synthesis; the formation method for these phases is described in the methodology section of this work. By analogy with layered compounds, three-dimensional  $\alpha$ -type phases should have a porous structure, which leads to the possibility of decreasing the total energy of the lattices of these phases during their mutual penetration. Therefore, in this work, the structural and energy characteristics of three new SI phases  $bct$ -C<sub>16</sub> ( $P4_2/nmm$ ),  $sh$ -C<sub>24</sub>-I ( $P6_4/22$ ) and  $sh$ -C<sub>24</sub>-II ( $P6_4/22$ ) were also calculated, the unit cells of which are shown in Fig. 3c-e, respectively. The calculations showed that the mutual penetration of the  $sh$ -C<sub>24</sub> and  $bct$ -C<sub>16</sub> lattices in the SI- $sh$ -C<sub>24</sub>-II and SI- $bct$ -C<sub>16</sub> structure, indeed, leads to a decrease in the total energy of these phases by 14-43 meV/atom, respectively. However, despite the presence of additional interactions between the sublattices in the three new SI phases, the sublimation energies of these phases range from 7.674 to 7.821 eV/atom, which is lower than the sublimation energy of 3D-SI- $\alpha$ G1. Thus, the phase of interpenetrating  $\alpha$ G1 layers has the highest stability in comparison with the layered and covalently bonded three-dimensional (isolated and self-intercalated)  $\alpha$ -type hybrids. It is also worth noting that the sublimation energies of the SI phases considered in this article are more than 32 meV/atom higher than the calculated value of  $E_{\text{sub}}$  of yne-diamond (daimondiyne), which is a carbon phase of the SI sublattices of  $\delta$ -carbynodiamond-2.

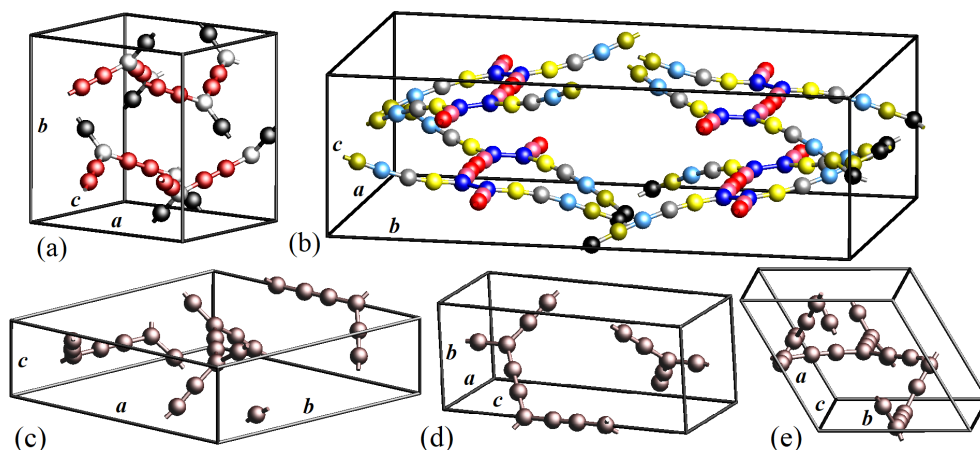


FIG. 3. Geometrically optimized structures and unit cells of 3D-SI- $\alpha$ G1 (a), 3D-SI- $\beta$ 1G2 (b), SI- $sh$ -C<sub>24</sub>-I (c), SI- $bct$ -C<sub>16</sub> (d), SI- $sh$ -C<sub>24</sub>-II (e) (atoms belonging to each nonequivalent position are highlighted in the same color)

To assess layer deformations in the structure of hypothetical phases, graphs of distributions of interatomic distances (Fig. 4) and angles between carbon-carbon bonds (Fig. 5) were constructed for isolated graphyne layers and their corresponding self-intercalated phases. During the structural relaxation of 3D-SI- $\alpha$ G1, the layers in it undergo weak deformations manifested as changes in the angles of interatomic bonds. This is evidenced by the splitting of the initial maxima

in the bond angle distribution within the isolated layer structure (Fig. 5), with minimal changing of the maxima of the interatomic distance distribution across the length range from 2.40 to 2.62 Å (Fig. 4). The interlocking of  $\alpha$ G1 layers leads to the emergence of new peaks in the  $N = f(R)$  diagram within the 3.5 – 4.0 Å range (Fig. 4), which correspond to distances between covalently unbound atoms of adjacent layers.

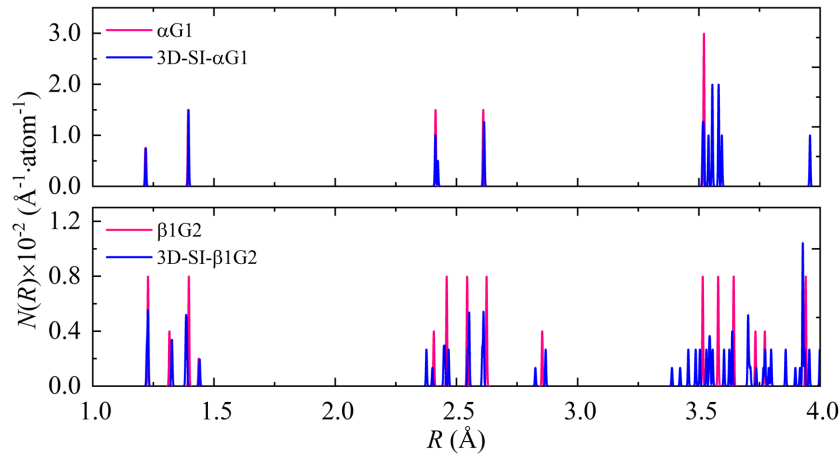


FIG. 4. Interatomic distance distribution in graphyne monolayers and 3D-SI phases

The interlocking of crystal lattices of  $\beta$ 1G2 layers results in their corrugated deformation, which is accompanied by multiple splitting and displacement of the maxima in the distribution of bond angles and interatomic distances within the range of 3.3 to 4.0 Å. At the same time, the distances between adjacent layers in the three-dimensional phase structure shift towards smaller values, starting from the value  $\approx 3.38$  Å (see Fig. 4). It should be noted that the covalent bond lengths in the structure of the both phases are close to the corresponding bond lengths in isolated layers, as can be observed in the graphs from Fig. 4 in the interatomic distance range from 1.2 to 1.6 Å.

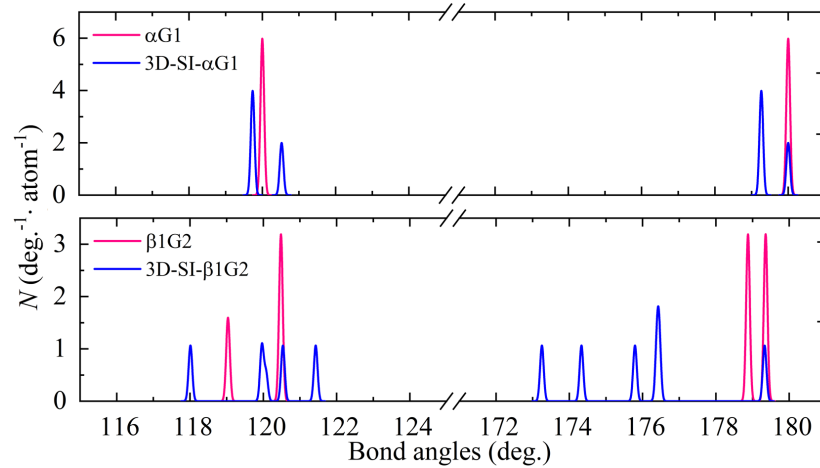


FIG. 5. Distribution of bond angles in graphyne monolayers and 3D-SI phases

Since the sublimation energy of the 3D-SI- $\alpha$ G1 phase is 0.784 eV/atom lower than the corresponding energy of hexagonal graphene, it is necessary to study the thermal stability of the crystal lattice of the new phase. Molecular dynamics simulations of the annealing process at 550 K for 7 ps demonstrated that the structure of the 3D-SI- $\alpha$ G1 phase is thermally stable, since no bond ruptures or formation of new covalent bonds within layers and between adjacent layers are observed (Fig. 6). At the same time, the structural elements of this tetragonal phase in the form of  $\alpha$ G1 layers undergo significant deformations and bend in a wave-like manner. This particular type of deformation behavior was observed in the works [32, 35] during the calculation of the phase structure via molecular mechanics methods and simulation of its thermal annealing at 400 K.

Theoretical investigation of volumetric compression of 3D-SI- $\alpha$ G1 revealed that the calculated bulk modulus of this phase is lower than that of hexagonal graphite and diamond (Fig. 7a), with the  $B_0$  value calculated by the Vinet equation being 31.0 GPa and its first pressure derivative being 2.28. During hydrostatic compression, both parameters  $a$  and  $b$  of the 3D-SI- $\alpha$ G1 unit cell demonstrate identical nonlinear decreases as pressure increases (Fig. 7b). This indicates



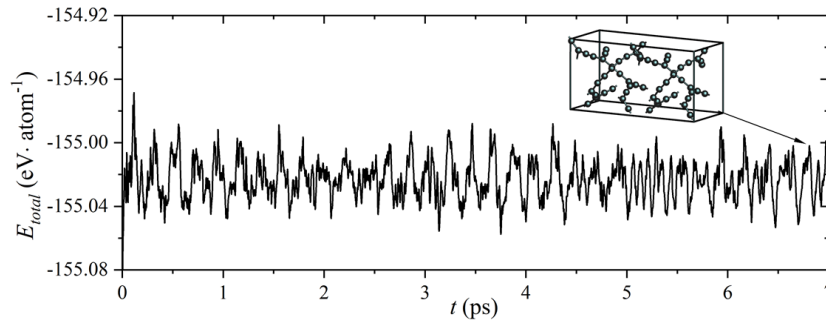


FIG. 6. Plot of the total energy versus time for 3D-SI- $\alpha$ G1 phase within thermal annealing simulation at 550 K

the preservation of the tetragonal symmetry of the phase and also the positive values of linear compressibilities  $K_a$  and  $K_b$ . The maximum value of linear compressibility  $K_a$  is observed in the region of  $P < 2.5$  GPa and amounts to  $18.2 \text{ TPa}^{-1}$ . The unit cell parameter  $c$  of the 3D-SI- $\alpha$ G1 phase exhibits nonlinear increase under volumetric compression, demonstrating the presence of a rare mechanical property in the crystalline compound – negative linear compressibility  $K_c$ . The minimum value of  $K_c = -11.7 \text{ TPa}^{-1}$  is observed at minimum pressure.

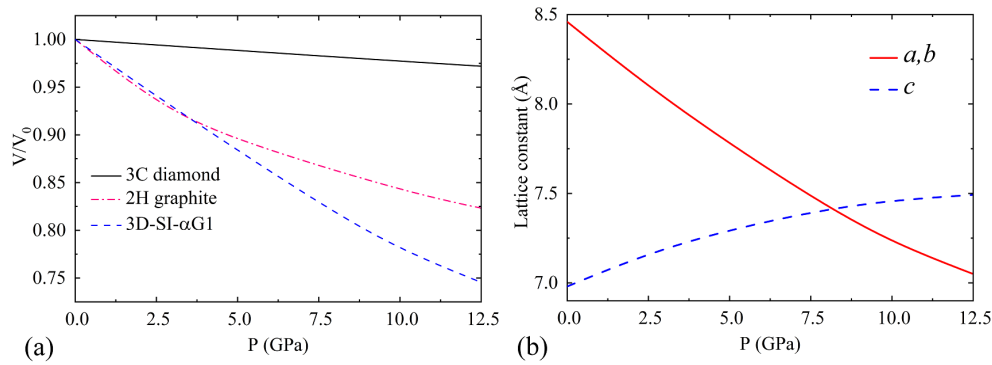


FIG. 7. Dependences of the relative volume (a) and unit cell parameters (b) versus pressure for the 3D-SI- $\alpha$ G1 phase under hydrostatic compression

Simulation of stretching of 3D-SI- $\alpha$ G1 along the [001] direction revealed that the Young's modulus of this phase in the elastic deformation region is 106.6 GPa. This value is less than 11 % lower than the calculated values for the [100] crystallographic direction of the graphite-like phase composed of  $\alpha$ G1 layers [51], and is 4.4 times higher than the calculated Young's modulus value for 2H graphite under stretching in the [001] direction. The Poisson's ratios associated with 3D-SI- $\alpha$ G1 stretching along the [001] direction, calculated relative to the [100] and [010] directions, are equal to 0.89. During the uniaxial stretching of the 3D-SI- $\alpha$ G1 phase in the elastic deformation region along the [001] direction, an increase in its density by 2.5 % is observed. This result is consistent with the negative linear compressibility  $K_c$  and is typical for materials exhibiting this property [31]. Under uniaxial stretching up to relative elongation  $\varepsilon = 0.022$  along the [100] and [010] directions, the 3D-SI- $\alpha$ G1 hybrid phase deforms according to Hooke's law, when the Young's modulus reaches the value of 3.1 GPa. The Poisson's ratios during stretching of 3D-SI- $\alpha$ G1 along the [100] direction range from 0.01 ( $\mu_c^a$ ) to 0.98 ( $\mu_a^b$ ). These values are close to the Poisson's ratio values of thin anisotropic rods of single-crystal graphite, calculated based on experimentally determined elastic constants [52]. In uniaxial compression, the functional dependencies of the unit cell parameters  $a$  and  $c$  on pressure can be adequately approximated by third- and second-order polynomials, respectively, as follows:

$$a = -1.117 \cdot 10^{-3} \cdot P^3 + 3.154 \cdot 10^{-2} \cdot P^2 - 3.333 \cdot 10^{-1} \cdot P + 8.464,$$

$$c = -8.874 \cdot 10^{-5} \cdot P^2 - 5.749 \cdot 10^{-3} \cdot P + 6.979,$$

where  $[a] = [c] = \text{\AA}$ ;  $[P] = \text{GPa}$ .

The tetragonal phase composed of self-intercalated layers of  $\alpha$ G1 has extended pores in the form of channels along the  $c$ -axis in its structure (see Fig. 3a), which are presumably capable of serving as accumulation sites or diffusion pathways for small molecules or metal ions. In the tetragonal unit cell there are four pores with a radius of 3.15  $\text{\AA}$  at the following positions: (0, 0, 0), (0.5, 0.5, 0), (0, 0, 0.5), (0.5, 0.5, 0.5). Therefore, the maximum possible filling of the lattice with hydrogen cannot exceed 25 atomic percent (2.1 mass percent). Density functional theory calculations have shown that when an  $\text{H}_2$  molecule moves along the center of the 3D-SI- $\alpha$ G1 channel in the [001] direction, the system's energy changes sinusoidally (Fig. 8a). A unit cell with a doubled  $c$  parameter contains four positions of the  $\text{H}_2$  molecule with

minimal energy, corresponding to the pore positions. Shortest transition between minimal energy positions requiring an energy of 0.080 eV. This value is close to the energy barrier height for hydrogen molecule diffusion (0.05 eV) through the largest rings in the  $\gamma$ 1G2 layer [53]. Direct investigation of H<sub>2</sub> molecule trajectories in a 3D-SI- $\alpha$ G1 supercell using molecular dynamics simulations has shown that the hydrogen molecule is capable of moving along the channel at temperatures above room temperature. The trajectory of the molecule's motion represents an irregularly shaped spiral (Fig. 8b). This makes diffusion of molecules containing atoms of elements from the second period and higher practically impossible. The hydrogen permeability of the 3D-SI- $\alpha$ G1-based material can be controlled via uniaxial compression, which should lead to a decrease in pore diameters. In particular, at pressure of  $\sim 8$  kbar ( $P_{22}$  component), the structure of the phase undergoes a 13.9 % compression along the  $a$  axis and this deformation results in a substantial decrease (53 %) in the  $\Delta E$  value (0.037 eV). The dependence of the energy barrier height  $\Delta E$  on the value of  $a/a_0$  under uniaxial compression of 3D-SI- $\alpha$ G1 along the [100] direction is a fourth-order polynomial:

$$\Delta E = -572.0 \cdot x^4 + 2117 \cdot x^3 - 2935 \cdot x^2 + 1807 \cdot x - 416.9,$$

where  $x = a/a_0$ . Calculations of the diffusion energy barrier for a larger molecule, such as methane, have shown that the value of this barrier (0.20 eV) is 2.5 times higher than  $\Delta E$  for a hydrogen molecule (Fig. 8a).

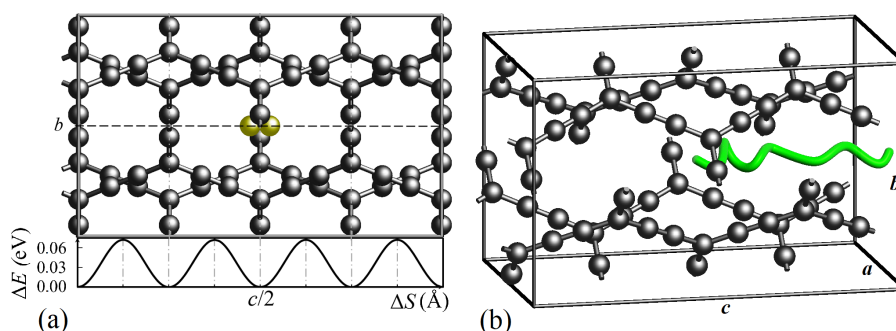


FIG. 8. (a) Dependence of the potential energy of the H<sub>2</sub> molecule versus its position along the channel axis in the crystal lattice of the 3D-SI- $\alpha$ G1 phase (the value of the  $c$  parameter of the supercell is 13.96 Å). (b) Standard trajectory of H<sub>2</sub> molecule movement within the structure of the 3D-SI- $\alpha$ G1 phase at  $T > 400$  K (the diffusion path of the molecule is marked in green)

The possibility of identifying new three-dimensional phases was investigated through the analysis of simulated powder X-ray diffraction patterns (Fig. 9), for which structural parameters were obtained from ab initio calculations. The X-ray patterns were calculated for the weighted average of the chromium  $K_{\alpha}$ -series radiation, as for characteristic radiation with a shorter wavelength, the maxima of phases with large crystal lattice parameters shift to the region of small diffraction angles, which leads to difficulties in detecting such materials. The calculated diffraction angles of the most intense maxima of the layer phase from  $\gamma$ 1G1 deviate from the experimentally observed values [27] by only  $0.2^{\circ}$ . In the case of hexagonal graphite, the calculated value of the diffraction angle characteristic of coherent scattering of radiation on the (002) crystal faces differs from the experimental value [54] by only  $1.7^{\circ}$ . The most intense maximum for 3D-SI- $\alpha$ G1 corresponds to the (110) crystal face with diffraction angle of  $2\theta = 22.1^{\circ}$ . The presence of this maximum is not sufficient for unambiguous identification of 3D-SI- $\alpha$ G1, since the maxima of phases  $\alpha$ G1 and  $\gamma$ 1G1 layered phases with AB stacking deviate from the position of this maximum by less than  $0.1^{\circ}$ . However, the 3D-SI- $\alpha$ G1 phase can be identified by maxima for the (200), (211), and (220) crystal faces, which correspond to diffraction angles of  $31.4$ ,  $40.3$ ,  $45.0^{\circ}$  and do not overlap with maxima of other phases with relative intensity exceeding 5 %. The most intense maximum of 3D-SI- $\beta$ 1G2 corresponds to the diffraction angle of  $10.9^{\circ}$ , which differs from the angle of the most intense maximum of the graphite-like phase composed of  $\beta$ 1G2 layers by less than 0.5 %, therefore these phases are indistinguishable in the region of small diffraction angles. The identification of 3D-SI- $\beta$ 1G2 can be performed based on the (110) diffraction maximum, which has the second highest intensity at a diffraction angle of  $18.6^{\circ}$ , as this maximum does not overlap with the high-intensity maxima of 2H-graphite, layered graphynes, and 3D-SI- $\alpha$ G1.

One of the possible methods for the synthesis of self-intercalated-type crystals is chemical carbonization of polymers, which can lead to the removal of non-carbon atoms and the partial formation of triple carbon-carbon bonds [55]. Another potential method of synthesis involves the polymerization of molecular precursors (monomers) with structural elements of graphyne layers [56] on a substrate with rectangular or trapezoidal protrusions. In this case, it is possible to form a three-dimensional self-intercalated phase through mutual penetration of graphyne layers into each other at the edges of the substrate material protrusions. The porosity of the forming hybrid phase should be determined by the distance between the protrusions. The synthesis of self-intercalated graphyne phases from molecular precursors can probably also be realized by their polymerization to form thin films on flat substrates in the presence of metal atoms. It is assumed that metal atoms can stabilize the structure of the films by preventing the binding of carbyne chains at low temperatures, in analogy with the mechanism of stabilization of the structure of carbynoid molecular crystals stable up to  $\sim 130^{\circ}\text{C}$  [19]. For example,

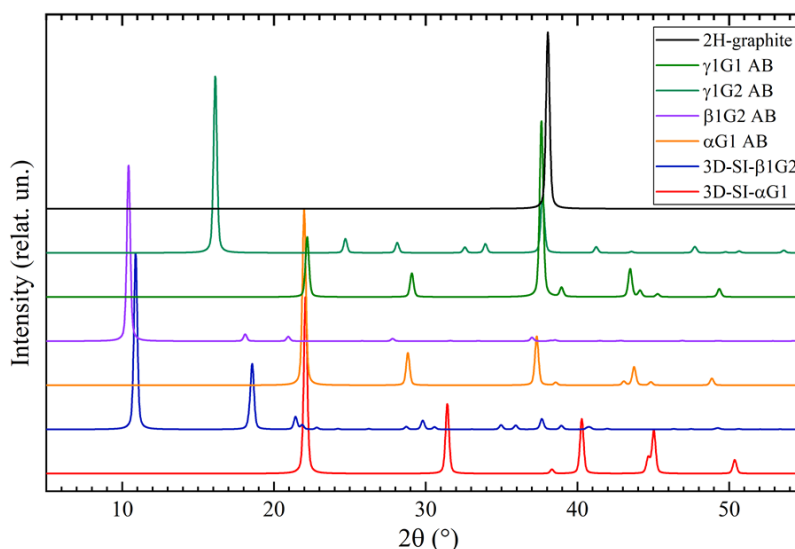


FIG. 9. Calculated powder X-ray diffraction patterns of graphite and graphyne phases

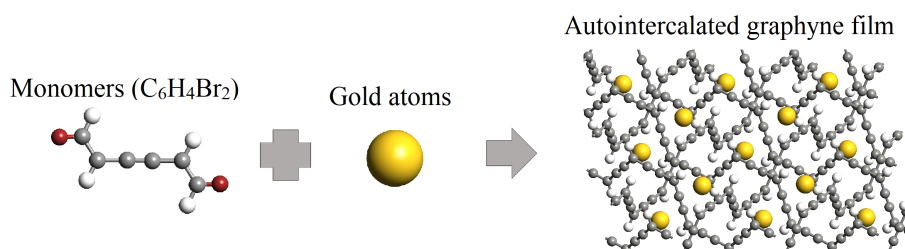


FIG. 10. Scheme of the formation of a thin 3D-SI- $\alpha$ G1 film from monomers (H atoms are shown in white, C atoms are shown in gray, Br atoms are shown in red, and Au atoms are shown in gold)

Fig. 10 shows a scheme of the formation of a 3D-SI- $\alpha$ G1-type film from  $C_6H_4Br_2$  molecules in the presence of stabilizing Au atoms film structure at the initial stage of growth.

#### 4. Conclusions

In this paper, the results of quantum-mechanical modeling of the structure and properties of graphyne compounds with covalent-van der Waals type of interatomic bonds of various crystallographic dimensions, which can be treated as self-intercalated, are presented. Ab initio calculations have shown that the most stable of the quasi-one-dimensional self-intercalated compounds are nanostructures based on  $\alpha$ -graphyne-1 and  $\beta$ 1-graphyne-2. It was found that a hybrid phase of interlocking  $\alpha$ -graphyne-1 layers, designated 3D-SI- $\alpha$ G1, should be more stable than the layered phase of  $\alpha$ -graphyne-1 and has the highest probability of formation among self-intercalated phases based on  $\alpha$ -type hybrid precursors. According to calculations, 3D-SI- $\alpha$ G1 has a tetragonal crystal lattice ( $I/4mcm$ ) formed by  $\alpha$ -graphyne-1 layers, the shape of which is close to the shape of flat isolated layers. The three-dimensional self-intercalated phase of  $\beta$ 1-graphyne-2 layers, designated as 3D-SI- $\beta$ 1G2, according to calculations, should be more stable than an isolated  $\beta$ 1-graphyne-2 monolayer, but less stable than a graphite-like phase with AB packing of layers of the same structural type. The 3D-SI- $\beta$ 1G2 phase is characterized by orthorhombic symmetry ( $Ibam$ ) and consists of wave-curved layers. The densities of 3D-SI phases based on graphyne layers range from 41 to 57 % of the graphite density. The tetragonal phase should be the most stable, as its structure does not break down at least up to 550 K, which is close to the temperature limit of  $\gamma$ 1-graphyne-1 [27].

Modeling of volumetric compression for the tetragonal phase 3D-SI- $\alpha$ G1 has demonstrated that the material has an elastic modulus value of 31.0 GPa. Furthermore, this phase should exhibit negative linear compressibility along the  $c$  axis, with the minimum value ( $-11.7 \text{ TPa}^{-1}$ ) observed at low pressures. Under uniaxial strains up to 19 %, the structure of 3D-SI- $\alpha$ G1 remains stable, with Young's moduli of this phase ranging from 3.1 to 106.6 GPa. A material based on the 3D-SI- $\alpha$ G1 phase can be used as a selective filter in hydrogen energetics, since the energy barrier to hydrogen penetration through pores is more than 2.5 times lower than the corresponding value for larger molecules. One of the unique features of this compound is that the energy barrier for hydrogen diffusion can be significantly reduced by 53 % over increasing the external stress applied perpendicular to the [001] axis to a relatively low value of  $\sim 8$  kbar.

A mechanism for the formation of thin films based on 3D-SI- $\alpha$ G1 is proposed, resulting from the polymerization of  $C_6H_4Br_2$  monomers in the presence of gold atoms. Since the studied nanostructured phases can be considered as a set of interlocked graphyne layers with the structure similar to isolated layers, the most accurate identification of hybrid self-intercalated phases is possible using X-ray diffraction analysis and high-resolution electron microscopy.

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## Theoretical investigation of the effects of viscosity variation, couple stress, and slip velocity on squeeze film lubrication of porous conical bearings

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**ABSTRACT** This study examines the effects of viscosity variation and velocity slip on the performance of porous conical bearings lubricated with a couple stress fluid. Darcy's law is used to describe fluid flow through the porous medium, while Stokes' couple stress theory accounts for the microstructure of the lubricant. A modified Reynolds equation is developed by incorporating viscosity variation and slip effects. Numerical results illustrate the influence of couple stress, slip velocity, permeability, and viscosity variation on pressure distribution, load-carrying capacity, and squeeze film time. It is observed that an increase in the couple stress parameter enhances the pressure and load capacity, while higher permeability tends to reduce the supporting ability of the bearing. The presence of slip at the boundary modifies the flow behaviour and contributes to improved lubrication characteristics. The combined effects of porous structure and slip lead to better aggregate performance, and the use of couple stress fluids significantly improves lubrication efficiency and operational reliability.

**KEYWORDS** couple stress fluid; viscosity variation; velocity slip; porous conical bearing.

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### 1. Introduction

Hydrodynamic lubrication of conical bearings is a significant area of research in tribology due to their ability to support both radial and axial loads in high-speed rotating machinery. The performance of such bearings is governed by the rheological properties of the lubricant and the flow characteristics within the thin film region. Classical lubrication theory assumes Newtonian fluids with constant viscosity; however, this assumption is not suitable for modern lubricants containing microstructural additives. To overcome this limitation, Stokes [1] introduced the couple stress fluid theory, which incorporates micro-continuum effects such as size dependency and particle rotation. This theory provides a more realistic representation of lubricant behaviour and improves the prediction of pressure distribution and load-carrying capacity in bearing systems. It is critical to note that Stokes' couple stress model specifically isolates fluid microstructure effects. It does not account for shear-thinning or non-linear shear-rate dependence. The viscosity coefficient in this formulation remains independent of the shear rate tensor. In engineering practice, this specialized model describes real-world lubricants containing long-chain polymer additives, synthetic oils with micro-particle suspensions, or bio-fluids where particle-rotation effects dominate.

The rheological behaviour of lubricants significantly affects the performance of tribological systems, particularly under high load and thin-film conditions. Modern lubricants containing polymer additives and microstructural particles often exhibit non-Newtonian characteristics such as shear-dependent viscosity and viscoelastic effects. Experimental studies have shown that lubricant viscosity varies with pressure, temperature, and shear rate, thereby influencing film formation and load-carrying capacity. Bair [2] experimentally emphasized the importance of pressure-dependent viscosity, while Spikes [3] reported that lubricant additives strongly affect rheological behaviour under severe operating conditions. These findings support the need for advanced lubrication models incorporating viscosity variation and non-Newtonian effects.

Viscosity variation is another crucial factor that significantly influences lubrication performance. In the present study, the lubricant dynamic viscosity ( $\mu$ ) is assumed to vary with pressure ( $p$ ) according to the Barus viscosity – pressure relation,

$$\mu = \mu_0 e^{\beta p} \quad (1)$$

where  $\mu_0$  is the reference viscosity at atmospheric pressure and  $\beta$  represents the pressure – viscosity coefficient. This piezo-viscous behaviour represents the increase in lubricant viscosity under high-pressure operating conditions. Furthermore, the lubricant rheology is described using Stokes' couple stress fluid theory, which models the lubricant as a non-Newtonian fluid with microstructural effects represented through the couple stress parameter material constant ( $\eta$ ), which

characterizes the microstructural properties of the fluid. The non-dimensional couple stress parameter ( $l^*$ ) is defined as  $l^* = \frac{l}{h_0}$ , where  $l = \sqrt{\frac{\eta}{\mu}}$  is the characteristic couple stress length scale and  $h_0$  is the initial lubricant film thickness. This relationship was first established by Barus [4] in his study on viscosity – pressure dependence. The importance of incorporating viscosity variation in lubrication analysis has been demonstrated by Sangeetha and Govindarajan [5] in their work on viscosity variation with magnetohydrodynamic effects, and by Naduvinamani and Kadadi [6] in their investigation of micropolar fluid lubrication in journal bearings. Dass et al. [7] further emphasized that variable viscosity plays a key role in enhancing load-carrying capacity. Additional studies by Naduvinamani et al. [8] and Salma and Hanumagowda [9] confirmed that neglecting viscosity variation leads to inaccurate predictions, particularly in thin film lubrication systems.

The boundary condition at the lubricant–surface interface is equally important. The classical no-slip condition becomes invalid in micro-scale flows, where velocity slip occurs due to fluid–surface interactions. Lauga et al. [10], in their work on microfluidics and the no-slip boundary condition, highlighted the limitations of classical assumptions. Similarly, Vinogradova [11] and Choi and Kim [12] demonstrated that slip flow significantly alters fluid motion and shear behaviour. The combined influence of viscosity variation and slip velocity has been studied by Dass et al. [13] and Kousar et al. [14], who showed that these effects improve pressure distribution and load-carrying capacity in lubrication systems.

The incorporation of porous materials into bearing design further enhances lubrication performance by enabling fluid flow through the bearing matrix. This behaviour is described using Darcy's law, as presented by Bear [15] in his comprehensive study on fluid flow in porous media. The non-dimensional permeability parameter ( $\psi$ ) is defined as  $\psi = \frac{k\delta}{h_0^3}$ , where  $k$  is the Darcy permeability of the porous matrix and  $\delta$  denotes the porous layer thickness. Boussaha et al. [16] investigated non-Newtonian couple-stress squeeze film behaviour between porous circular discs and demonstrated improved stability. Similarly, Naduvinamani and Siddangouda [17] analyzed porous lubrication with couple stress fluids and reported enhanced load-carrying capacity. Ramesh and Devakar [18] analyzed fluid transport within a non-Darcy porous matrix under electroosmotic forcing, utilizing lubrication approximation and perturbation techniques. Their study highlights how porous permeability and moving boundary interfaces significantly restrict the flow field profile. Salma and Hanumagowda [19] also emphasized the importance of viscosity variation in porous lubrication systems.

Recent studies have focused on advanced modeling approaches and lubrication configurations. Vinutha et al. [20] examined the effect of couple stress and slip velocity on squeeze film lubrication and reported improved performance characteristics. Hanumagowda B.N. et al. [21] studied the combined influence of surface roughness and MHD on porous conical bearings lubricated with a conducting couple-stress fluid and observed enhanced lubrication performance. Kashinath et al. [22] investigated the squeeze film characteristics of porous conical bearings with combined effects of piezo-viscous dependency and non-Newtonian couple stresses. Vadher et al. [23] studied the effect of transverse surface roughness on the performance of hydromagnetic squeeze films between conducting truncated conical plates, while Hanumagowda et al. [24] analyzed the effects of MHD and couple stress on conical bearings. More recently, Kempepatil et al. [25] examined the influence of magneto-hydrodynamic and couple stress squeeze film lubrication on conical bearing: A slip velocity model and reported significant improvements in pressure distribution and load-carrying capacity. B.Kashinath and Upadhya A.C. [26] recently analyzed the combined impacts of surface roughness and couple stress fluids on the performance of porous slider bearings. Their findings provide a foundation for extending these non-Newtonian squeeze film characteristics to more complex porous conical geometries.

A comprehensive analysis that incorporates viscosity variation, slip velocity, couple stress fluid behaviour, and porous effects in conical bearings remains limited. Since the present analysis considers laminar thin-film lubrication flow, the governing formulation is based on a modified Reynolds lubrication equation, derived from the continuity and momentum equations under lubrication approximations. The equation is modified to incorporate the effects of couple stress fluid rheology, viscosity variation, velocity slip, and porous media characteristics.

The present study develops a modified Reynolds equation, obtained by extending the classical Reynolds lubrication equation to incorporate the effects of couple stress fluid behaviour, pressure-dependent viscosity, velocity slip, and porous medium flow. This unified formulation enables the combined influence of these effects on bearing performance to be investigated. The model is employed to examine the combined influence of viscosity variation, slip velocity, permeability, and couple stress parameters on key performance characteristics, including pressure distribution, load-carrying capacity, and squeeze film time. This approach offers a more realistic and detailed understanding of lubrication behaviour, which is important for the optimal design and improved efficiency of porous conical bearing systems.

Based on the literature review, no study has yet analyzed the combined effects of viscosity variation, couple stress, and slip velocity on porous conical bearings. Therefore, the objective of this paper is to investigate these coupled effects on the squeeze film lubrication characteristics of porous conical bearings to provide a more realistic prediction of bearing performance.

## 2. Mathematical formulation and solution of the problem

Fig. 1 illustrates the geometrical configuration of the porous conical bearing and lubricant film region considered in the present study. The effects of non-Newtonian couple stress fluid behaviour and velocity slip are incorporated through

the governing equations and boundary conditions. The local lubricant film thickness between the conical surfaces is denoted by  $h$  and the non-dimensional film thickness parameter is expressed as  $h^* = \frac{h}{h_0}$ . The squeezing velocity of the upper surface is given by  $\sin \theta \frac{\partial h}{\partial t}$ , where  $\theta$  represents the semi-cone angle of the bearing. The present study examines the squeeze film lubrication characteristics of a porous conical bearing lubricated with a non-Newtonian couple stress fluid under viscosity variation and velocity slip. The lubricant is assumed to be thin, incompressible, axisymmetric, and laminar. The lower surface is porous and governed by Darcy's law, while the upper surface moves with squeezing motion.

The lubricant is modeled as an incompressible non-Newtonian couple stress fluid based on Stokes' couple stress fluid theory [1]. The constitutive relation for the stress tensor is given by

$$\tau_{ij} = -p\delta_{ij} + 2\mu d_{ij} - \eta \nabla^2 d_{ij} \quad (2)$$

where  $\tau_{ij}$  is the stress tensor,  $p$  is the pressure,  $\mu$  is the dynamic viscosity,  $d_{ij}$  is the rate of deformation tensor, and  $\eta$  is the couple stress material constant representing microstructural effects in the lubricant. Equation (2) represents a simplified form of the general constitutive relation proposed by Stokes [1]. Under the assumptions of incompressible thin-film lubrication flow, axisymmetry, negligible body couples, and lubrication approximations, the general couple stress constitutive equation reduces to the form employed in the present analysis. Therefore, Equation (2) should be regarded as a lubrication-theory representation derived from the original Stokes model rather than a direct reproduction of Equation (3.1) presented in Stokes [1].

It should be noted that the present study employs Stokes' couple stress fluid theory rather than micropolar fluid theory. Unlike micropolar fluids, which include independent microrotation and rotational viscosity effects, the couple stress fluid model accounts for microstructural behaviour through higher-order stress gradients characterized by the material constant  $\eta$ . Therefore, rotational viscosity is not considered in the present formulation. In the present formulation, the lubricant exhibits non-Newtonian rheology based on Stokes' couple stress fluid model, while viscosity variation is assumed to be pressure-dependent according to the Barus exponential law.

It should be emphasized that the pressure-dependent viscosity and couple stress effects represent two distinct physical mechanisms. The Stokes couple stress model accounts for the microstructural characteristics of the lubricant through the material parameter  $\eta$ , whereas the Barus relation  $\mu = \mu_0 e^{\beta p}$  is employed to describe the experimentally observed increase in viscosity under high-pressure conditions. Although the original Stokes theory is generally formulated for fluids with constant material properties, the incorporation of the Barus viscosity law is a commonly adopted engineering approximation in lubrication analysis to account for piezo-viscous effects. Therefore, the present study considers a lubricant exhibiting both couple stress and pressure-dependent viscosity characteristics, providing a more realistic representation of practical lubricants used in bearing applications. Based on lubrication theory, the governing equations are obtained from momentum and continuity equations. Equation (3) represents the radial momentum equation for a couple stress fluid, Equation (4) assumes negligible pressure variation across the film thickness, and Equation (5) represents mass conservation within the lubricant film.

$$\mu \frac{\partial^2 u}{\partial z^2} - \eta \frac{\partial^4 u}{\partial z^4} = \frac{\partial p}{\partial r} \quad (3)$$

$$\frac{\partial p}{\partial z} = 0 \quad (4)$$

$$\frac{1}{r} \frac{\partial(ru)}{\partial r} + \frac{\partial w}{\partial z} = 0 \quad (5)$$

The flow of lubricant through the porous matrix is modeled using Darcy's law. The lower conical surface is assumed to be porous, homogeneous, and isotropic, allowing lubricant seepage through the porous medium. For consistency with the governing momentum and continuity equations presented earlier, the porous-medium flow equations are first expressed in dimensional form. The seepage velocity components in the radial and transverse directions are denoted by  $u_p$  and  $w_p$ , respectively. Accordingly, the Darcy flow equations governing lubricant transport through the porous matrix are written as follows:

$$u_p = -\frac{k}{\mu(1-\beta)} \frac{\partial p}{\partial r} \quad (6)$$

$$w_p = -\frac{k}{\mu(1-\beta)} \frac{\partial p}{\partial z} \quad (7)$$

$$\frac{1}{r} \frac{\partial(ru_p)}{\partial r} + \frac{\partial w_p}{\partial z} = 0 \quad (8)$$

It should be noted that Equations (3)–(8) are expressed in dimensional form. The velocity distribution and the modified Reynolds equation are first derived using dimensional variables. Subsequently, appropriate nondimensional variables and parameters are introduced to obtain the final nondimensional governing equation.

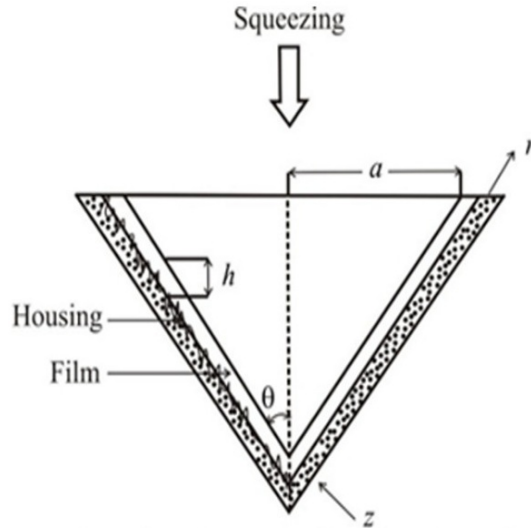


FIG. 1. Geometrical representation of the porous conical bearing

The relevant boundary conditions for the velocity components are:

(i) At the lower surface:  $y = 0$

$$\frac{\alpha}{\sqrt{k}}(u - u_p) = \left(\frac{\partial u}{\partial z}\right), \quad \frac{\partial^2 u}{\partial z^2} = 0 \quad (9)$$

$$w = w_p \quad (10)$$

(ii) At the upper surface:  $z = h \sin \theta$

$$u = 0, \quad \frac{\partial^2 u}{\partial z^2} = 0 \quad (11)$$

$$w = \sin \theta \frac{\partial h}{\partial t} \quad (12)$$

By solving equations (3) and (4) with given boundary conditions (9) and (11), the velocity component  $u$  can be obtained as follows.

$$u = \left[ \frac{1}{2\mu_0 e^{\beta p}} \frac{\partial p}{\partial r} \right] \left\{ z(z - h) + 2l^2 \left[ 1 - \frac{\cosh\left(\frac{2z-h}{2l}\right)}{\cosh\left(\frac{h}{2l}\right)} \right] + \xi_1 h - \xi_2 h l \tanh\left(\frac{h}{2l}\right) \right\} \quad (13)$$

where  $\xi_1 = \frac{3[2s^2\alpha^2 + (1 - \beta)sh]}{h(h + s)(1 - \beta)}$  and  $\xi_2 = \frac{s}{h + s}$ .

To obtain the equation for pressure, we first substitute Equation (13) into the continuity equation (5) and then perform the integration. By incorporating the boundary conditions given in Equations (10) and (12), the final form of the modified Reynolds lubrication equation for laminar thin-film flow is obtained as:

The modified Reynolds type equation for pressure is:

$$\frac{1}{r} \frac{\partial}{\partial r} \left[ \frac{r f(h, \xi_1, \xi_2, l)}{12\mu_0 e^{\beta p}} \frac{\partial p}{\partial r} \right] + \frac{k\delta}{1 - \beta} \nabla^2 p = 12 \frac{\partial h}{\partial t}, \quad (14)$$

where,

$$f(h, \xi_1, \xi_2, l) = (1 + \xi_1)h^3 - 6l^2h \left[ h - \xi_2 l \tanh\left(\frac{h}{2l}\right) \right] - 12l^3 \tanh\left(\frac{h}{2l}\right)$$

The volume flux of the lubricant is given by the following formula:

$$Q = 2\pi r \int_0^h u \, dz \quad (15)$$

where  $u$  is the velocity component given in Eq. (13).

After obtaining the dimensional modified Reynolds equation (14), the following nondimensional variables and parameters are introduced to facilitate the analysis and numerical computation.

$$r^* = \frac{r}{R}, \quad h^* = \frac{h}{h_0}, \quad l^* = \frac{l}{h_0}, \quad p^* = \frac{ph_0^3}{\mu_0 R^2 \left(\frac{\partial h}{\partial t}\right) \sin \theta}, \quad G = \frac{\beta \mu_0 R^2 \left(\frac{\partial h}{\partial t}\right) \sin \theta}{h_0^3}, \quad \psi = \frac{k\delta}{h_0^3}, \quad \sigma^* = \frac{s}{h_0}$$

The characteristic quantities used for nondimensionalization are the bearing radius  $R$  and the initial lubricant film thickness  $h_0$ . Thus, the radial coordinate, film thickness, couple stress parameter, and slip length are scaled by  $R$  and  $h_0$  according to  $r^* = r/R$ ,  $h^* = h/h_0$ ,  $l^* = l/h_0$ , and  $\sigma^* = s/h_0$ . The dimensionless slip parameter  $\sigma^*$  therefore, represents the ratio of the slip length to the initial film thickness. For example,  $\sigma^* = 0.6$  indicates that the slip length is 60% of the initial lubricant film thickness. Such values correspond to relatively strong slip conditions that may occur in highly smooth, porous, hydrophobic, or micro-/nano-scale lubricated interfaces.

Substituting the non-dimensional variables into Eq. (14), the non-dimensional modified Reynolds lubrication equation, valid for laminar thin-film flow in porous conical bearings, is obtained in the form

$$\frac{\partial}{\partial r^*} \left[ e^{-Gp^*} (f^*(h^*, \chi_1, \chi_2, l^*, G, \psi)) r^* \frac{\partial p^*}{\partial r^*} \right] = 12r^* \quad (16)$$

where

$$f^*(h^*, \chi_1, \chi_2, l^*, G, \psi) = \left[ (h^* \sin \theta)^3 (1 + \chi_2) - 6(h^* \sin \theta)^2 l^* \chi_1 \tanh \left( \frac{h^* \sin \theta}{2l^*} \right) - 12l^{*2} \left[ h^* \sin \theta - 2 \tanh \left( \frac{h^* \sin \theta}{2l^*} \right) \right] + \frac{12\psi}{1 - \beta} \right].$$

and

$$\chi_1 = \frac{\sigma^*}{h^* \sin \theta + \sigma^*}, \quad \chi_2 = \frac{3(1 - \beta)^2 (\sigma^*)^2 \alpha^2}{h^{*2} \sin^2 \theta + \sigma^* h^* \sin \theta + (1 - \beta) \sigma^* (h^* \sin \theta + \sigma^*)}.$$

The pressure boundary conditions are:

$$\frac{\partial p^*}{\partial r^*} = 0 \quad \text{at} \quad r^* = 0 \quad (17)$$

$$p^* = 0 \quad \text{at} \quad r^* = 1 \quad (18)$$

By performing an integration of the nondimensional modified lubrication equation in relation to  $r^*$  and incorporating the pressure boundary conditions, one obtains

$$p^* = -\frac{1}{G} \ln \left[ \frac{3G(r^{*2} - 1)}{f^*(h^*, \chi_1, \chi_2, l^*, G, \psi)} + 1 \right] \quad (19)$$

The non-dimensional load-carrying capacity  $w^*$ , is obtained by integrating the film pressure over the bearing area:

$$W^* = \frac{2\pi}{G} \int_0^1 \ln \left[ \frac{3G(r^{*2} - 1)}{f^*(h^*, \chi_1, \chi_2, l^*, G, \psi)} + 1 \right] r^* dr^* \quad (20)$$

The squeeze film time is obtained by integrating the velocity equation:

$$T^* = \frac{2\pi}{G} \int_{h_f^*}^1 \int_0^1 \ln \left[ \frac{3G(r^{*2} - 1)}{f^*(h^*, \chi_1, \chi_2, l^*, G, \psi)} + 1 \right] r^* dr^* dh^* \quad (21)$$

Following the numerical resolution of the film pressure distribution, the integrated bearing metrics can be determined. The total load-carrying capacity of the bearing is evaluated in its dimensionless form as  $w^*$ , while the total operational duration of the squeezing film is represented by the non-dimensional squeeze film time ( $T^*$ ).

### 3. Results and discussion

The effects of viscosity variation, slip velocity, couple stress fluid behaviour, and permeability on the squeeze film characteristics of porous conical bearings are analyzed using the modified Reynolds equation through numerical evaluation of pressure distribution, load-carrying capacity, and squeeze film time. Physically, an increase in the viscosity variation parameter enhances the effective lubricant viscosity under pressure, thereby increasing resistance to flow and promoting greater pressure development within the lubricant film. Consequently, both the load-carrying capacity and squeeze film time increase. Similarly, increasing the couple stress parameter strengthens the microstructural interactions within the lubricant, resulting in higher fluid stiffness and greater resistance to film thinning. This leads to improved pressure generation, enhanced load support, and longer squeeze film duration. In contrast, slip velocity reduces the shear resistance at the lubricant-surface interface, facilitating fluid motion and reducing pressure build-up. Likewise, increasing the permeability of the porous matrix allows greater lubricant seepage through the bearing surface, thereby reducing fluid retention within the film and lowering the load-carrying ability of the bearing. These observations indicate that lubricants possessing microstructural characteristics and pressure-dependent viscosity can significantly improve bearing performance compared with conventional Newtonian lubricants, while slip and permeability effects tend to moderate these improvements.

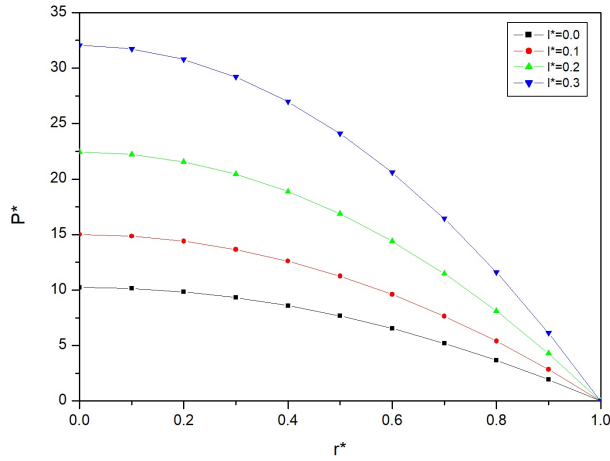


FIG. 2. Variation of non-dimensional pressure  $P^*$  with  $r^*$  for different values of  $l^*$  with  $G = 0.03$ ,  $h^* = -0.7$ ,  $\sigma = 0.2$ ,  $\psi = 0.01$ ,  $\theta = \frac{\pi}{3}$ .

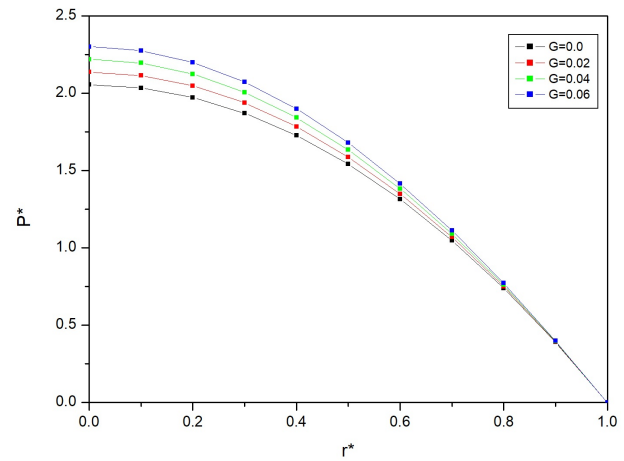


FIG. 3. Variation of non-dimensional pressure  $P^*$  with  $r^*$  for different values of  $G$  with  $h^* = -0.7$ ,  $l^* = 0.2$ ,  $\sigma = 0.2$ ,  $\psi = 0.01$ ,  $\theta = \frac{\pi}{3}$ .

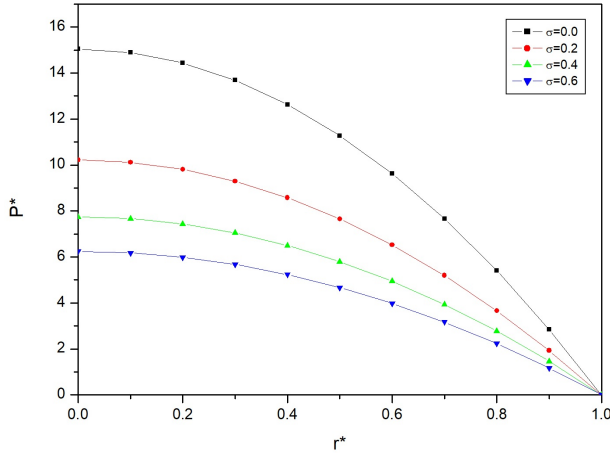


FIG. 4. Variation of non-dimensional pressure  $P^*$  with  $r^*$  for different values of  $\sigma$  with  $l^* = 0.2$ ,  $h^* = 0.7$ ,  $G = 0.03$ ,  $\psi = 0.01$ ,  $\theta = \frac{\pi}{3}$ .

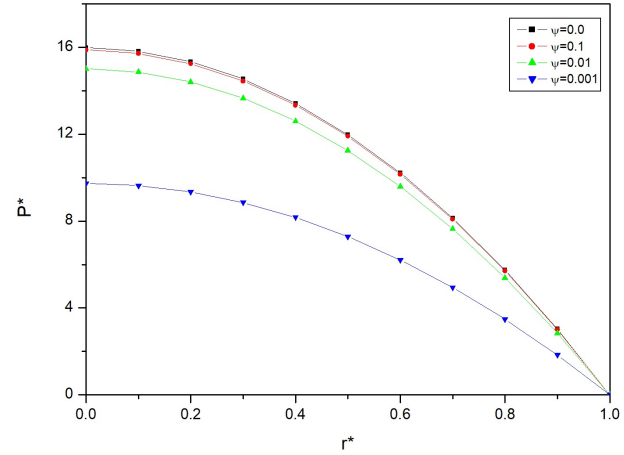


FIG. 5. Variation of non-dimensional pressure  $P^*$  with  $r^*$  for different values of  $\psi$  with  $h^* = 0.7$ ,  $l^* = 0.2$ ,  $\sigma = 0.2$ ,  $G = 0.03$ ,  $\theta = \frac{\pi}{3}$ .

### 3.1. Squeeze film pressure

Figure 2 illustrates the distribution of dimensionless pressure  $P^*$  across the dimensionless radial coordinate  $r^*$ . The data reveals that  $P^*$  rises from 0 to 0.3. This enhancement is attributed to the increased internal resistance characteristic of micro-structure fluids, which necessitates higher pressure gradients to maintain flow. Physically, increasing the couple stress parameter enhances the microstructural resistance of the lubricant due to suspended additives or long-chain molecules, thereby strengthening momentum transfer and promoting higher pressure generation within the lubricant film. Similarly, Fig. 3 indicates that an increase in the viscosity variation parameter significantly boosts the dimensionless pressure, as higher local viscosity offers greater resistance to lubricant deformation, a typical non-linear behaviour in non-Newtonian lubrication regimes. Physically, increasing viscosity under pressure increases internal flow resistance, thereby restricting lubricant motion and enhancing pressure development in the squeeze film region.

Figure 4 illustrates the effect of the dimensionless slip length parameter  $\sigma^*$ , varied from 0 to 0.6, where  $\sigma^* = 0$  corresponds to the classical no-slip condition. The upper limit  $\sigma^* = 0.6$  represents relatively strong interfacial slip conditions, which may occur in lubricated systems with highly smooth or hydrophobic surfaces, porous interfaces, polymer-enhanced lubricants, or micro-/nano-scale thin-film applications where slip effects become significant. It is observed that increasing  $\sigma^*$  results in a reduction of  $P^*$ , as interfacial slip decreases flow resistance at the boundary. Physically, larger slip lengths reduce shear resistance at the lubricant–surface interface, allowing easier fluid motion and reducing pressure build-up



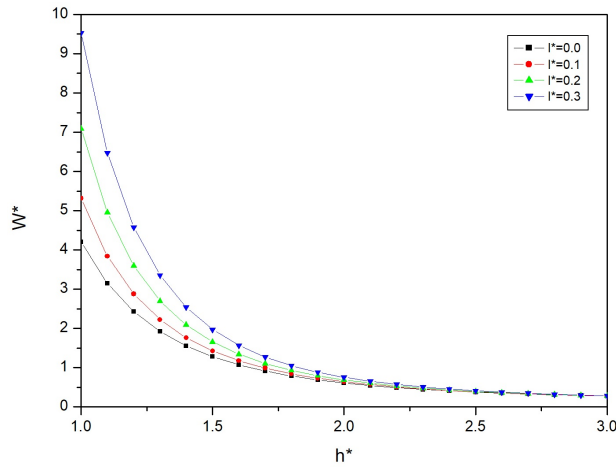


FIG. 6. Variation of non-dimensional Load carrying capacity  $W^*$  with  $h^*$  for different values of  $l^*$  with  $G = 0.03$ ,  $\sigma = 0.2$ ,  $\psi = 0.01$ ,  $\theta = \frac{\pi}{3}$ .

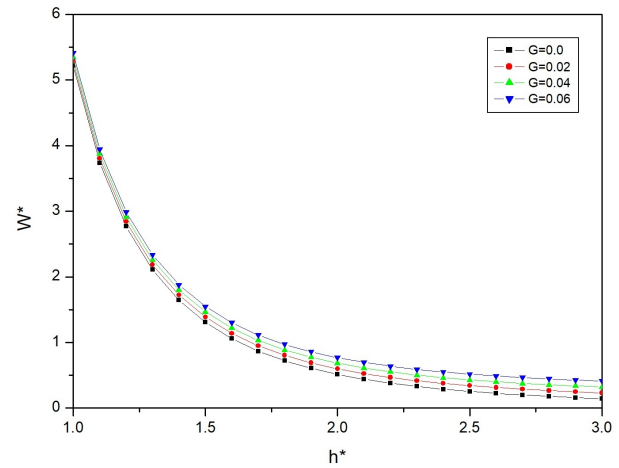


FIG. 7. Variation of non-dimensional Load carrying capacity  $W^*$  with  $h^*$  for different values of  $G$  with  $l^* = 0.2$ ,  $\sigma = 0.2$ ,  $\psi = 0.01$ ,  $\theta = \frac{\pi}{3}$ .

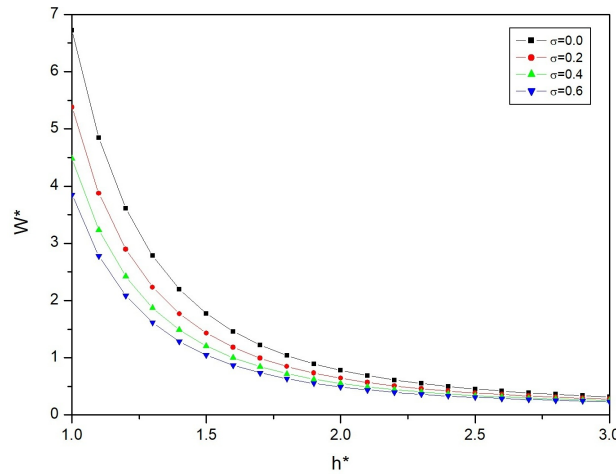


FIG. 8. Variation of non-dimensional Load carrying capacity  $W^*$  with  $h^*$  for different values of  $\sigma$  with  $l^* = 0.2$ ,  $G = 0.03$ ,  $\psi = 0.01$ ,  $\theta = \frac{\pi}{3}$ .

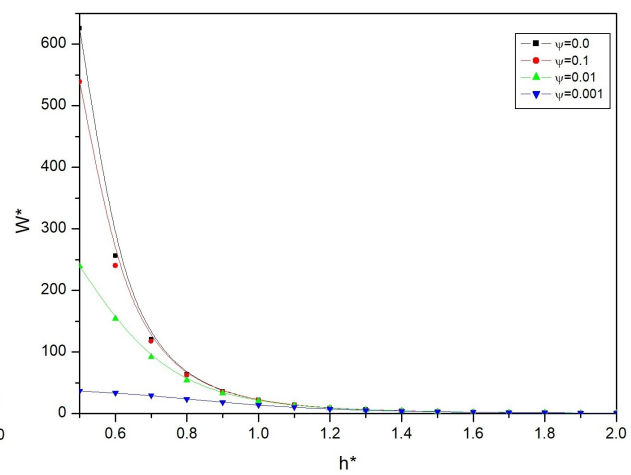


FIG. 9. Variation of non-dimensional Load carrying capacity  $W^*$  with  $h^*$  for different values of  $\psi$  with  $l^* = 0.2$ ,  $G = 0.03$ ,  $\sigma = 0.2$ ,  $\theta = \frac{\pi}{3}$ .

within the lubricant film. Consequently, the load-carrying capacity of the bearing decreases under stronger slip conditions. Finally, in the present analysis, porous effects are represented through the non-dimensional permeability parameter  $\psi$ , which characterizes the ease of lubricant flow through the homogeneous porous matrix. Different values of  $\psi$  are considered to examine the influence of porous structure on bearing performance. Fig. 5 demonstrates that an increase in the permeability parameter  $\psi$  leads to a decrease in dimensionless pressure, highlighting that higher permeability in the porous medium facilitates fluid flow and lowers the pressure within the film. From a physical perspective, increasing permeability allows greater lubricant seepage through the porous matrix, reducing lubricant retention within the film and consequently lowering pressure generation.

### 3.2. Load carrying capacity

Figures 6–9 illustrate the relationship between the minimum film height and the dimensionless load-carrying capacity ( $W^*$ ) for various values of the couple stress parameter ( $l^*$ ), viscosity variation ( $G$ ), slip velocity ( $\sigma$ ), and permeability ( $\psi$ ). As shown in Figs. 6,7,  $W^*$  increases as  $l^*$  increases and  $G$  increases. This behavior is attributed to the fact that higher couple stresses introduce internal micro-rotational effects that enhance fluid stiffness, while increased viscosity strengthens resistance to flow; both factors improve the lubricant's ability to support applied loads. Fig. 8 reveals that  $W^*$  decreases as the dimensionless slip length parameter ( $\sigma^*$ ) increases, since greater interfacial slip reduces pressure build-up within the lubricant film. The relatively higher value  $\sigma^* = 0.6$  corresponds to conditions of enhanced slip, which may



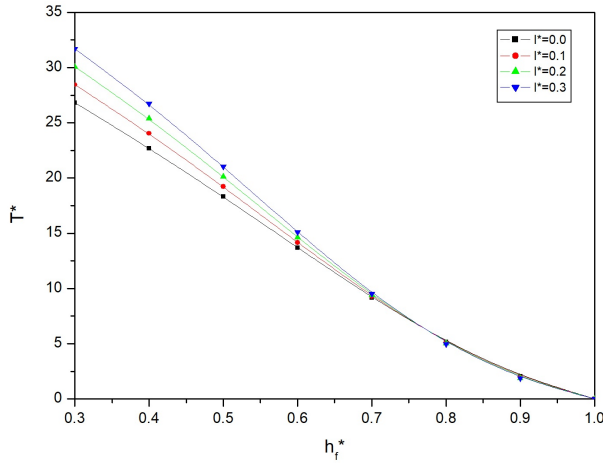


FIG. 10. Variation of squeeze film time  $T^*$  with  $h_f^*$  for different values of  $l^*$  with  $G = 0.03$ ,  $\sigma = 0.2$ ,  $\psi = 0.01$ ,  $\theta = \frac{\pi}{3}$ .

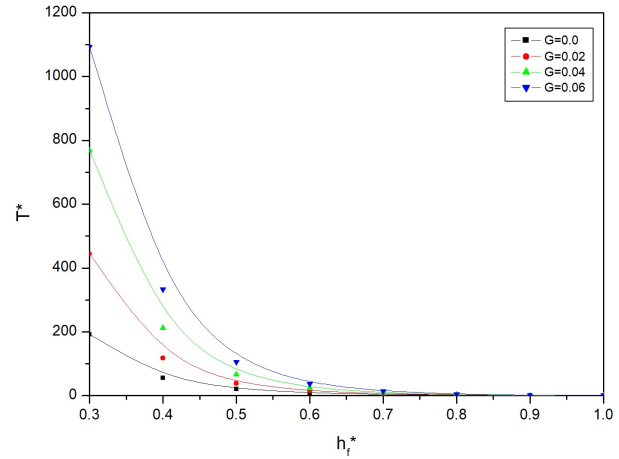


FIG. 11. Variation of squeeze film time  $T^*$  with  $h_f^*$  for different values of  $G$  with  $l^* = 0.2$ ,  $\sigma = 0.2$ ,  $\psi = 0.01$ ,  $\theta = \frac{\pi}{3}$ .

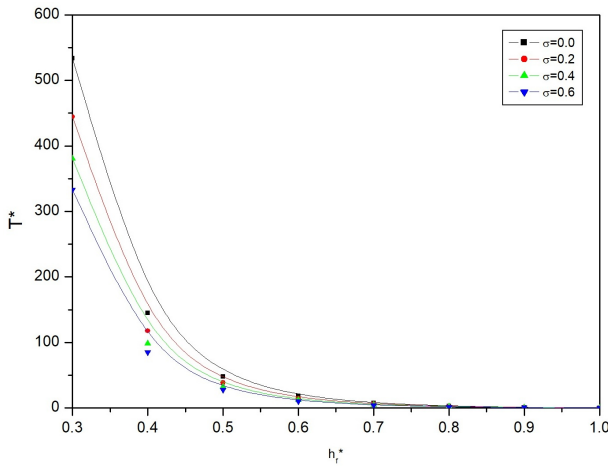


FIG. 12. Variation of squeeze film time  $T^*$  with  $h_f^*$  for different values of  $\sigma$  with  $l^* = 0.2$ ,  $G = 0.03$ ,  $\psi = 0.01$ ,  $\theta = \frac{\pi}{3}$ .

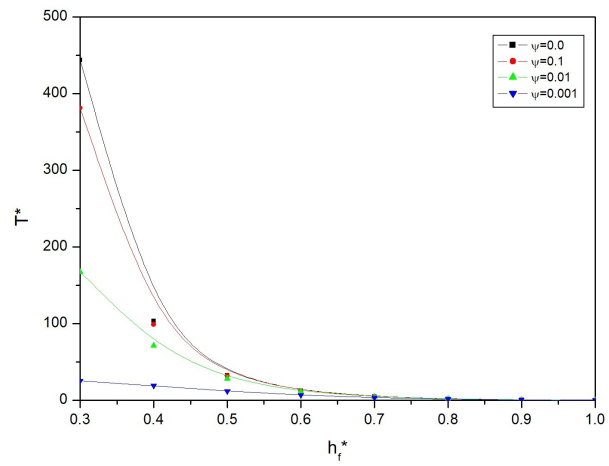


FIG. 13. Variation of squeeze film time  $T^*$  with  $h_f^*$  for different values of  $\psi$  with  $l^* = 0.2$ ,  $G = 0.03$ ,  $\sigma = 0.2$ ,  $\theta = \frac{\pi}{3}$ .

arise in highly smooth, porous, or hydrophobic bearing interfaces and in thin-film lubrication systems containing polymer additives. Finally, Fig. 9 demonstrates that an increase in the permeability parameter ( $\psi$ ) leads to a decrease in  $W^*$ , as higher permeability allows more lubricant to pass into the porous medium, thereby reducing hydrodynamic pressure and load-carrying capacity.

### 3.3. Squeeze film time

In Fig. 10, the dimensionless squeeze film duration ( $T^*$ ) is shown to increase as the couple stress parameter ( $l^*$ ) rises from 0 to 0.3. A similar trend is observed in Fig. 11, where  $T^*$  increases with the viscosity variation parameter ( $G$ ). This behavior occurs because both couple stress effects and higher viscosity increase the internal resistance to fluid motion, thereby stiffening the lubricant film and extending the time required for film thinning. Fig. 12 shows that the squeeze film duration decreases as the dimensionless slip velocity ( $\sigma$ ) increases, since boundary slip promotes faster fluid escape from the bearing gap. Finally, Fig. 13 illustrates that an increase in the permeability parameter ( $\psi$ ) further reduces the squeeze film time, as the porous medium provides an additional path for fluid flow, leading to a more rapid reduction of the lubricant film thickness.

#### 4. Conclusions

This research provides a comprehensive analysis of the squeeze film characteristics in porous conical bearings by extending the classical Reynolds lubrication equation to include the effects of pressure-dependent viscosity, couple stress fluid behaviour, velocity slip, and porous medium permeability. The results demonstrate that viscosity variation and couple stress effects significantly enhance pressure distribution, load-carrying capacity, and squeeze film time by increasing flow resistance and fluid stiffness. Conversely, slip velocity reduces these parameters by lowering interfacial shear resistance, while higher permeability decreases pressure and load support by facilitating lubricant escape through the porous matrix. The use of non-Newtonian lubricants together with viscosity variation enhances bearing performance, while slip and permeability diminish these improvements. The findings contribute to a better understanding of lubrication behaviour and may aid in the design and optimization of porous conical bearings.

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## Effect of roughness geometry and temperature on adsorption of argon flow in Nano-channels: A molecular dynamics approach

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**ABSTRACT** Nanochannels have surface roughness due to their non-ideal surfaces. These roughnesses on the surface of nanochannels have an important effect on the flow behavior of argon atoms. This study examined the argon flow in nanochannels under various roughness geometries via molecular dynamics simulation. Also, the researchers investigated the adsorption rate, density, and diffusion of argon atoms under different temperatures and height roughness in nanochannels. The results showed that nanochannels with cylindrical roughness exhibit higher levels of interaction energy (adsorption) ( $-149$  kcal/mol) and density ( $144$  g/cm<sup>3</sup>) compared to nanochannels with square and conical roughness. Furthermore, as the height roughness of the nanochannels is increased ( $11$  to  $20$  Å), the amount of adsorption (interaction energy) and density rise as well. By comparing the MSD (mean square displacement) diagram of nanochannels, the nanochannels with the highest diffusion of argon atoms have cone roughness in contrast to square and cylinder nanochannel roughness.

**KEYWORDS** adsorption; diffusion coefficient; roughness geometry; argon; nanochannels.

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### 1. Introduction

Over the past decade, significant advancements in nanoscale science have enabled researchers to investigate the behavior of nanofluid flow in nanochannels more precisely. Investigating fluid flow behavior in nanochannels is a highly practical and compelling issue [1–8]. Roughness is always present on the surface of nanochannels due to their non-ideality, significantly affecting the flow behavior of nanoparticles in nanochannels. Also, these roughnesses directly affect the adsorption and diffusion of nanoparticles in nanochannels. As a result, it is essential to investigate nanoparticle adsorption and diffusion in nanochannels. Compared to experimental methods, nano-scale simulation methods provide a cost-effective and highly accurate alternative, eliminating environmental errors and enabling researchers to precisely investigate particle flow behaviors in nanochannels. In previous studies on nanoparticle flow behavior in nanochannels, Chen et al. [9] found that an increase in obstacles in nanochannels leads to a change in the density of argon atoms from  $0.099$  to  $0.093$  atoms/Å<sup>3</sup>. Also, Pang et al.'s study [10] on the flow of gases in nanochannels with different geometries shows that the geometry of nanochannels has a significant effect on the speed of gas flow.

In a molecular dynamics study, Motlagh and Kalteh [11] investigated the convective heat transfer of argon in nanochannels with different roughness effects. Their results show that increasing the roughness in nanochannels raises the Nusselt number (displacement heat transfer). In another molecular dynamics study, Rashidi et al. [12] indicate that the roughness and unevenness of nanochannels reduce the fluctuations in the density of argon atoms. Also, increasing the height of the roughness results in a greater impact on the flow. In addition, the findings of the study by Motlagh and Kalte [13] on the behavior of argon poise flow in copper nanochannels reveal that the roughness of the nanochannels improves the heat transfer between the argon atoms and the walls of the nanochannels. In the same vein, it was demonstrated that the presence of aluminium nanoparticle barriers in zigzag nanochannels increases the density and temperature of argon fluid [14]. Increasing the surface roughness of nanochannels reduces the length of the thermal gradient and escalates the Nusselt number [15]. In addition, raising the number of layers in nanochannels increases nanofluids (accumulation) to the nanochannel wall [16]. Reducing the surface roughness in copper nanochannels enhances the average velocity of water nanofluid [17]. Furthermore, the results of the study by Meng et al. [18] show that by raising the roughness of nanochannels, the density of atoms increases and also improves heat transfer. In another study, Akbari et al. [19] demonstrated that wall temperature and obstacles in nanochannels significantly affect the flow parameters. Obstacles reduce the range of motion fluctuations of argon atoms and improve the thermal conductivity coefficient. The results of Qin et al. [20] show that the fluid growth rate of the hot wall is  $10.5\%$  higher than that of the cold wall in nanochannels. Among the nanostructures (square and triangular), the triangular nanostructure has the least resistance and friction against the flow. Furthermore, the presence of holes in the nanochannels causes the argon atoms to absorb additional energies

from the walls of the nanochannels, which improves the heat transfer efficiency [21]. In a molecular dynamics study on copper/argon nanochannels, Akbari et al [22] show that with larger barriers in the structure of nanochannels, the attractive force is stronger compared to smooth nanochannels (increase in the density of argon atoms around 17.3%). The roughness of the surfaces in the nanochannels can prevent the reduction of the pressure drop [23]. Another study shows that the fluid viscosity and, consequently, the flow resistance in a nanochannel can be modified by changing the material of the nanochannel walls [24]. In the present study, we used molecular dynamics simulation to examine the adsorption rate, diffusion, and density of argon flow in nanochannels with different surface roughness (square, cone, smooth, cylinder) and temperatures. Given the significance of this subject and the findings of previous studies, it was imperative to investigate these parameters.

## 2. Method and simulation

The nanochannels are modeled with argon flow using Lammmps molecular dynamics simulation software [25]. The dimensions of the nanochannels are modelled as  $100 \times 100 \times 240$  Angstrom. Each nanochannel contains 500 argon atoms. Also, nanochannels have different roughness geometries, including conical, square, cylindrical and smooth (without roughness). The nanochannel surface was designed as a square area of  $100 \times 100$  Å and was divided into four equal sections to incorporate roughness geometries. Three different roughness shapes were modeled: a square with dimensions of  $10 \times 10$  Å, a cylinder with a diameter of 10 Å, and a cone with a base diameter of 10 Å. For each geometry, roughness heights of 11, 14, 17, and 20 Å were considered. The roughness structures were arranged such that the center-to-center distance between adjacent geometries was 50 Å. Also, these roughnesses are created on both sides of the bottom and top of the nanochannel as four pieces in the nanochannels. Fig. 1 shows the graphical output of different nanochannels under different roughnesses. The simulation system is configured as an NVT ensemble with constant atom number, constant volume, and temperature. The pressure of argon inside the nanochannels was maintained at 1 atmosphere, and the simulations were conducted at a temperature of 125 K. The temperatures of the nanochannel walls and the argon fluid were assumed to remain identical throughout the simulation. Furthermore, the system energy was equilibrated using the energy minimization command. Additionally, the boundary conditions in both the X and Y directions of the nanochannels are assumed to be periodic. Also, run repetitions and the rate of time steps were considered to be 200,000 and 0.001 for all the simulations, respectively. Also, the total simulation time lasted 300 picoseconds.

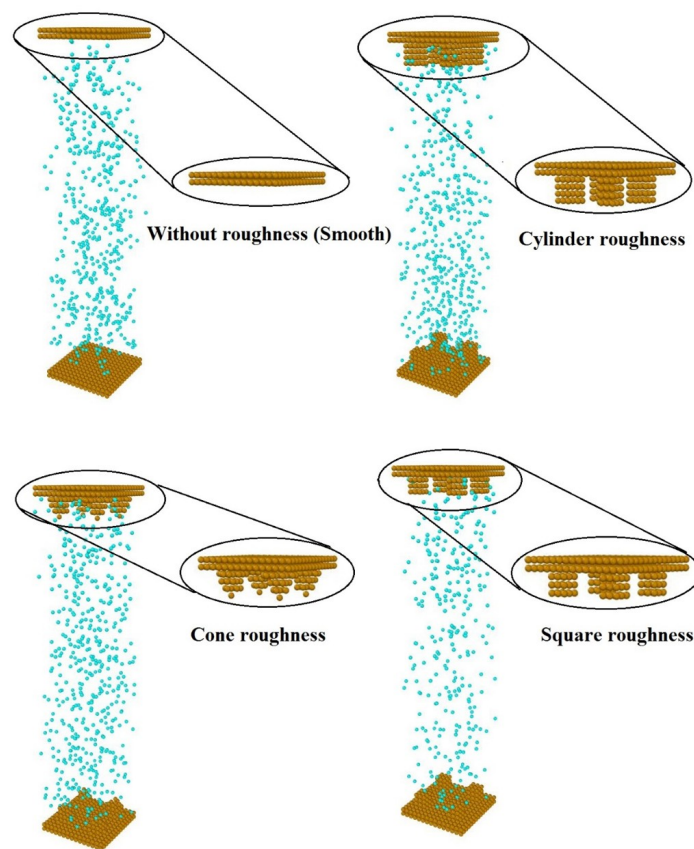


FIG. 1. The graphical output of different nanochannels under different roughnesses

### 2.1. Force fields

The nanochannels were composed of platinum metal (Pt) atoms, and the interaction between atoms was defined using the EAM force potential [26]. Equation 1 presents the EAM force potential.

$$E_i = F_\alpha \left( \sum_{i \neq j} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{\alpha\beta}(r_{ij}). \quad (1)$$

In this equation,  $E_i$  represents the total energy.  $F_\alpha$  is the embedded energy.  $r_{ij}$  shows the distance between two atoms of  $i$  and  $j$ . Also, the Lennard-Jones potential [27] was used to define the interaction between argon atoms and platinum atoms of nanochannels. The force potential equation of Leonard-Jones is given in Equation 2.

$$\phi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (2)$$

In this Equation,  $R_c$  is the cutoff radius,  $r$  is the distance between atoms,  $\varepsilon$  is the interaction strength ratio, and  $\sigma$  represents the diameter of the atom. Also, the cutoff radius of 4.5 Å was considered in this simulation. The Velocity-Verlet algorithm was employed to solve Newton's equations of motion [28]. This algorithm numerically integrates the trajectories of particles over successive time steps ( $\Delta t$ ) in molecular dynamics simulations. The positions and velocities of the particles are updated through three sequential steps using Equations 3 and 4.

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2, \quad (3)$$

$$v(t + \Delta t) = v(t) + \frac{1}{2}[a(t) + a(t + \Delta t)]\Delta t. \quad (4)$$

### 2.2. Calculation of system density (Argon density) in Z direction

Equation (5) was used to calculate the system density in the Z direction by dividing the total sampled mass within a given bin by the volume of that bin.  $N_{Samples}$  is the number of sampled atoms (Argon atom) in the specific Z-slab.  $N_A$  The Avogadro constant  $6.022 \times 10^{23} \text{ mol}^{-1}$  used to convert from moles to individual atoms.  $L_x$  and  $L_y$  represent the length dimensions in the X and Y directions, respectively.  $M$  denotes the mass of the Atoms (mass of the argon atom (39.95 g/mol)),  $N_z$  represents the number of available atoms.

$$\rho(z) = \frac{N_{Zi}(z)m\sigma^3 M}{N_{Sample}L_xL_y\Delta z\sigma^3 N_A}. \quad (5)$$

The number of available argon atoms ( $N_z$ ), represent the total number of argon atoms within the entire simulation box, while the thickness of the sampled region corresponds to the thickness of the Z-direction slab.

### 2.3. Calculation of the interaction energy between argon atoms and nanochannels

Equation (6) is recruited in order to calculate the amount of interaction energy for adsorption. According to Equation (6), the interaction energy is determined by subtracting the total potential energy of the system (nanochannel with argon atoms) from the potential energy of argon atoms and the nanochannel separately. As a result, the obtained value shows the amount of surface adsorption of argon atoms to the nanochannels. As the negative value of the interaction energy increases, the surface absorption also intensifies [29].

$$E_{interaction} = E_{Pt/Ar} - (E_{Pt} + E_{Ar}). \quad (6)$$

### 2.4. Calculation of mean square displacement (MSD)

Equations (7) and (8) show the mean square displacement equation, which refer the diffusion of argon atoms to the surface of nanochannels by using the slope of the MSD diagram [30].

$$MSD = \frac{1}{N} \sum_{i=1}^N (R_{i(t)} - R_{0(t)})^2, \quad (7)$$

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt}(MSD). \quad (8)$$

In these equations,  $N$  denotes the number of atoms in the system and  $R_i$  represents the distance.



## 2.5. Radial distribution function (RDF)

Equation (9) presents the radial distribution function, which indicates the probability of finding argon atoms near platinum atoms at a distance  $r$  from each other.

In this equation,  $V$  is the total volume of the system.  $dr$  is the thickness of the spherical shell used to sample atom positions [31]. Also, the radial displacement function (RDF) was considered for argon atoms with the upper rough wall surface of the nanochannels.

$$g(r) = \frac{V}{4\pi r^2 dr} \quad (9)$$

## 3. Results and discussion

### 3.1. Investigating the effect of different roughness geometries in nanochannels

Figure 2 shows the diagram of the amount of interaction energy between argon atoms and different roughness geometries in nanochannels. According to Fig. 2, the interaction energy of the cylinder roughness geometry is higher than that of the cone and square roughness geometries over time. This means the nanochannel with cylinder roughness adsorption ( $-149$  kcal/mol) has more argon atoms than the nanochannel with cone and square roughness. Also, the lowest amount of adsorption (interaction energy) is related to smooth nanochannels (without roughness) which adsorb the least amount of argon atoms.

In addition, Fig. 2b shows the density distribution of argon within the nanochannels. The argon density varies because the nanochannels were considered periodic condition in the X and Y directions, and the geometry of the surface roughness along the Z direction influences surface adsorption and the local argon density. As shown in Fig. 2b, the argon density is higher near the beginning and end regions of the nanochannel along the Z direction, where rough surfaces with different geometries are present. This increase in density is attributed to the stronger adsorption of argon atoms on the rough surfaces. In contrast, in the central region of the nanochannel, the argon density decreases significantly. Also, Fig. 2b shows the density along the Z-direction of different nanochannels under different roughness geometries. Based on this diagram, at the beginning and end of the nanochannel where roughnesses exist, the density in these two regions is higher than that in other regions of the Z direction. The nanochannels with cylinder roughness geometry have the highest density ( $144$  g/cm<sup>3</sup>) of argon atoms compared to cone and square roughness geometries. This occurs due to the geometry of the cylinder roughness, the nanochannel with cylinder roughness have more adsorption of argon atoms than the other nanochannels. As a result, the nanochannel with cylinder roughness have a higher density of argon atoms than the other nanochannels. Also, it is observed that the lowest density of argon atoms belongs to smooth nanochannels (without roughness).

According to the graphs in Fig. 2, parts a and b, it can be seen that, compared to cone and square roughness geometry, nanochannels with a cylinder roughness geometry have the greatest effect on the flow of argon atoms. Therefore, this effect results in a greater adhesion of argon atoms to the surface of the nanochannels. Nanochannels with conical roughness exhibited the lowest surface adsorption and density compared to other nanochannels. Nanochannels with triangular roughness have the least effect on the flow of argon atoms due to less friction and impact on argon atoms [20].

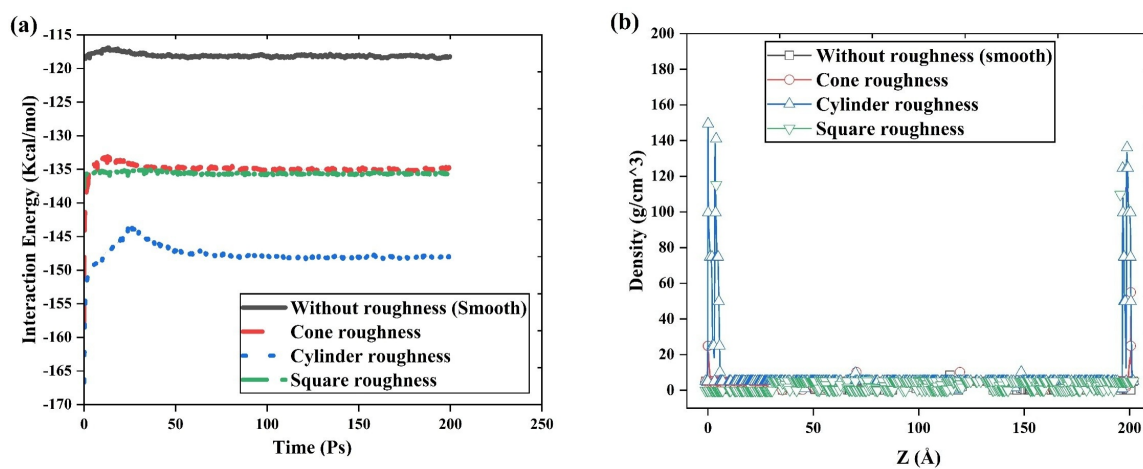


FIG. 2. Diagrams of the amount of (a) interaction energy (b) Density between argon atoms and different roughness geometries in nanochannels at a temperature of 125 K

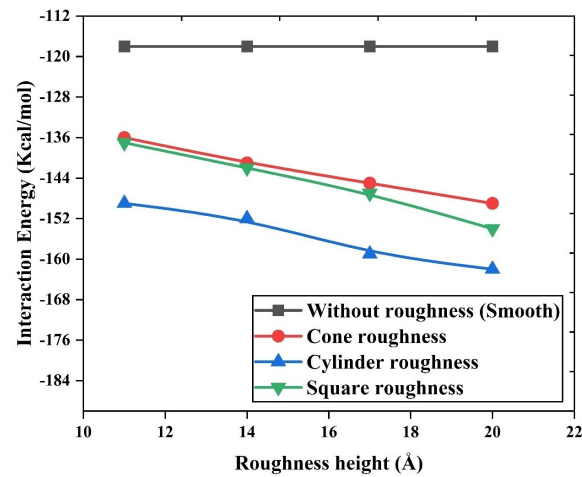


FIG. 3. The amount of interaction energy changes according to the different heights of roughness at a temperature of 125 K and at 1 atm

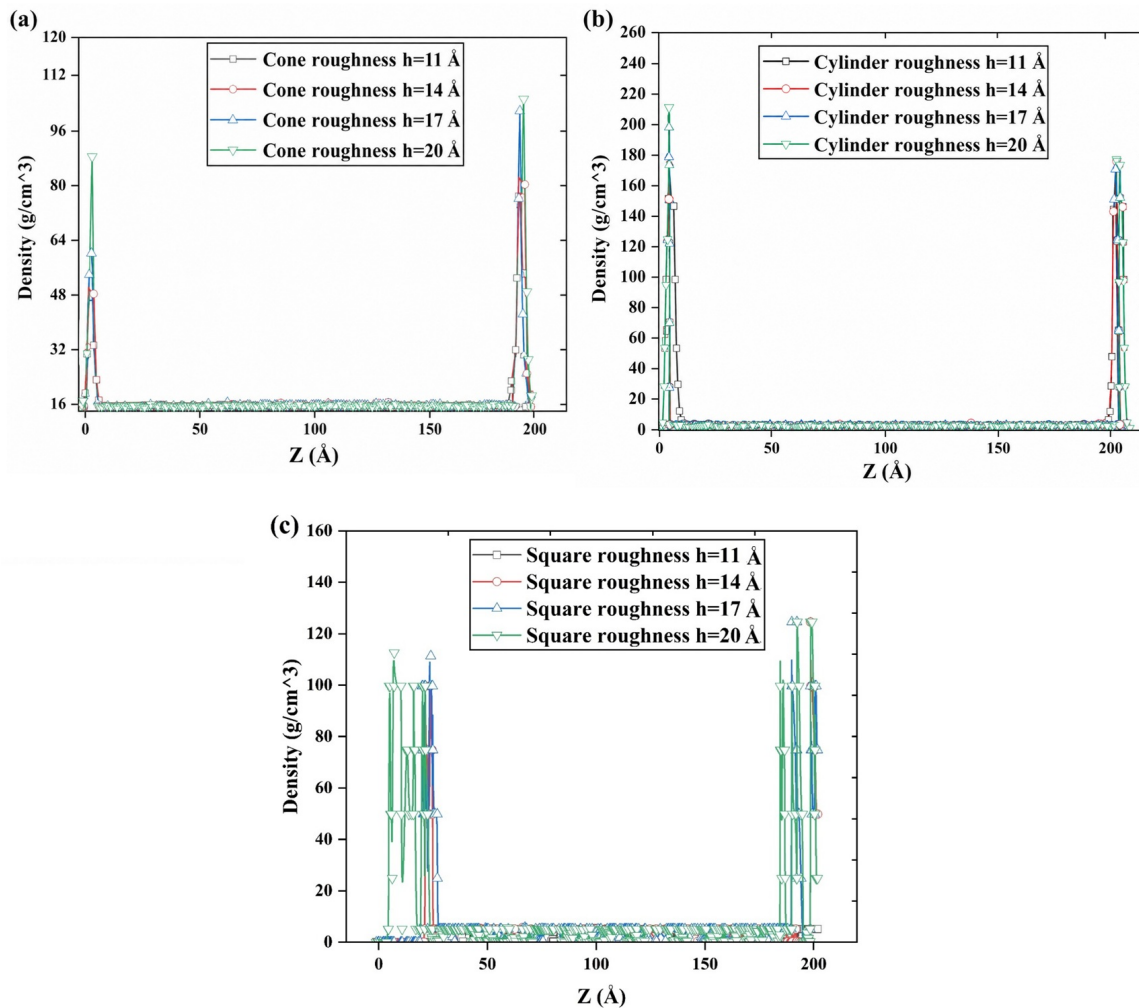


FIG. 4. The density with the increase of height roughness of the nanochannels in the Z direction (a) Cone roughness (b) Cylinder roughness (c) Square roughness at a temperature of 125 K



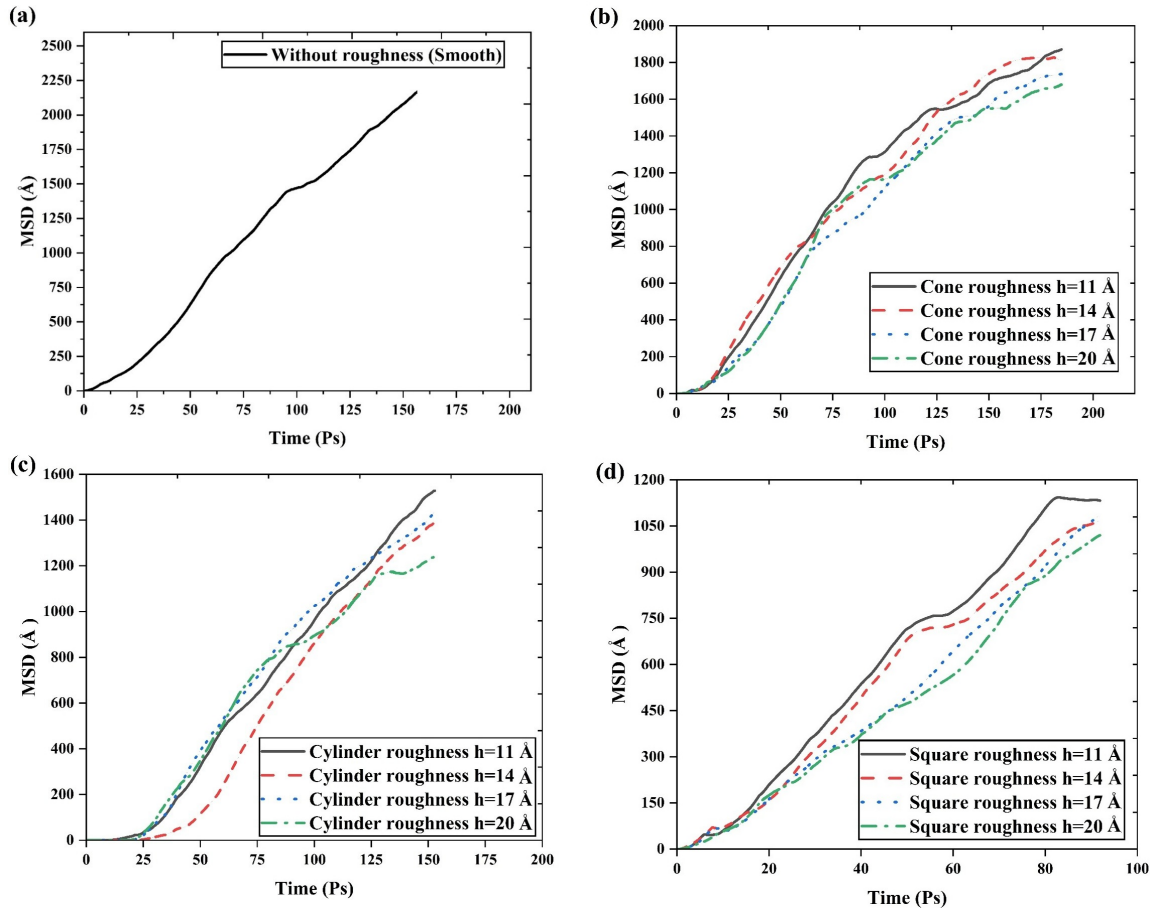


FIG. 5. The Mean Square Displacement (MSD) diagram based on different height roughness. (a) Without roughness (b) Cone roughness (c) Cylinder roughness (d) Square roughness at a temperature of 125 K

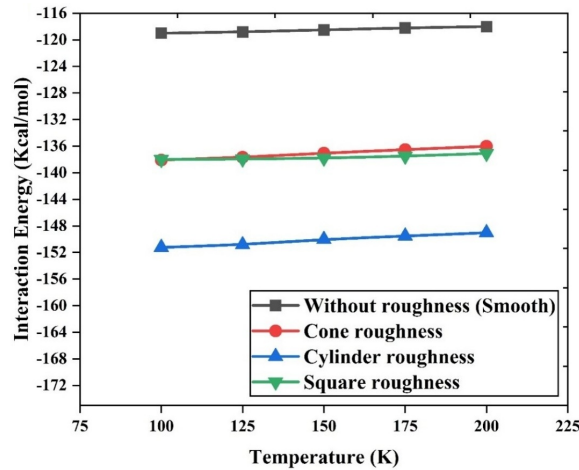


FIG. 6. The amount of interaction energy in terms of different temperatures in nanochannels

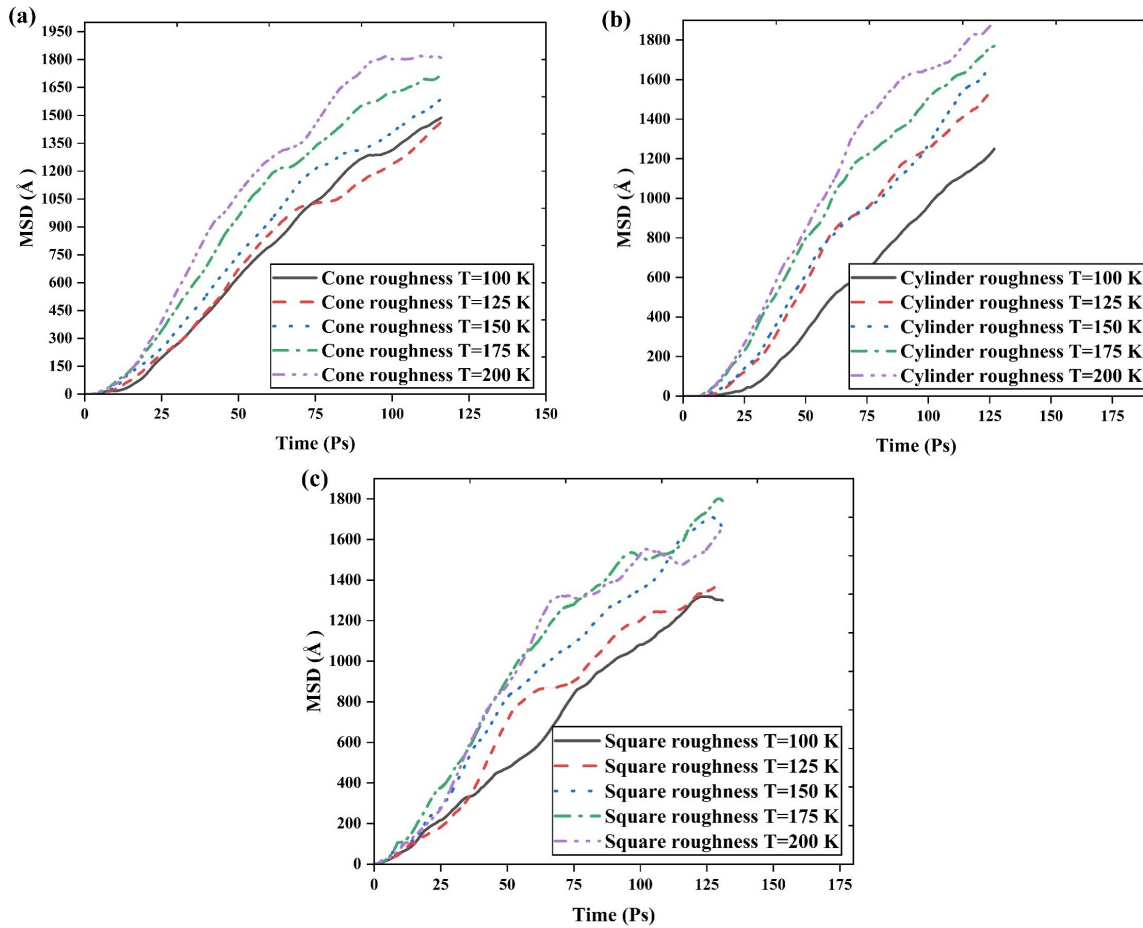


FIG. 7. The Mean Square Displacement (MSD) diagram of argon atoms in nanochannels under different temperatures

### 3.2. Investigating the effect of height roughness in nanochannels

The diagram in Fig. 3 shows the amount of interaction energy changes according to the different heights of roughness. According to Fig. 3, the interaction energy (adsorption) increases with the greater height of nanochannel roughness. As the height of roughness increases, among the nanochannels those with cylinder roughness exhibit the highest level of adsorption in comparison to cone and square roughness variations. This occurs due to the geometry of the cylinder roughness, as increasing the height roughness of nanochannels with cylinder roughness have more friction between argon atoms and nanochannels. Also, the lowest amount of adsorption (interaction energy) is related to nanochannels with cone roughness. Also, in general, the increase in interaction energy with increasing roughness height can be attributed to enhanced friction and greater contact between the rough surfaces and argon atoms. In addition, Fig. 4 diagrams a, b, and c illustrate the highest density with the increase of height roughness at the beginning and end of the nanochannels in the Z direction. By increasing the height of the roughness in nanochannels ( $h = 11 \text{ Å}$  to  $h = 20 \text{ Å}$ ), the density rises. The highest density profile occurs at the roughness height  $h = 20 \text{ Å}$ . On the other hand, the lowest density corresponds to  $h = 11 \text{ Å}$ .

### 3.3. Investigating the effect of roughness height on the diffusion of argon atoms

Figure 5 shows the Mean Square Displacement (MSD) diagram based on different height roughness. According to Fig. 5, the diffusion of argon atoms decreases as the nanochannel height roughness ( $11 \text{ Å}$  to  $20 \text{ Å}$ ) increases. By comparing the diffusion of nanochannels, smooth (without roughness) and cone-shaped nanochannels exhibit higher diffusion rates than other nanochannels. Compared to other types (square and cylinder), the higher diffusion of cone and smooth roughness is due to their peak-like geometry which results in less contact and friction with argon atoms. However, square and cylinder roughness geometry have the most friction and impact. This is because the diffusion of cone roughness geometry is higher than square and cylinder roughness. Surface roughness is directly correlated with the diffusion of nanoparticles. Diffusion increases as the diameter of the surface geometry decreases [32].

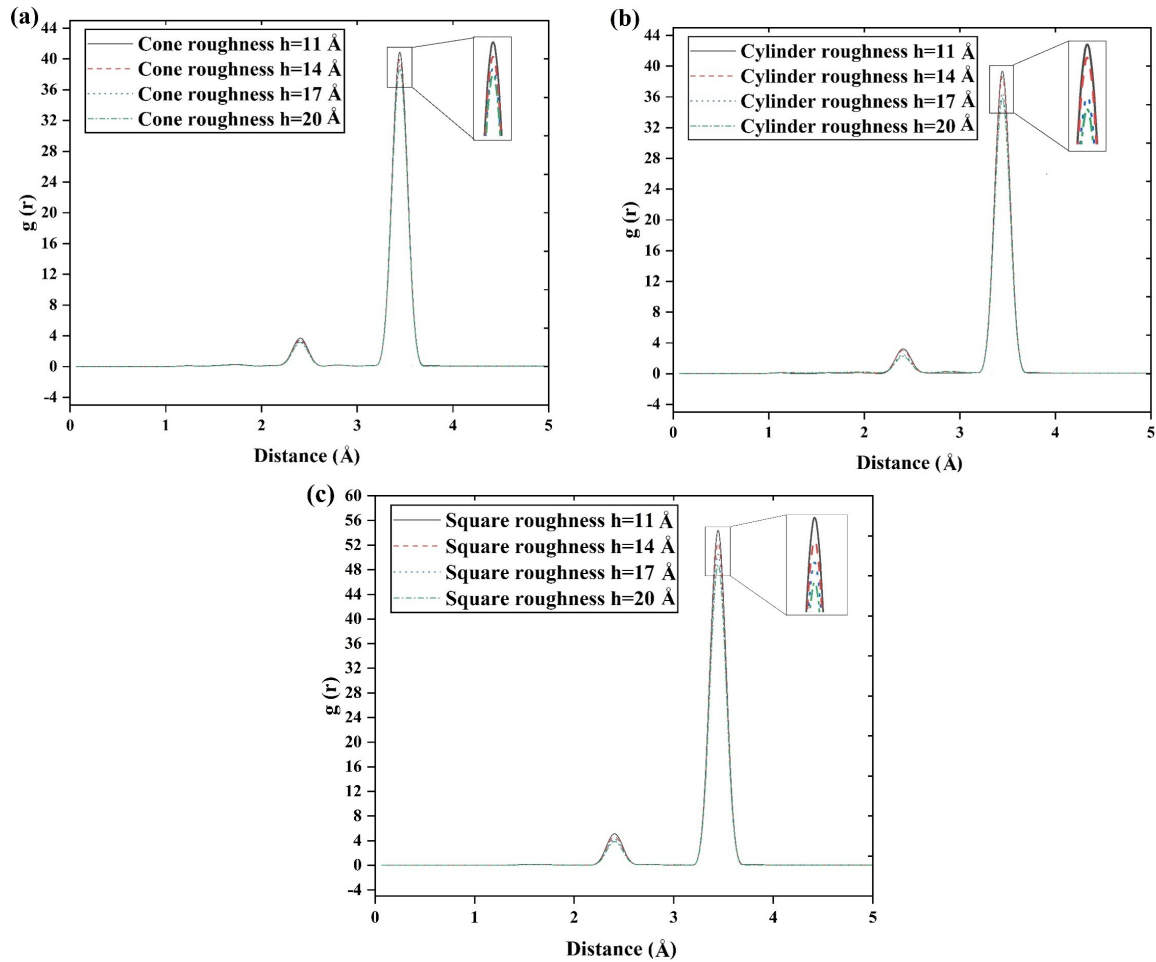


FIG. 8. The radial distribution function between the argon atom and the platinum atom under different heights of roughness

#### 3.4. Investigating the effect of different temperatures on the adsorption and diffusion of argon atoms in nanochannels

Figure 6 depicts the amount of interaction energy in terms of different temperatures in nanochannels. Also, the interaction energy (adsorption) between argon atoms and nanochannels decreases as the temperature increases. The decrease in adsorption and adhesion between argon atoms and nanochannels is due to the increase in kinetic energy and mobility of argon atoms in nanochannels [33]. A rise in temperature causes an increase in the kinetic energy and speed of argon atoms in nanochannels, which reduces the adhesion (adsorption) of argon atoms to the surface of nanochannels. In addition, Fig. 7 shows the diffusion of argon atoms in nanochannels under rough geometries and different temperatures. According to Fig. 7, with escalating the temperature, the diffusion of argon atoms in nanochannels increases. The results of these graphs are in agreement with the findings of liquid aluminum diffusion to the copper surface by Mao et al. [34] under different temperatures. The reason for the rise in diffusion with increasing temperature is due to that temperature escalates the kinetic energy and mobility of argon atoms, which raises the diffusion of argon to the rough surface of nanochannels.

#### 3.5. Investigation of radial distribution function (RDF) between argon and platinum atoms

Figure 8 shows the radial distribution function between the argon atom and the platinum atom (under different heights of roughness). According to Fig. 8, parts a, b, and c, the distance between argon atoms and platinum atoms is around 3.5 Å, which agrees with the results of the RDF diagram of the distance between argon atoms and platinum atoms by Zeng et al [35]. In RDF diagrams, as the distance increases, the simulation system's  $g(r)$  tends to reach equilibrium [36]. According to the diagrams in Fig. 8, the simulation system has reached equilibrium, and  $g(r)$  tends to a constant number as the distance increases. Also, with the rise in the height of the roughness of the nanochannels, the proximity between argon atoms and platinum atoms decreases.

#### 4. Conclusion

In this study, molecular dynamics simulation has been used to investigate the behavior of argon flow in nanochannels under different roughness geometries. The effect of temperature, and height roughness on diffusion and adsorption of argon atoms in nanochannels was investigated. The results indicate that the interaction energy (adsorption) in nanochannels is higher in cylinder roughness geometry compared to square and cone roughness geometries. Also, the lowest adsorption of argon atoms belongs to smooth nanochannels (without roughness). Furthermore, the highest amount of density in the nanochannels at the beginning and end of the nanochannels in the z direction was related to the nanochannels with cylinder roughness. In addition, as the roughness of the nanochannels increases, the amount of adsorption and density increases as well. Moreover, with the rise in height roughness, the diffusion of argon atoms in nanochannels decreases. By comparing nanochannels with different roughness geometries, nanochannels with cone and smooth roughness (without roughness) have more diffusion than square and cylinder roughness geometries. In addition, increasing the temperature decreases the surface adsorption between nanochannels with argon atoms. Besides, with escalating the temperature, the diffusion of argon atoms in different nanochannels increases.

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# On the validity of 2D reduction of the Fournier-Galatola planar anchoring model for polymer-dispersed nematic liquid crystals

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**ABSTRACT** The validity of directly reducing the three-dimensional Fournier-Galatola model of planar anchoring to two-dimensional nematic systems is investigated analytically and numerically. An alternative two-dimensional formulation based on a direct target surface  $Q$ -tensor is introduced for comparison. Analytical calculations reveal that the reduced Fournier-Galatola functional yields a cubic restoring torque at the poles of an elliptical droplet, whereas the direct tensor formulation preserves a linear response along the entire boundary. The influence of this difference on orientational relaxation is studied using the Landau-de Gennes simulations of mesoscale elliptical 5CB droplets. The reduced Fournier-Galatola model is shown to enhance boojum mobility, alter the final bipolar orientation at moderate aspect ratios, and systematically predict lower equilibrium energies. The results indicate that direct projection-based reduction can lead to qualitatively different relaxation scenarios in two-dimensional nematic models.

**KEYWORDS** bipolar structure, planar anchoring,  $Q$ -tensor, boojums, mesoscale nematic droplets.

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## 1. Introduction

Polymer-dispersed liquid crystals (PDLC) represent a class of composite materials in which liquid crystal droplets are dispersed within a polymer matrix. Due to a combination of a pronounced electro-optic response, ease of fabrication, and the ability to retain formed orientational states for a long time, such systems are widely considered as a basis for information display devices, switchable optical elements, and memory materials [1–3]. In composites based on 5CB within a polymer matrix, mesoscale nematic droplets are formed, the internal orientational structure of which is determined by the interplay of elastic interactions, surface anchoring, and boundary geometry. Elliptical and elongated droplets are characterized by the formation of bipolar textures with surface defects of the boojum type, whose position significantly affects the configuration stability, optical characteristics, and relaxation processes after the external field is removed [4]. Consequently, a correct description of boundary orientational processes and surface defect dynamics is a prerequisite for building predictive models of such systems, especially since different surface anchoring models may predict qualitatively different relaxation scenarios. Establishing the range of applicability of these models is therefore important before using them for quantitative comparison with experiment.

The Landau-de Gennes theory, based on the tensor order parameter  $Q$ , serves as the most universal continuum approach to describing defect structures in nematics. Unlike the Frank-Oseen approach, this method allows for a local reduction of the order parameter down to its vanishing at defect cores, thereby naturally capturing the topological features of the texture [5–7]. Several surface anchoring formulations have been developed within the  $Q$ -tensor framework. One of the most well-known is the Nobili-Durand model [8], designed to specify a fixed preferred director orientation at the surface. For the case of degenerate planar anchoring, the Fournier-Galatola projection formulation [9] is widely used; it does not select a preferred direction in the tangent plane and is therefore convenient for modeling droplets and colloidal systems.

When moving to two-dimensional (2D) and quasi-2D formulations, the corresponding surface functional must be transferred to a 2D geometry, raising the question of the validity of such an operation. During the transition from 3D to 2D, the dimensionality of the tangent space decreases from two to one, causing the structure of the projection operator to change qualitatively, not just quantitatively. It remains unclear whether the 2D reduction of the Fournier-Galatola functional retains the same restoring torque properties inherent in the original 3D formulation, or if such a reduction leads to additional dynamical effects. This question is of particular interest for systems with a curved boundary and pronounced

geometric anisotropy, specifically for elliptical nematic droplets, where even small changes in the surface torque structure can significantly affect the dynamics of surface defects and the selection of the final equilibrium state. To the authors' knowledge, this issue has not received systematic analytical investigation to date.

The aim of this work is to investigate the 2D reduction of the Fournier-Galatola projection model and determine its affect on the relaxation dynamics of the orientational structure in an elliptical nematic liquid crystal droplet. To this end, an analytical investigation of the restoring torque is performed and compared with an alternative anchoring formulation based on the direct specification of a target surface  $Q$ -tensor. Next, using a numerical solution of the relaxation equations, the director field evolution after switching off the external aligning field is investigated, and the influence of the chosen anchoring model on boojum migration and the formation of the final bipolar configuration is analyzed. The theoretical formulation is presented in Section 2. Section 3 analyzes the boundary torque structure. Numerical implementation and simulation results are discussed in Sections 4 and 5, respectively.

## 2. Theoretical Formulation

### 2.1. $Q$ -tensor parameterization

The tensor order parameter  $Q_{ij}$  is a symmetric traceless matrix that describes the local degree of orientational order and the direction of the preferred molecular orientation in a nematic. In the 3D case, a nematic is characterized by five independent degrees of freedom, and the  $Q$ -tensor is typically written as:

$$Q_{ij} = \frac{3}{2}S \left( n_i n_j - \frac{1}{3} \delta_{ij} \right), \quad (1)$$

where  $S$  is the scalar order parameter, and  $\mathbf{n}$  is the unit director vector. This normalization ensures that in the fully ordered state ( $S = 1$ ), the largest eigenvalue of the tensor equals one, and the other two equal  $-1/2$ .

Upon transitioning to 2D geometry, the system possesses only two translational degrees of freedom, and the tensor  $Q_{ij}$  becomes a  $2 \times 2$  matrix. Symmetry and tracelessness requirements are preserved, but the condition on the eigenvalues changes: there are now only two, and they must equal  $\pm S$ . This leads to a different normalization factor. In the 2D case, the  $Q$ -tensor is parameterized as:

$$Q_{ij} = S \begin{pmatrix} \cos 2\phi & \sin 2\phi \\ \sin 2\phi & -\cos 2\phi \end{pmatrix} = S (2n_i n_j - \delta_{ij}), \quad (2)$$

where  $\phi$  is the angle of preferred molecular orientation relative to the  $x$ -axis, and  $\mathbf{n} = (\cos \phi, \sin \phi)$  is the unit director vector. The eigenvectors coincide with  $\mathbf{n}$  and the direction orthogonal to it.

### 2.2. Bulk free energy

The free energy in the domain  $\Omega$  includes bulk and elastic contributions. The bulk contribution governs the thermodynamics of the isotropic-nematic phase transition and in the 2D reduction takes the form [11]:

$$f_{bulk} = \frac{A}{2} \left( 1 - \frac{U}{3} \right) Q_{ij} Q_{ij} - \frac{AU}{3} Q_{ij} Q_{jk} Q_{ki} + \frac{AU}{4} (Q_{ij} Q_{ij})^2 = A \left( 1 - \frac{U}{3} \right) S^2 + AU S^4, \quad (3)$$

here  $A$  is the energy scale (for 5CB  $A = 1.17 \times 10^5$  J/m<sup>3</sup>), and  $U$  is a dimensionless parameter controlling the depth of the nematic minimum. Minimization with respect to  $S$  shows that for  $U > 3$ , the isotropic state  $S = 0$  loses stability, and a non-zero equilibrium value emerges:

$$S_0 = \sqrt{\frac{U-3}{6U}}. \quad (4)$$

For the characteristic value  $U = 3.5$ , corresponding to 5CB [11], we obtain  $S_0 \approx 0.154$ . This value is lower than the typical one for bulk 5CB ( $S_0 \approx 0.53$ ), which is due to the specifics of the 2D reduction of the bulk functional and does not contradict the physics of thin films, where the order parameter can be reduced.

The elastic contribution in the one-constant approximation is written in terms of the  $Q$ -tensor gradients [11]:

$$f_{elastic} = \frac{L}{2} \frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k}, \quad (5)$$

where  $L$  is the elastic constant (for 5CB  $L \approx 6$  pN). Direct calculation of the gradients of  $Q_{ij}$  leads to the form:

$$f_{elastic} = L [(\nabla S)^2 + 4S^2(\nabla \phi)^2]. \quad (6)$$

The first term is associated with inhomogeneities of the order amplitude, and the second with orientational distortions. As  $S \rightarrow 0$  (defect core), the orientational elasticity contribution automatically vanishes, eliminating the elastic energy singularity in regions with disrupted order.

### 2.3. Relaxation equations

The system dynamics are defined within the framework of linear nonequilibrium thermodynamics. The dissipative function, quadratic in the rate of change of the Q-tensor, takes the following form in the 2D case:

$$R = \frac{\gamma}{2} \text{tr}(\dot{Q}^2) = \gamma \dot{S}^2 + 4\gamma S^2 \dot{\phi}^2. \quad (7)$$

Here and below, the overdot denotes differentiation with respect to time. In the Onsager formalism, the generalized dissipative forces are balanced by the variational derivatives of the total free energy  $F = \int_{\Omega} (f_{\text{bulk}} + f_{\text{elastic}}) d\Omega$  [11]:

$$\frac{\partial R}{\partial \dot{S}} = -\frac{\delta F}{\delta S}, \quad \frac{\partial R}{\partial \dot{\phi}} = -\frac{\delta F}{\delta \phi}. \quad (8)$$

Calculating the variational derivatives yields the following system of coupled relaxation equations:

$$2\gamma \frac{\partial S}{\partial t} = 2L\nabla^2 S - 2A \left(1 - \frac{U}{3}\right) S - 4AUS^3 - 8LS(\nabla\phi)^2, \quad (9)$$

$$8\gamma S^2 \frac{\partial \phi}{\partial t} = 8L\nabla \cdot (S^2 \nabla \phi). \quad (10)$$

The coefficient of  $\partial\phi/\partial t$  is proportional to  $S^2$ , so the director dynamics slow down in regions with a small order parameter. This property is particularly important when modeling topological defect cores.

### 2.4. Surface anchoring

The surface free energy is given by an integral over the boundary:

$$F_{\text{surface}} = \int_{\partial\Omega} f_{\text{surface}} dS. \quad (11)$$

This work compares two formulations of degenerate planar anchoring that translate boundary conditions into bulk equations via fluxes: the projection model (hereafter the FG model) and the direct target tensor model (DT model).

The FG model is based on the standard Fournier-Galatola approach [9]. The surface energy has the form:

$$f_{\text{surface}}^{FG} = W \left( \tilde{Q}_{ij} - \tilde{Q}_{ij}^{\perp} \right)^2, \quad (12)$$

where  $W > 0$  is the anchoring energy,

$$\tilde{Q}_{ij} = Q_{ij} + \frac{1}{2} S_0 \delta_{ij}, \quad (13)$$

$$\tilde{Q}_{ij}^{\perp} = P_{ik} \tilde{Q}_{kl} P_{lj}, \quad (14)$$

$$P_{ij} = \delta_{ij} - \nu_i \nu_j, \quad (15)$$

$\nu_i$  are the components of the outward unit normal to the boundary. In the 2D case, the tensor  $P_{ij}$  projections onto the tangent direction  $t_i = (-\nu_y, \nu_x)$ . Substituting the parameterization of  $Q_{ij}$  leads to the expression for the torque  $g_{\phi} = -\partial f_{\text{surface}} / \partial \phi$ :

$$g_{FG} = -4WS \sin 2\phi (S \cos 2\phi \mp S_0), \quad (16)$$

where the “−” sign applies at boundary points where the equilibrium director is perpendicular to the normal (ellipse equator), and the “+” sign applies at points where the equilibrium director is parallel to the normal (pole).

Direct 2D anchoring (DT model) is based on explicitly specifying a target surface Q-tensor. The requirement that the director be tangent to the boundary yields the form:

$$Q_{ij}^{\text{surf}} = S_0 (2t_i t_j - \delta_{ij}). \quad (17)$$

In components relative to the global basis  $(x, y)$ , taking into account  $t_x = -\nu_y$ ,  $t_y = \nu_x$ :

$$Q_{xx}^{\text{surf}} = S_0 (\nu_y^2 - \nu_x^2), \quad Q_{xy}^{\text{surf}} = -2S_0 \nu_x \nu_y. \quad (18)$$

The surface energy in the DT model is defined as a quadratic form of the difference between the actual and target tensors:

$$f_{\text{surface}}^{DT} = 2WS_0^2 (\Delta_{xx}^2 + \Delta_{xy}^2), \quad (19)$$

where the dimensionless residuals are:

$$\Delta_{xx} = \frac{S}{S_0} \cos 2\phi - (\nu_y^2 - \nu_x^2), \quad \Delta_{xy} = \frac{S}{S_0} \sin 2\phi + 2\nu_x \nu_y. \quad (20)$$

The corresponding torque is:

$$g_{DT} = 4WS_0^2 \frac{S}{S_0} (-\Delta_{xx} \sin 2\phi + \Delta_{xy} \cos 2\phi). \quad (21)$$



For  $S = S_0$ , the expression simplifies to the compact form:

$$g_{DT} = -2WS_0^2 \sin 2(\phi - \phi_{eq}), \quad (22)$$

where  $\phi_{eq}$  is the angle of the tangent to the boundary at the given point. This form is used in Section 3 for analytical comparison with the projection model.

The obtained expressions for the restoring torque allow for an analytical comparison of the two anchoring models in a specific geometry. Below, this analysis is performed for an elliptical droplet.

The one-constant approximation is adopted in order to isolate the influence of the surface anchoring model on the relaxation dynamics. Although the elastic constants of 5CB are anisotropic, the same bulk elastic properties (Eq. (5)) are used for both anchoring models. Therefore, the observed differences arise solely from the form of the surface free-energy functional, as reflected in the corresponding expressions for the restoring torque (Eqs. (16) and (21)). The inclusion of elastic anisotropy would likely affect quantitative characteristics, such as relaxation times and defect trajectories, but does not affect the qualitative distinction between the anchoring models.

### 3. Boundary torque asymmetry: analytical derivation

Consider a 2D elliptical nematic droplet with semi-axes  $a$  (horizontal) and  $b$  (vertical),  $a > b$ . Degenerate planar anchoring is realized at the boundary, so the equilibrium director orientation at each point is tangent to the surface. Two characteristic boundary points define the limiting cases:

- the poles  $(0, b)$  with normal  $\nu = (0, 1)$ , tangent  $t = (1, 0)$ , and equilibrium angle  $\phi_{eq} = 0$ ;
- the equator  $(a, 0)$  with normal  $\nu = (1, 0)$ , tangent  $t = (0, 1)$ , and equilibrium angle  $\phi_{eq} = \pi/2$ .

This section investigates the local structure of the restoring torque near the equilibrium director orientations at the boundary.

At the initial time, the director is uniform and oriented vertically. Such a configuration models the state of the droplet immediately after switching off a strong external electric field applied across the long axis of the ellipse. After the field is removed, the system must relax to an equilibrium bipolar structure, and the nature of this relaxation is determined solely by the properties of the surface anchoring.

Let us write the initial condition as:

$$\phi = \frac{\pi}{2} + \delta\psi, \quad \delta\psi \ll 1, \quad S \approx S_0, \quad (23)$$

where  $\delta\psi$  is a small deviation arising from thermal fluctuations or residual field inhomogeneity.

Using expressions (16) and (22) for the restoring torques and expanding in the small parameter  $\delta\psi$ , we obtain the asymptotics for the two models. For the FG model, one has:

$$g_{FG}^{pole} \approx 16WS_0^2(\delta\psi)^3, \quad (24)$$

$$g_{FG}^{eq} \approx -16WS_0^2\delta\psi. \quad (25)$$

For the DT model, we obtain:

$$g_{DT}^{pole} \approx 4WS_0^2\delta\psi, \quad (26)$$

$$g_{DT}^{eq} \approx -4WS_0^2\delta\psi. \quad (27)$$

Thus, in the DT model, the torque remains linear in  $\delta\psi$  in both cases and differs only in sign. Whereas in the FG model, the torque at the pole is cubic in  $\delta\psi$ , unlike the linear torque at the equator. For a characteristic  $\delta\psi=0.1$ , the ratio of the torque scales in the projection model is:

$$\frac{g_{DT}^p}{g_{FG}^p} \sim \frac{1}{(\delta\psi)^2} \sim 100. \quad (28)$$

Thus, direct reduction of the 3D Fournier-Galatola functional to the 2D case leads to a cubic dependence of the restoring torque at the poles of an elliptical droplet when starting from a vertical position.

Two qualitative predictions follow from the obtained asymptotics. First, the weakening of the restoring torque at the poles should increase the mobility of surface defects and facilitate their displacement along the boundary. Second, the influence of this effect should be most pronounced in droplets with moderate geometric anisotropy, where the competition between surface anchoring and boundary shape is most distinct. These assumptions are verified in the subsequent numerical experiments.

#### 4. Numerical experiment setup

To test the analytical predictions of Section 3, numerical simulations of the director relaxation in a 2D elliptical droplet were performed after switching off an external electric field that initially oriented the director vertically. Two surface anchoring models are compared: FG (projection) and DT (direct 2D anchoring).

Calculations were carried out for two sets of semi-axes: a moderate ellipse ( $a = 3.0 \mu\text{m}$ ,  $b = 2.5 \mu\text{m}$ ,  $a/b = 1.2$ ) and an elongated ellipse ( $a = 6.25 \mu\text{m}$ ,  $b = 2.5 \mu\text{m}$ ,  $a/b = 2.5$ ), which corresponds to the mesoscale range typical for experimental PDLC systems. The second geometry corresponds to highly elongated droplets observed in polymer matrices [4], while the first allows for investigating the transition regime where the difference between the models is most pronounced.

The model parameters correspond to the 5CB nematic (Table 1). The anchoring energy is chosen in the strong anchoring regime ( $W = 10^{-3} \text{ J/m}^2$ , extrapolation length  $\xi = L/W \ll a$ ). The initial state is specified by a vertical director with a small spatial modulation. The system of relaxation equations (Section 2.3) with the corresponding boundary conditions (Section 2.4) is integrated using the finite element method on a triangular mesh refined near the boundary. A second-order implicit time-stepping scheme is used. All quantities are non-dimensionalized using the scales  $x_c = a$ ,  $t_c = \gamma/A$ ,  $S_c = S_0$ ,  $f_c = AS_0^2$ .

TABLE 1. Model parameters

| Parameter                   | Symbol   | Value                           |
|-----------------------------|----------|---------------------------------|
| Thermodynamic parameter     | $U$      | 3.5                             |
| Energy scale                | $A$      | $1.17 \cdot 10^5 \text{ J/m}^3$ |
| Elastic constant            | $L$      | 6 pN                            |
| Anchoring energy            | $W$      | $10^{-3} \text{ J/m}^2$         |
| Equilibrium order parameter | $S_0$    | 0.154                           |
| Rotational viscosity        | $\gamma$ | 0.1 Pa·s                        |

To prevent numerical instabilities associated with the abrupt onset of boundary conditions, the surface fluxes defined by expressions (16) and (22) were introduced smoothly. During the interval  $0 \leq t \leq t_{\text{ramp}}$ , they were multiplied by a monotonically increasing function  $\text{ramp}(t) = t/t_{\text{ramp}}$ , and for  $t > t_{\text{ramp}}$ , they took their full values. The ramp time is  $t_{\text{ramp}} = 0.01 \text{ s}$ , which in dimensionless units corresponds to approximately  $10^4$ .

#### 5. Results and discussion

The numerical simulation results for the two droplet geometries and the two surface anchoring models are presented in Figs. 1-3. In all cases, after the external field is turned off, the director relaxes to a bipolar configuration; however, the nature of this relaxation and the final state qualitatively depend on the choice of the anchoring model and the aspect ratio of the ellipse semi-axes.

For moderate elongation ( $a/b = 1.2$ ), the difference between the models is most pronounced. In the FG model, the bipolar axis is oriented horizontally (Fig. 1a): two surface defects – boojums, identified by the regions  $S \rightarrow 0$  – are localized near the ends of the major axis of the ellipse at the equator, at points  $(\pm a, 0)$  (Fig. 1c). In the DT model, the bipolar axis is oriented vertically (Fig. 1b), and the boojums are located at the poles  $(0, \pm b)$  (Fig. 1d). Thus, with identical parameters and identical initial states, the choice of the surface anchoring model leads to different equilibrium orientations of the bipolar structure.

For strong elongation ( $a/b = 2.5$ ), both models yield a horizontal bipolar structure (Fig. 2a,b). In both cases, boojums are localized near the ends of the equator, at points  $(\pm a, 0)$  (Fig. 2c,d).

The dynamics of the free energy  $F$  are shown in Fig. 3 on a logarithmic scale of dimensionless time  $t/t_c$ . In all cases, three characteristic regions can be distinguished on the plots. The first region is a rapid energy drop by several orders of magnitude (up to  $t/t_c \sim 10^{-2} - 10^{-1}$ ), corresponding to the initial stage of relaxation. The second region is an intermediate plateau in the interval  $t/t_c \sim 10^{-1} - 10^4$ , where the energy changes weakly. These two regions span the entire period of the smooth introduction of the boundary conditions (ramping), which is completed by  $t/t_c \sim 10^4$  ( $t = 0.01 \text{ s}$ ). After full anchoring is turned on, the energy increases to values corresponding to the true free energy minimum under fully developed boundary conditions, and levels off at a final plateau for  $t/t_c > 10^4$ .

For  $a/b = 1.2$ , the DT model curve, upon leaving the intermediate plateau, reaches the final stationary level  $F \approx 2.1 \times 10^{-2} \text{ J}$ . In the FG model, the transition from the intermediate plateau reaches a value of  $F \approx 1.1 \times 10^{-2} \text{ J}$ , which is 48% lower than in the DT model.

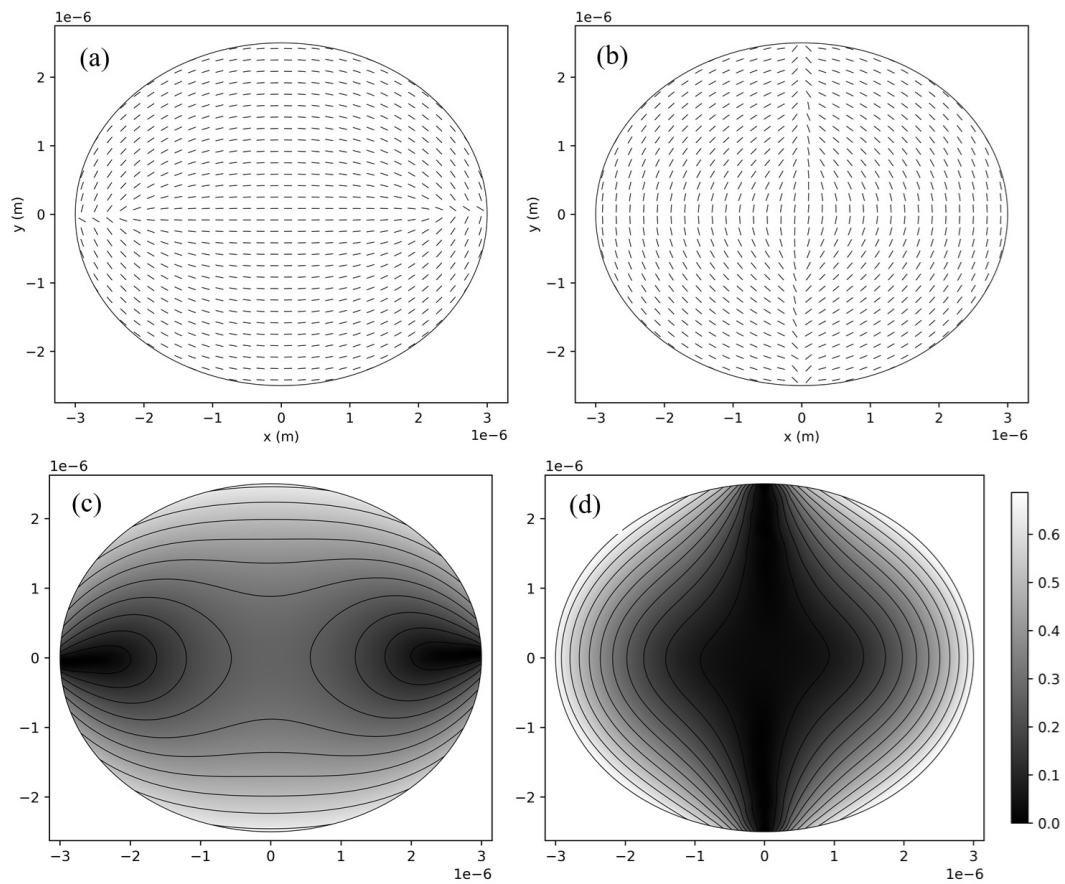


FIG. 1. Director field and order parameter for a moderately elongated droplet: FG model (a, c); DT model (b, d)

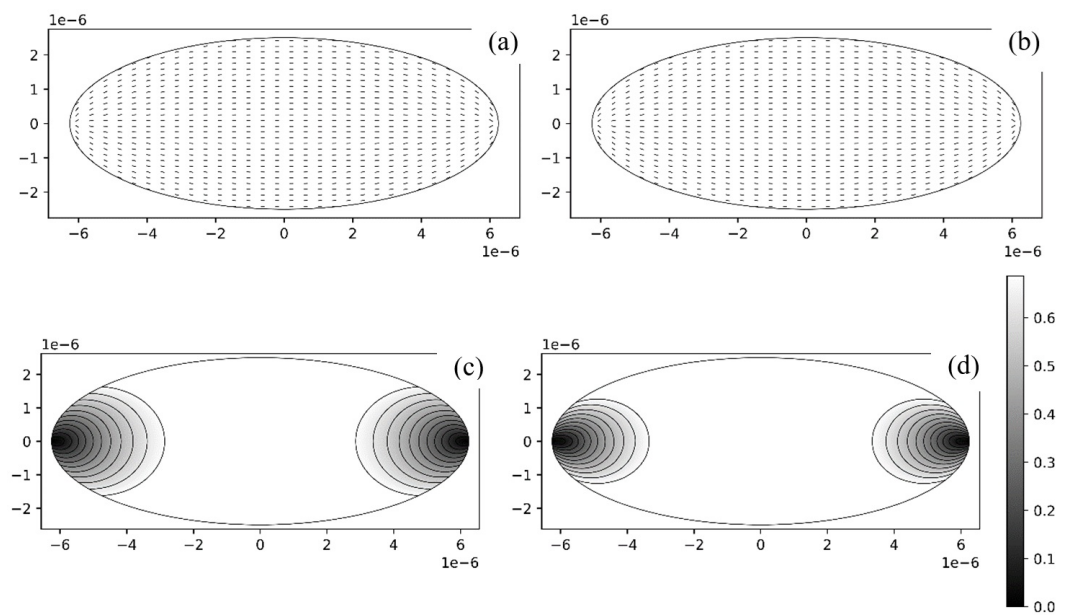


FIG. 2. Director field and order parameter for a strongly elongated droplet: FG model (a, c); DT model (b, d)

For  $a/b = 2.5$ , the DT model curve reaches a plateau  $F \approx 1.7 \times 10^{-2}$  J. The FG model again yields a lower final value  $F \approx 1.1 \times 10^{-2}$  J – a difference of about 35%.

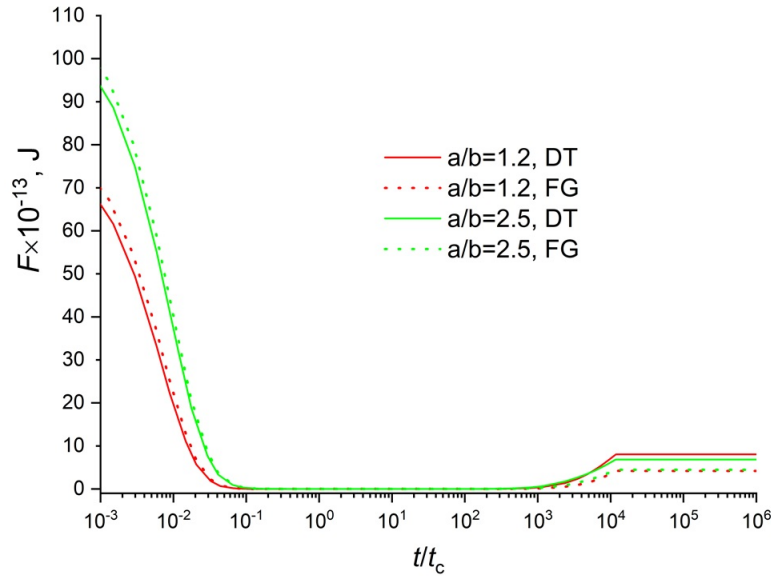


FIG. 3. Free energy relaxation plot for two droplet geometries and two anchoring models on a logarithmic time scale

Analytical estimates combined with numerical modeling provide a clear physical picture of how the form of surface anchoring affects director relaxation in an elliptical droplet. It was previously shown that in the FG model, the restoring torque at the ellipse poles for a vertical start is cubic with respect to the small deviation  $\delta\psi$ , whereas in the DT model it is linear. Numerical experiments indicate that this difference plays a dominant role in determining the mobility of surface defects and, consequently, the orientation of the resulting bipolar structure.

Regardless of the chosen anchoring model and droplet elongation, the early stage of relaxation is universal. As the boundary conditions are smoothly applied (ramping), the equatorial torque, which is linear in both models, keeps the director near the vertical at the equator, and a vertical bipolar configuration with two boojums at the poles forms in the system. This stage concludes around  $t/t_c \sim 300$ .

The subsequent system behavior is governed by the migration of boojums along the boundary from the poles to the equator, driven by geometric anisotropy. The long sides of the ellipse create a larger boundary area for which tangential orientation is energetically favorable, and in the absence of a restraining force, the boojums shift, transforming the vertical bipolar configuration into a horizontal one.

In the FG model, the weak cubic polar torque provides substantially less resistance to boojum migration than the linear torque of the DT model. At both aspect ratios, boojums move along the boundary and reach the equator by the time anchoring is fully applied, forming a horizontal bipolar structure.

In the DT model, the linear polar torque actively resists boojum migration. At moderate elongation ( $a/b = 1.2$ ), this resistance completely blocks the movement: the boojums remain at the poles throughout the entire simulation time, and the vertical bipolar structure is preserved as a stable state. At strong elongation ( $a/b = 2.5$ ), the geometric anisotropy is large enough to overcome the linear torque, and the boojums migrate to the equator, forming a horizontal bipolar structure.

The significant difference in equilibrium energies indicates that the considered models lead to different stationary states. Since the respective configurations differ in boojum placement and bipolar axis orientation, these results point to a substantial modification of the system's energy landscape when transitioning from the DT formulation to the 2D reduction of the Fournier-Galatola model. A more detailed analysis of the structure of the respective minima requires a separate investigation.

The obtained results are consistent with previous studies showing that increasing aspect ratio promotes defect displacement toward the ends of the major axis [11]. However, unlike previously published works, the present study demonstrates that the choice of a specific degenerate planar anchoring model can alter not only the quantitative relaxation characteristics but also the orientation of the final bipolar structure.

Numerical calculations indicate that the direct use of the 3D Fournier-Galatola projector in 2D models leads to a qualitative difference in relaxation dynamics compared to the DT model: at moderate elongation, a horizontal bipolar structure forms instead of a vertical one, and for any geometry, the final energy is systematically underestimated. The DT formulation preserves a linear restoring torque along the entire boundary and may therefore provide a useful alternative framework for quasi-2D nematic modeling.

## 6. Conclusion

This work analyzes the validity of directly transferring the 3D formulation of Fournier-Galatola degenerate planar anchoring to 2D models of nematic liquid crystals. It is analytically shown that reducing the 3D projector to the 2D case yields a cubic dependence of the restoring torque on the director deviation at the poles of an elliptical droplet when starting from a vertical position. In the direct target tensor model, the torque remains linear at all boundary points. For characteristic deviations, the cubic torque in the FG model is roughly two orders of magnitude weaker than the linear torque of the DT model.

Numerical modeling of director relaxation in elliptical 5CB droplets with aspect ratios  $a/b = 1.2$  and  $2.5$  revealed that this difference directly dictates the mobility of surface boojums and, consequently, the orientation of the final bipolar structure. In all cases, a vertical bipolar configuration forms during the early stage. In the FG model, the cubic polar torque does not provide substantial resistance to boojum migration toward the ends of the major axis, and the system transitions to a horizontal bipolar structure at any elongation. In the DT model, the linear polar torque blocks migration at  $a/b = 1.2$ , maintaining the vertical bipolar configuration, whereas at  $a/b = 2.5$  the geometric anisotropy is strong enough to induce migration in this case as well.

The equilibrium energy in the FG model is systematically lower than in the DT model (by 35–48%), indicating a structural difference in the achieved minima. The findings demonstrate that directly utilizing the 3D projector in a 2D framework yields results that qualitatively differ from those of the direct target tensor model. The DT formulation, wherein the restoring torque is linear along the entire boundary, provides a more reliable basis for modeling quasi-2D nematic systems. A quantitative comparison of the predicted director dynamics with the experimental data reported in Ref. [4], including relaxation times and defect evolution, constitutes an important direction for future research.

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## Carbon diffusion in $\alpha$ -Ti and $\alpha_2$ -Ti<sub>3</sub>Al

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**ABSTRACT** The interstitial defect formation energies of carbon in various interstices, crystal orbital Hamilton populations, electron localization function, Voronoi volumes, and other characteristics in  $\alpha$ -Ti and  $\alpha_2$ -Ti<sub>3</sub>Al were calculated by the projector augmented wave method. The climbing image nudged elastic band method was used to estimate migration barriers along paths between stable interstitials. The temperature-dependent diffusion coefficients of carbon were evaluated along two nonequivalent crystallographic directions (*a* and *c*) in  $\alpha$ -Ti and, for the first time, in  $\alpha_2$ -Ti<sub>3</sub>Al. The energetically preferred site in both  $\alpha$ -Ti and  $\alpha_2$ -Ti<sub>3</sub>Al is an octahedral one, whose local environment contains only Ti atoms. This preference depends on material and is primarily due to low mechanical contribution to the defect formation energy in  $\alpha$ -Ti and chemical one in the case of the alloy. The presence of Al leads to an increase in the defect formation energy in the alloy. In the case of  $\alpha$ -Ti, the obtained diffusion coefficients are in good agreement with experiment. Aluminum in the alloy leads to a slowdown in carbon diffusion due to higher both defect formation and migration energies.

**KEYWORDS** titanium, titanium aluminide, carbon diffusion, ab-initio calculations

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## 1. Introduction

Titanium aluminides are attractive structural materials for use in the aerospace industry due to their low density, high melting point, high specific strength, creep resistance at high temperatures, and other good mechanical properties. For example, the  $\alpha_2$ -Ti<sub>3</sub>Al alloy has an elastic modulus and tensile strength comparable to those of nickel superalloys; however, a complete lack of ductility at room temperature is a major problem in its use [1]. The addition of alloying elements and some heat treatment can significantly improve the mechanical properties of Ti<sub>3</sub>Al [2, 3]. It is known that atomic diffusion determines a number of mechanical properties of materials [4, 5]. For example, the thermal stability of coatings and creep resistance depend on the diffusion, interdiffusion, and self-diffusion rate. Interstitial impurities can affect the mechanical properties of alloys, phase stability, and resistance to environmental degradation. Experimental measurement of the diffusion coefficient is quite difficult, and its experimental evaluation is accompanied by a number of problems related to purity of samples, availability of radioactive tracers, etc. As a result, the spread in the values of diffusion coefficients and activation energies is significant. Moreover, experimental methods allow one to estimate the diffusion rate, but not to determine its microscopic mechanisms. The results of an experimental study of the diffusion of Fe, Ni, Nb, Al, Ga, Si, and O in  $\alpha_2$ -Ti<sub>3</sub>Al are presented in [6–10]. For example, it was shown that O diffusion in both *a* and *c* directions occurs faster than self-diffusion of Ti and Al [10] or diffusion of impurities such as Nb, Si, and Ga, but slower than Fe and Ni. It should be emphasized that both groups of elements are substitutional impurities, while O is an interstitial one. From the reviews given in [10, 11], it is clear that a similar phenomenon also occurs in  $\alpha$ -Ti. In the latter case, the formation energies of interstitial and substitutional defects, their migration energies, and the exponential part of the diffusion coefficient at 1000 K were calculated for a number of impurities in paper [12]. The authors concluded that a small difference in the formation energies of interstitial and substitutional defects in the case of fast diffusers may be the main reason for the anomalously high diffusion rate via the interstitial mechanism. In our previous studies [13, 14], the temperature-dependent diffusion coefficient of a number of metal impurities within vacancy and interstitial mechanisms in  $\alpha$ -Ti was calculated. It was shown that fast impurities prefer to diffuse via interstices, but the preferred site differs from that for non-metallic interstitial impurities. The diffusion coefficients of *d*-metals (Co and Fe) obtained within the interstitial mechanism are in good agreement with the available experimental values. At the



same time, normal diffusers migrate via interstitial sites more slowly than via vacancies. Similar calculations in the  $\alpha_2$ -Ti<sub>3</sub>Al alloy [15, 16] demonstrated that Al in the local environment of the impurity leads to an increase in the interstitial defect formation energy compared to  $\alpha$ -Ti and, as a consequence, to an increase in the diffusion coefficients. Despite the significant scattering in the diffusion coefficients of carbon in different experimental studies [17–20], carbon, which is a classic interstitial impurity, has a diffusion coefficient several orders of magnitude lower than that of some *d*-metals (Fe, Co, etc.).

The diffusion of C along with O and N in  $\alpha$ -Ti was studied using an analytical model, the multi-state diffusion method as well as kinetic Monte Carlo simulations in the paper [21]. The obtained results showed the reliability of these two methods with respect to the experimental data [20]. It was demonstrated that C is the faster diffuser in comparison with O and N. However, the comparison diffusion coefficient of C within one theoretical approach in  $\alpha$ -Ti and  $\alpha_2$ -Ti<sub>3</sub>Al and with that for metallic impurities was not carried out. The aim of this work is a comparative study of C diffusion coefficients in both  $\alpha$ -Ti and  $\alpha_2$ -Ti<sub>3</sub>Al materials.

## 2. Computational details

The atomic and electronic structure of  $\alpha$ -Ti and  $\alpha_2$ -Ti<sub>3</sub>Al was calculated using the projector augmented wave (PAW) method [22, 23] in the plane-wave basis set with the generalized gradient approximation (GGA-PBE) [24] for the exchange-correlation functional. In the case of  $\alpha$ -Ti with an HCP structure, a  $4 \times 4 \times 3$  supercell containing 96 Ti atoms was used. The atomic structure of the  $\alpha_2$ -Ti<sub>3</sub>Al alloy with the same crystal structure was modeled by a  $2 \times 2 \times 3$  supercell also containing 96 atoms (72 Ti and 24 Al atoms). A full optimization scheme including relaxation of both atomic positions and supercell volume was used. The energy cutoff for the plane-wave basis set was 400 eV. Integration over the Brillouin zone was performed using a  $3 \times 3 \times 3$   $\Gamma$ -centered mesh of *k*-points. Convergence was considered achieved if the difference in the total energies of two consecutive iterations did not exceed  $10^{-6}$  eV. Relaxation of atomic positions was carried out until the forces on the atoms reached approximately  $10^{-4}$  eV/Å.

The defect formation energy ( $E^f$ ) in  $\alpha$ -Ti and  $\alpha_2$ -Ti<sub>3</sub>Al was calculated using the following formula:

$$E^f = E^{def} - E^{id} - E(C) + nE(\text{Ti}/\text{Al}), \quad (1)$$

where  $E^{def}$  and  $E^{id}$  are the total energies of the defect and ideal supercells;  $E(C)$  and  $E(\text{Ti}/\text{Al})$  are the total energies of C and Ti or Al in the ground state per atom; the parameter *n* is equal to 0 or 1 in the case of interstitial or substitutional defect, respectively. With this definition, the smaller  $E^f$ , the easier it is for the defect to form.

To explain the preference for defect formation, the mechanical (*MC*) and chemical (*CC*) contributions to  $E^f$  [25], the crystal orbital Hamilton population (COHP) curves [26–28] and the integral from these curves to the Fermi level (ICOHP), as well as the electron localization function (ELF) [29] were calculated. Since on the COHP curve the negative values correspond to the bonding states, while historically these states are depicted as positive, the  $-\text{COHP}$  curves and  $-\text{ICOHP}$  values will be shown and discussed in the figures. The charge transfer and overlap population were estimated by DDEC6 method that is a refinement of the Density Derived Electrostatic and Chemical (DDEC) approach [30, 31].

The migration energies ( $E^m$ ) were calculated using the nudged elastic band method with a climbing image [32]. For each migration path, five images were used, in which the positions of the diffusing atom along the migration path were determined by linear interpolation between its initial and final positions. By simultaneously relaxing all five images, each atom was assumed to be elastically bound to the same atom in adjacent images. This approach allows one to determine the minimum energy path, as well as the saddle point. Note that the difference in the total energies of system with diffusing atoms in the saddle point and in the initial position is equal to the height of the migration barrier.

The following positions of carbon in  $\alpha$ -Ti were considered (Fig. 1a): octahedral (*O*); tetrahedral (*T*); hexahedral, located between *O*-sites ( $H_O$ ) and *T*-sites ( $H_T$ ); crowdions, in which the impurity atom is located between the nearest Ti atoms in a basal plane (*Cb*) and in adjacent planes (*C*). The substitution position is designated as *S*. Since the atomic structure of  $\alpha_2$ -Ti<sub>3</sub>Al and  $\alpha$ -Ti are similar, the same interstitial sites were considered in the alloy, but due to the presence of Al there are two sites of each type, differing in the Ti content in the local environment. Sites with a higher Ti content are designated as 1, and those with a lower Ti content as 2. Figure 1b shows all considered interstitial sites in the  $\alpha_2$ -Ti<sub>3</sub>Al alloy: octahedral (*O1* and *O2*, in the centers of octahedra of the Ti<sub>6</sub> and Ti<sub>4</sub>Al<sub>2</sub> compositions); tetrahedral (*T1* and *T2*, in the center of tetrahedrons of the Ti<sub>3</sub>Al<sub>1</sub> composition, the difference between which lies in the position of the Al atom); hexahedral, located between the *O*-sites ( $H_{O1}$  and  $H_{O2}$ ) and *T*-sites ( $H_{T1}$  and  $H_{T2}$ ); crowdions, in which the impurity atom is located between the nearest Ti atoms in the same basal plane (*Cb1* and *Cb2*) and in adjacent planes (*C1* and *C2*). Positions *S1* and *S2* correspond to the substitution of Al and Ti atoms, since in the first case the nearest ones are 12 Ti atoms, and in the second case 8 Ti atoms and 4 Al atoms.

## 3. Results and discussion

### 3.1. Carbon diffusion in $\alpha$ -Ti

The calculated values of the carbon defect formation energies in  $\alpha$ -Ti are given in Table 1. The most preferred position is the *O*-interstice. It is characterized by a negative value of  $E^f$ , which is due to the lowest value of *MC* contribution.

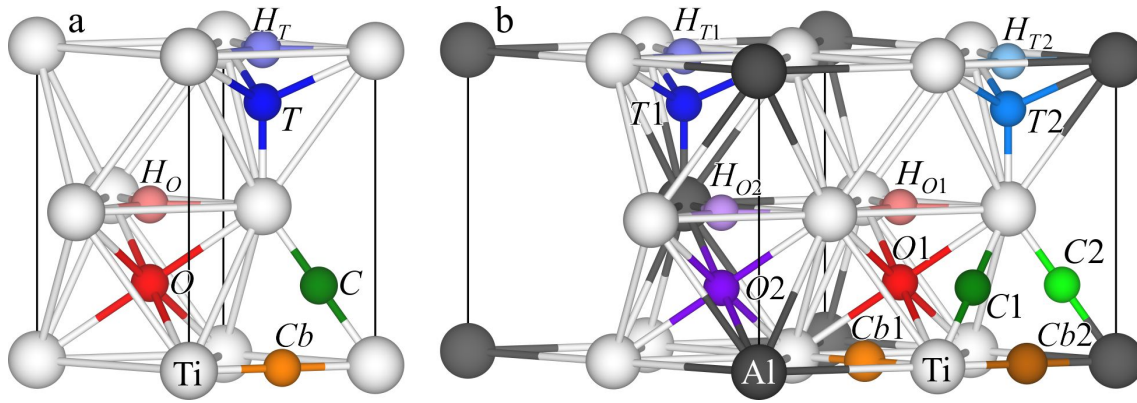
FIG. 1. Unit cell of  $\alpha$ -Ti (a) and  $\alpha_2$ -Ti<sub>3</sub>Al (b) with considered interstitial sites

TABLE 1. The defect formation energy ( $E^f$ ), the mechanical ( $MC$ ) and chemical ( $CC$ ) contributions to this energy, the changes in the Voronoi volume ( $\Delta V_V$ ) of the interstices due to carbon atom incorporation, interatomic distance between carbon and nearest titanium atoms ( $d$ ), overlap population of these bonds ( $\theta$ ), charge state of carbon atom ( $q$ ), integrated crystal orbital Hamilton population ( $-ICOHP$ ). In the case of substitutional defect subscripts “in” and “out” indicate position of C and Ti atoms in the same (0001) plane and adjacent planes

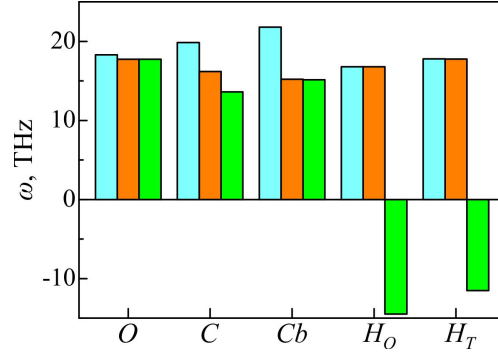
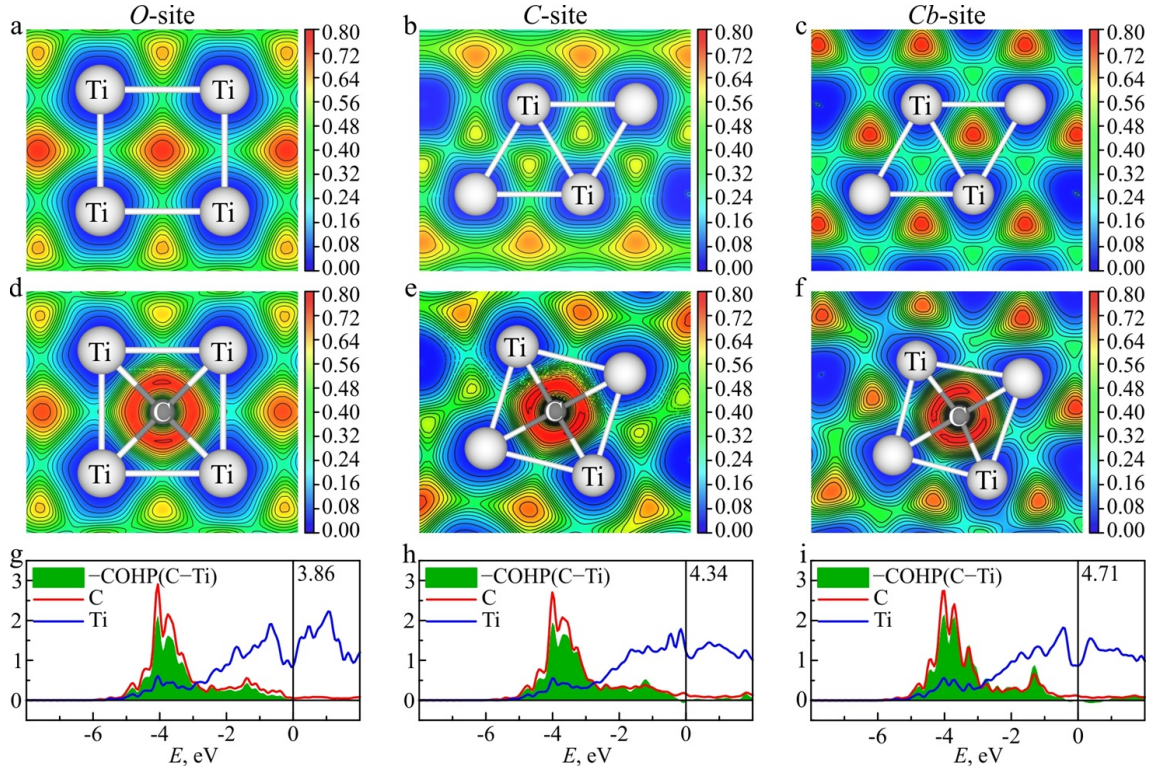
| Site  | $E^f$ , eV | $MC$ , eV | $CC$ , eV | $\Delta V_V$ , Å <sup>3</sup> | $d$ , Å                                     | $\theta$ , el.                              | $q$ , el. | $-ICOHP$ , eV                               |
|-------|------------|-----------|-----------|-------------------------------|---------------------------------------------|---------------------------------------------|-----------|---------------------------------------------|
| $O$   | −1.56      | 0.13      | −1.69     | +1.61                         | 2.10                                        | 0.55                                        | −1.18     | 3.86                                        |
| $C$   | −0.13      | 1.46      | −1.59     | +2.47                         | 2.05                                        | 0.60                                        | −1.17     | 4.34                                        |
| $Cb$  | −0.13      | 1.27      | −1.40     | +0.34                         | 2.00                                        | 0.63                                        | −1.15     | 4.71                                        |
| $H_O$ | 1.72       | 1.07      | 0.66      | +2.69                         | 2.00                                        | 0.64                                        | −0.94     | 5.21                                        |
| $H_T$ | 0.59       | 0.54      | 0.05      | +1.39                         | 1.97                                        | 0.65                                        | −1.06     | 5.17                                        |
| $S$   | 2.36       | 0.72      | 1.64      | −3.75                         | 2.81 <sub>in</sub> ,<br>2.64 <sub>out</sub> | 0.16 <sub>in</sub> ,<br>0.22 <sub>out</sub> | −0.78     | 1.15 <sub>in</sub> ,<br>1.74 <sub>out</sub> |

Another stable insertion positions are crowdion  $C$  and basal crowdion  $Cb$  (Table 1). These defects are characterized by the same values of the formation energy because of close  $MC$  and  $CC$  contribution. It should be noted that structure relaxation results in the movement of carbon atom from  $T$ -site into  $H_T$ . For hexahedral positions  $H_O$  and  $H_T$  the defect formation energies equal to 1.72 and 0.52 eV, respectively. Table 1 also presents the results of some electronic and structural characteristics of carbon in  $\alpha$ -Ti. The high value of the  $MC$  contribution among interstitial positions in the case of the  $C$ -site (1.46 eV) is manifested by a pronounced structural distortion and is a consequence of the smaller volume of the  $C$ -interstice compared to other positions. The  $O$ ,  $C$  and  $Cb$  positions are characterized by a negative and high absolute value of the chemical contribution as well as almost the same charge state of the carbon atom. Calculation of the phonon frequencies of carbon revealed the presence of only one imaginary frequency in  $H_O$  and  $H_T$  sites (Fig. 2). It means that these hexahedral positions can be considered as the first-order transition states. Thus, in  $\alpha$ -Ti the  $O$ ,  $C$  and  $Cb$  sites have to be considered as interstitial positions for carbon diffusion. Note that, unlike metallic impurities, carbon has difficulty substituting for Ti, and the defect formation energy reaches 2.36 eV (Table 1).

The introduction of carbon into the  $O$ -position only slightly, up to 0.79, increases the value of electron localization function in the interstitial site (Fig. 3a,d), and the localization region has a spherical shape that is typical for ionic-covalent interaction. Calculations have shown that a charge of  $\sim 1.2$  electrons is transferred to carbon, and the  $-ICOHP$  value reaches 3.86 eV (Table 1). Although both crowdions in pure  $\alpha$ -Ti are characterized by a low ELF (Fig. 3b,c), the C atom induces charge transfer and the formation of an electron localization region (Fig. 3e,f). The COHP curves for these positions (Fig. 3g–i) show a virtually complete absence of antibonding states as well as a low density of states at the Fermi level that indicates strong C–Ti interactions at these sites, consistent with the values of the chemical contributions (Table 1).

Table 2 presents the migration barriers for all considered jumps of carbon between stable interstices. It is seen that there are four paths oriented along the basal plane ( $\parallel a$ ):  $O \rightarrow C$  (and reverse jump  $C \rightarrow O$ ),  $C \rightarrow C$  and two variants of  $Cb \rightarrow Cb$  which differ by saddle point given in brackets. Carbon diffusion along  $[0001]$  direction can occur via only two paths:  $C \rightarrow C$  and  $O \rightarrow (H_O) \rightarrow O$ . Other four jumps allow carbon to move simultaneously along both  $a$  and  $c$  axes. Due to



FIG. 2. Phonon frequencies of C atom in interstitial sites in  $\alpha$ -TiFIG. 3. Distribution of ELF in ideal  $\alpha$ -Ti (a–c) and near the C interstitial atom (d–f), as well as the local DOS of the C and nearest Ti atoms and the corresponding COHP curves (g–i)

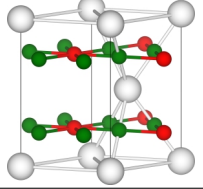
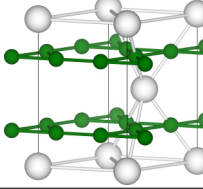
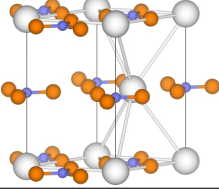
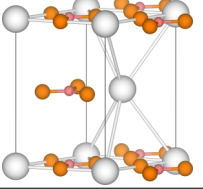
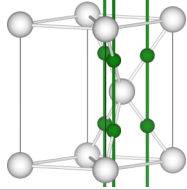
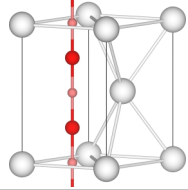
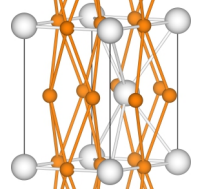
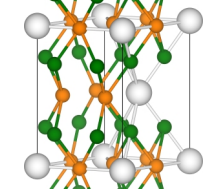
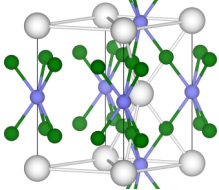
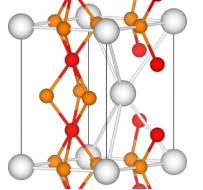
the highest preference for absorption in the  $O$ -site,  $E^m$  along the  $a$ -axis for the  $O \rightarrow C$  path is 1.54 eV, while for the reverse path,  $C \rightarrow O$ , it is only 0.11 eV. The  $C \rightarrow C$  jump along the  $a$ -axis requires 1.42 eV that is 0.3 eV more than this jump along the  $c$ -axis. The migration energy for the  $Cb \rightarrow (H_T) \rightarrow Cb$  path (0.72 eV) is minimal, while for the  $Cb \rightarrow (H_O) \rightarrow Cb$  path (1.85 eV) is maximal among atomic jumps oriented along basal plane (Table 2). The migration energy for the  $C \rightarrow C$  and  $O \rightarrow (H_O) \rightarrow O$  paths along  $c$ -axis are 1.12 and 3.28 eV, respectively. It should be noted that the high value of  $E^m$  for the  $O \rightarrow (H_O) \rightarrow O$  jump allows us to exclude it from further consideration as the slowest but not the only diffusion channel along  $c$ -axis. The jumps between both crowdions, when carbon displacement occurs in both directions simultaneously, require 0.37–0.72 eV. Taking into account difference in  $E^f$  for  $C(Cb)$  and  $O$  sites (1.43 eV), it is possible to conclude that  $O \rightarrow Cb$  jump can make main contribution to diffusion among mixed paths.

Additionally, Table 2 includes the values of the migration energy and the attempt frequency ( $\nu$ ) obtained in paper [21]. It is seen that almost all present  $E^m$  values agree well with earlier data. Exception is  $C \rightarrow Cb$  jump for which the migration energy is found to be about twice less than that from [21]. Difference in the attempt frequencies is connected with different approach for their estimation. In the present paper, the classical expression [4] was applied:

$$\nu = \sqrt{\frac{E^m}{2md^2}}, \quad (2)$$

where  $m$  is mass of C atom,  $d$  is jump distance; whereas in [21] Vineyard's definition [33] was used.

TABLE 2. Migration energies ( $E^m$ ), jump length ( $d$ ) and attempt frequency ( $\nu$ ) for all considered jumps of carbon in  $\alpha$ -Ti. The values in parentheses are given for the reverse jump. Results from paper [21] are marked by \*

| Path                             | $O \rightarrow C \parallel a$                                                       | $C \rightarrow C \parallel a$                                                       | $Cb \rightarrow (H_T) \rightarrow Cb \parallel a$                                    | $Cb \rightarrow (H_O) \rightarrow Cb \parallel a$                                     |
|----------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| $E^m$ , eV                       | 1.54 (0.11),<br>1.42* (0.12*)                                                       | 1.42                                                                                | 0.72                                                                                 | 1.85                                                                                  |
| $d$ , Å                          | 1.460                                                                               | 1.460                                                                               | 1.685                                                                                | 1.685                                                                                 |
| $\nu$ , $10^{12} \text{ s}^{-1}$ | 17.03 (4.55),<br>94.57* (3.21*)                                                     | 16.36                                                                               | 10.09                                                                                | 16.18                                                                                 |
| Network                          |    |    |    |    |
| Path                             | $C \rightarrow C \parallel c$                                                       |                                                                                     | $O \rightarrow (H_O) \rightarrow O \parallel c$                                      |                                                                                       |
| $E^m$ , eV                       | 1.12                                                                                |                                                                                     | 3.28, 3.40*                                                                          |                                                                                       |
| $d$ , Å                          | 2.319                                                                               |                                                                                     | 2.319                                                                                |                                                                                       |
| $\nu$ , $10^{12} \text{ s}^{-1}$ | 9.15                                                                                |                                                                                     | 15.65, 16.70*                                                                        |                                                                                       |
| Network                          |   |                                                                                     |  |                                                                                       |
| Path                             | $Cb \rightarrow Cb$                                                                 | $C \rightarrow Cb$                                                                  | $C \rightarrow (H_T) \rightarrow C$                                                  | $O \rightarrow Cb$                                                                    |
| $E^m$ , eV                       | 0.38                                                                                | 0.38 (0.38),<br>0.85* (0.84*)                                                       | 0.72                                                                                 | 1.77 (0.35),<br>1.69* (0.38*)                                                         |
| $d$ , Å                          | 2.467                                                                               | 1.433                                                                               | 2.867                                                                                | 1.433                                                                                 |
| $\nu$ , $10^{12} \text{ s}^{-1}$ | 5.01                                                                                | 8.62 (8.62),<br>10.85* (33.68*)                                                     | 5.93                                                                                 | 18.60 (8.27),<br>70.87* (17.60*)                                                      |
| Network                          |  |  |  |  |

The diffusion coefficients within the interstitial mechanism were calculated using the Landman method [34,35]. Since  $O$ ,  $C$  and  $Cb$  sites in  $\alpha$ -Ti correspond to  $2a$ ,  $6g$  and  $6h$  Wyckoff positions, the Fourier transform matrix of displacement,  $\tilde{p}(\mathbf{k})$ , and the Laplace transform matrix of waiting-time function,  $\tilde{\psi}(u)$ , in the considered jump network have a dimension of  $14 \times 14$ . We do not present these matrices in the present paper because they are very cumbersome. The propagator matrix is calculated using the following expression:

$$R(\mathbf{k}, u) = E - \tilde{\psi}(u) \circ \tilde{p}(\mathbf{k}), \quad (3)$$

where  $E$  is the identity matrix; the symbol " $\circ$ " denotes the Hadamard (element-wise) product of matrices.

The root-mean-square displacement of a diffusing atom in the  $\mathbf{r}$  direction over time  $t$  is estimated as

$$\langle \sigma_{\mathbf{r}}^2(t) \rangle = \lim_{\mathbf{k} \rightarrow 0} \left( t \frac{1}{\Delta_0} \frac{\delta^2 \det R(\mathbf{k}, u)}{\delta \mathbf{k}_{\mathbf{r}}^2} \right), \quad (4)$$

where

$$\Delta_0 = \lim_{\mathbf{k} \rightarrow 0} \left( \frac{\partial \det R(\mathbf{k}, u)}{\partial u} \right). \quad (5)$$

According to the Einstein–Smoluchowski relation, the root-mean-square displacement over time  $t$  is:

$$\langle \sigma^2(t) \rangle = 2ntD, \quad (6)$$

where  $n$  is the dimension of the system and  $D$  is the diffusion coefficient.

The attempt frequencies (eq. (2)) are included in the formula for the jump rate  $\Gamma$ :

$$\Gamma = \nu \exp\left(-\frac{E^m}{k_B T}\right), \quad (7)$$

where  $k_B$  is the Boltzmann constant and  $T$  is the temperature. So, each jump are characterized by own rate determined by the values of  $E^m$  and  $\nu$  (Fig. 4a). The ratio of polynomials composed of different  $\Gamma$ 's gives the diffusion coefficient.

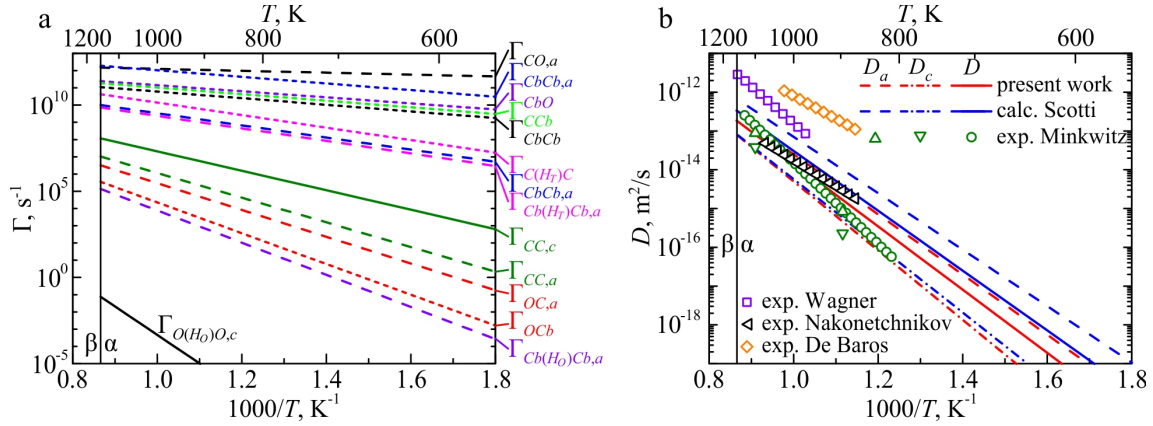


FIG. 4. Temperature-dependent jump rate (a) and diffusion coefficient (b) of carbon in  $\alpha$ -Ti in comparison with earlier calculations of Scotti [21] and experimental data of Wagner [17], Nekonetchnikov [18], Minkwitz [19] and De Baros [20]

From Fig. 4a it is seen that, as expected, jumps from the  $O$ -site are slower than from both crowdions and the  $O \rightarrow H_O \rightarrow O$  jump is the slowest. For convenient we use following designation:  $\Gamma_{ij,k}$  is the rate of the  $i \rightarrow j$  jump oriented along  $k$ -direction, the notation  $\Gamma_{i(h)j,k}$  denotes a jump with a saddle point in position  $h$ . To apply obtained expressions for diffusion coefficients along  $a$ - and  $c$ -axis ( $D_a$  and  $D_c$ ), they should be simplified. Since  $O$ -site is the preferable one and  $\Gamma_{OC,a}$  and  $\Gamma_{OCb,a}$  are the lowest one excepting  $\Gamma_{O(H_O)O,c}$  and  $\Gamma_{Cb(H_O)Cb}$ , the expressions for  $D_a$  and  $D_c$  were expanded in a Taylor series for these rates:

$$D_a = a_0^2 \Gamma_{OC}, \quad (8)$$

and

$$D_c = c_0^2 \Gamma_{OCb}, \quad (9)$$

where  $a_0$  and  $c_0$  are the Ti lattice parameters.

By approximating the temperature dependence of  $D_a$  and  $D_c$  according to the Arrhenius equation using the least squares method over points with a step of 50 K, we obtain the final expressions for the diffusion coefficients of carbon within the framework of the interstitial mechanism:

$$\begin{aligned} D_a &= 1.45 \cdot 10^{-6} \exp\left(-\frac{1.54}{k_B T}\right) \text{ m}^2/\text{s}, \\ D_c &= 4.16 \cdot 10^{-6} \exp\left(-\frac{1.77}{k_B T}\right) \text{ m}^2/\text{s}. \end{aligned} \quad (10)$$

Figure 4b shows the calculated results of the carbon diffusion coefficients in  $\alpha$ -Ti. It is evident that C diffusion is faster along the  $a$ -axis than along  $c$ -axis that is in agreement with calculations from [21] and experimental data for single crystal diffusion from [19]. The diffusion anisotropy ( $D_c/D_a$ ) is 0.27–0.29 for the temperatures of 896–1100 K (0.27–0.43 for the same temperature range [19]). The values for polycrystalline  $D$  (solid line in Fig. 4b) estimated as geometric mean of  $D_a$  and  $D_c$  are in good agreement with the experiments [18, 19] and 1–2 orders of magnitude lower than in the experimental works [17, 20].

Figure 5 demonstrates the polycrystalline diffusion coefficient of C in comparison with those for other impurities obtained previously by the same method in [13, 14, 36] and with the self-diffusion coefficient of Ti from the paper [37]. It is seen that the diffusion rate of C is 4–6 and 4–8 orders of magnitude higher than the self-diffusion of Ti and diffusion of normal metal impurities (Al and Ga) at the temperature of 600–1155 K, respectively. Compared to oxygen, carbon diffuses 2–3 orders of magnitude faster that is in agreement with experiment [10]. At the same time, the C diffusion coefficient is found to be somewhat lower than that of the anomalously fast  $d$ -metal impurities (Fe and Co).

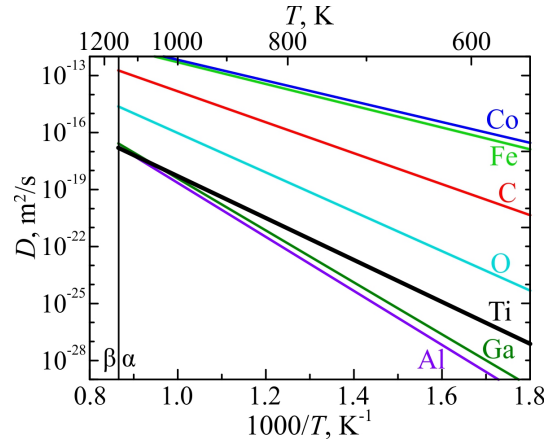


FIG. 5. Temperature-dependent diffusion coefficients of C in  $\alpha$ -Ti and their comparison with the diffusion coefficients of Fe, Co, Ga, Al, O [13, 14, 36] and the Ti self-diffusion coefficient [37]

### 3.2. Carbon diffusion in $\alpha_2$ -Ti<sub>3</sub>Al

Similar calculations of the C diffusion coefficient were performed in the  $\alpha_2$ -Ti<sub>3</sub>Al alloy as well. It should be noted that the same interstitial sites were considered in this alloy as in  $\alpha$ -Ti, but due to the presence of Al, there are two sites of each type, differing in the Ti content in the local environment. Sites with a higher Ti content are designated 1, and those with a lower Ti content are designated 2 (Fig. 1b). As in  $\alpha$ -Ti, in the alloy during structural optimization carbon atom moves from  $T1$  and  $T2$  sites into  $H_{T1}$  and  $Cb1$  ones. Similarly, both  $H_{O1}$  and  $H_{O2}$  sites are dynamically unstable with respect to vibrations along the [0001] direction, whereas unlike  $\alpha$ -Ti the  $H_{T1}$  and  $H_{T2}$  sites are stable (Fig. 6a). The  $C1$  crowdion is unstable and, during structural optimization, the carbon atom shifted to the  $O1$ -site. Thus, in  $\alpha_2$ -Ti<sub>3</sub>Al the stable interstices are the  $O1$ ,  $O2$ ,  $C2$ ,  $Cb1$ ,  $Cb2$ ,  $H_{T1}$  and  $H_{T2}$ .

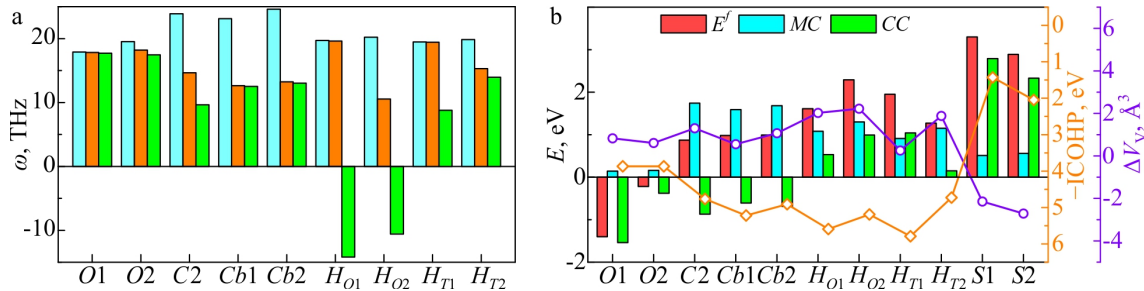


FIG. 6. Phonon frequencies of carbon atom (a) as well as defect formation energies, mechanical and chemical contributions in comparison with the change in the Voronoi volume and the average population of the Hamiltonian crystal orbitals (b) in interstitial sites in the  $\alpha_2$ -Ti<sub>3</sub>Al alloy

The calculated defect formation energies and several additional data for these sites are given in Table 3. It is evident that the  $O1$ -site is the most preferred for carbon due to the high absolute negative value of the  $CC$  contribution. Despite low  $MC$  in  $E^f$  in both  $O1$  and  $O2$  sites (almost the same as in  $\alpha$ -Ti), the difference in  $CC$  contribution is quite large. The insertion of carbon into the  $O1$ -site induces a large charge transfer to it (Fig. 7), with the charge accumulation region consistent with the electron pair localization region, indicating the covalent polar nature of the C–Ti bond. It should be noted that, as in the case of  $\alpha$ -Ti, carbon induced enough high charge transfer (Table 3), and a correlation between the  $MC$  contribution to  $E^f$  and the increase in interstitial volume ( $\Delta V_V$ ) also occurs (Fig. 6b). In general, the covalency of bonds in  $\alpha_2$ -Ti<sub>3</sub>Al is higher than in  $\alpha$ -Ti due to the presence of Al, which leads to higher  $E^f$  values in the alloy. The mechanical contribution to the defect formation energy for C as well as Fe, Co, Al, Ga [15] correlates with the change in the volume of the Voronoi polyhedron in both studied materials, but for the same  $|\Delta V_V|$  the  $MC$  contribution in the alloy is higher (Fig. 8). It can be seen that the slope of the trend line for the  $\alpha_2$ -Ti<sub>3</sub>Al alloy ( $0.65 \text{ eV}/\text{\AA}^3$ ) is almost twice as large as that for  $\alpha$ -Ti ( $0.36 \text{ eV}/\text{\AA}^3$ ), indicating higher rigidity of the alloy. The latter is consistent with the higher Young's modulus of the alloy (185 GPa [38]) compared to the metal (113 GPa [39]). The correlation coefficients for titanium and the alloy are 0.92 and 0.90, respectively.

Constructing a similar graph for the  $CC$  contribution is significantly more difficult, since it is determined by several factors, including charge transfer, which explained well the observed trends in the case of non-metallic impurities (O, H, B, C) [40, 41]. In addition, the appearance of aluminum near the defect leads to an increase in its formation energy along with an increase in the strength of the bonds, which should lead to a decrease in the diffusion coefficient.



TABLE 3. The defect formation energy ( $E^f$ ), the mechanical ( $MC$ ) and chemical ( $CC$ ) contributions to this energy, the changes in the Voronoi volume ( $\Delta V_V$ ) of the interstices due to carbon atom incorporation, charge state of carbon atom ( $q$ ), interatomic distance between carbon and nearest titanium/aluminum atoms ( $d$ ), overlap population of these bonds ( $\theta$ ), integrated crystal orbital Hamilton population ( $-\text{ICOHP}$ ). In the case of substitutional defect subscripts “*in*” and “*out*” indicate position of C and Ti/Al atoms in the same (0001) plane and adjacent planes

| Site     | $E^f$ , eV | $MC$ , eV | $CC$ , eV | $\Delta V_V$ , Å <sup>3</sup> | $q$ , el. | $d$ , Å                                     |                                             | $\theta$ , el.                              |                                             | $-\text{ICOHP}$ , eV                        |                                             |
|----------|------------|-----------|-----------|-------------------------------|-----------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
|          |            |           |           |                               |           | C–Ti                                        | C–Al                                        | C–Ti                                        | C–Al                                        | C–Ti                                        | C–Al                                        |
| $O1$     | −1.40      | 0.14      | −1.54     | +0.83                         | −1.35     | 2.10                                        | –                                           | 0.26                                        | –                                           | 3.87                                        | –                                           |
| $O2$     | −0.22      | 0.16      | −0.38     | +0.61                         | −1.08     | 2.07                                        | 2.04                                        | 0.55                                        | 0.51                                        | 4.10                                        | 3.40                                        |
| $C2$     | 0.87       | 1.74      | −0.87     | +1.30                         | −1.09     | 1.97                                        | 1.92                                        | 0.66                                        | 0.62                                        | 5.20                                        | 4.33                                        |
| $Cb1$    | 0.98       | 1.59      | −0.61     | +0.55                         | −1.15     | 1.91                                        | –                                           | 0.66                                        | –                                           | 5.22                                        | –                                           |
| $Cb2$    | 0.99       | 1.68      | −0.69     | +1.07                         | −1.12     | 1.94                                        | 1.92                                        | 0.69                                        | 0.61                                        | 5.49                                        | 4.33                                        |
| $H_{O1}$ | 1.61       | 1.08      | 0.53      | +2.02                         | −1.10     | 1.96                                        | –                                           | 0.67                                        | –                                           | 5.59                                        | –                                           |
| $H_{O2}$ | 2.29       | 1.30      | 0.99      | +2.22                         | −0.92     | 2.00                                        | 1.91                                        | 0.62                                        | 0.63                                        | 5.39                                        | 4.80                                        |
| $H_{T1}$ | 1.95       | 0.91      | 1.04      | +0.25                         | −0.87     | 1.93                                        | –                                           | 0.65                                        | –                                           | 5.79                                        | –                                           |
| $H_{T2}$ | 1.27       | 1.15      | 0.15      | +1.88                         | −1.07     | 1.99                                        | 1.94                                        | 0.63                                        | 0.60                                        | 4.95                                        | 4.28                                        |
| $S1$     | 3.30       | 0.51      | 2.79      | −2.15                         | −0.87     | 2.76 <sub>in</sub> ,<br>2.72 <sub>out</sub> | –                                           | 0.18 <sub>in</sub> ,<br>0.20 <sub>out</sub> | –                                           | 1.36 <sub>in</sub> ,<br>1.49 <sub>out</sub> | –                                           |
| $S2$     | 2.89       | 0.56      | 2.33      | −2.71                         | −0.97     | 2.26 <sub>in</sub> ,<br>2.42 <sub>out</sub> | 3.11 <sub>in</sub> ,<br>3.45 <sub>out</sub> | 0.42 <sub>in</sub> ,<br>0.33 <sub>out</sub> | 0.09 <sub>in</sub> ,<br>0.05 <sub>out</sub> | 3.33 <sub>in</sub> ,<br>2.63 <sub>out</sub> | 0.28 <sub>in</sub> ,<br>0.10 <sub>out</sub> |

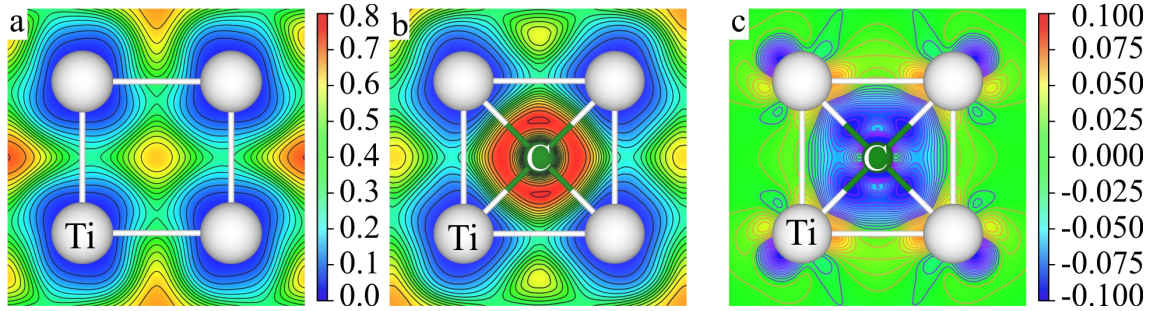


FIG. 7. ELF in ideal  $\alpha_2$ -Ti<sub>3</sub>Al (a) and near the carbon interstitial atom (b) as well as  $\Delta\rho$  (c) at the  $O1$ -site

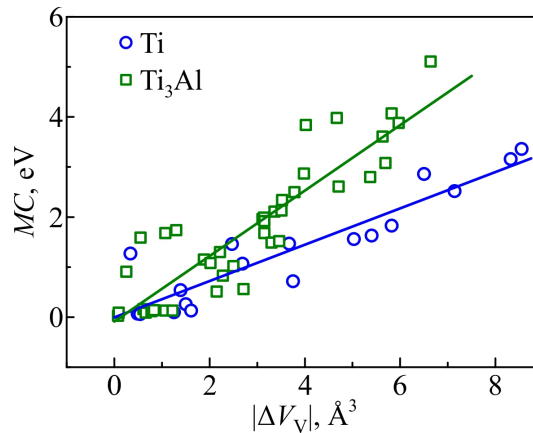


FIG. 8. Correlation between the mechanical contribution to the interstitial defect formation energy and the change in the modulus of the Voronoi volume of corresponding interstices in  $\alpha$ -Ti and  $\alpha_2$ -Ti<sub>3</sub>Al

The possible migration paths between stable positions are shown in Fig. 9, 10. It is seen that there are several migration paths along the  $[0001]$  direction. There are the paths from preferable  $O1$  and  $O2$  sites: direct ones  $O1 \rightarrow O1$  and  $O2 \rightarrow O2$  with  $H_{O1}$  and  $H_{O2}$  saddle points, indirect ones  $O1 \rightarrow Cb1 \rightarrow O1$ ,  $O2 \rightarrow Cb1 \rightarrow O2$  and  $O2 \rightarrow Cb2 \rightarrow O2$  (Fig. 9a). There are also path without any  $O$  sites, this is  $C2 \rightarrow Cb1 \rightarrow C2 \rightarrow Cb2 \rightarrow C2$  (Fig. 9b). It should be noted that only such a long path satisfies translation invariance. Diffusion along basal plane (0001) can pass through  $O1$  and  $O2$  sites –  $O1 \rightarrow O2 \rightarrow O1$ ,  $O2 \rightarrow C2 \rightarrow O2$  and  $O1 \rightarrow C2 \rightarrow C2 \rightarrow O1$  (Fig. 10a), as well as bypassing them –  $Cb1 \rightarrow Cb1 \rightarrow Cb2 \rightarrow Cb2 \rightarrow Cb1$  (Fig. 10b). Migration through positions  $H_{T1}$  and  $H_{T2}$  only results in an increase in the number of jumps, so these positions should not be considered as intermediate ones. Nevertheless,  $H_{T2}$ -site can be considered as initial one for a diffusion path  $H_{T2} \rightarrow Cb2 \rightarrow Cb2 \rightarrow H_{T2}$  (Fig. 10b). The migration energies and the attempt frequencies for all possible carbon atom jumps are given in Table 4.

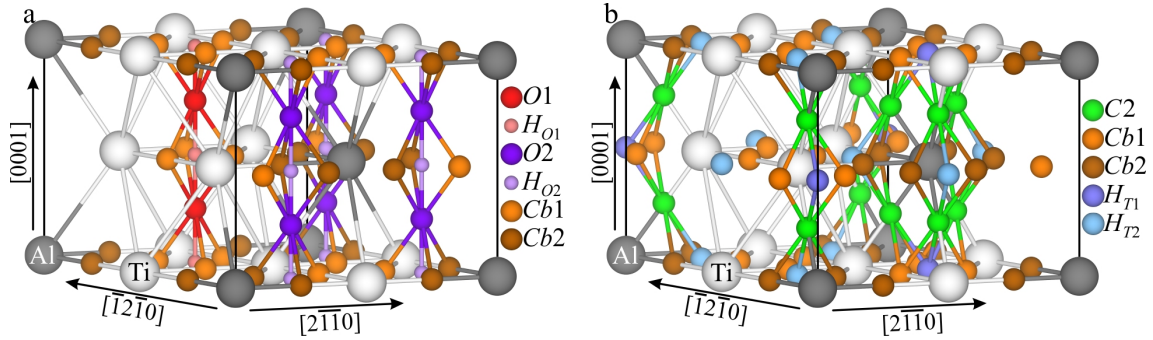


FIG. 9. Migration paths in the  $\alpha_2$ -Ti<sub>3</sub>Al alloy oriented along the  $[0001]$  direction and passing through octahedral sites (a) or bypassing them (b)

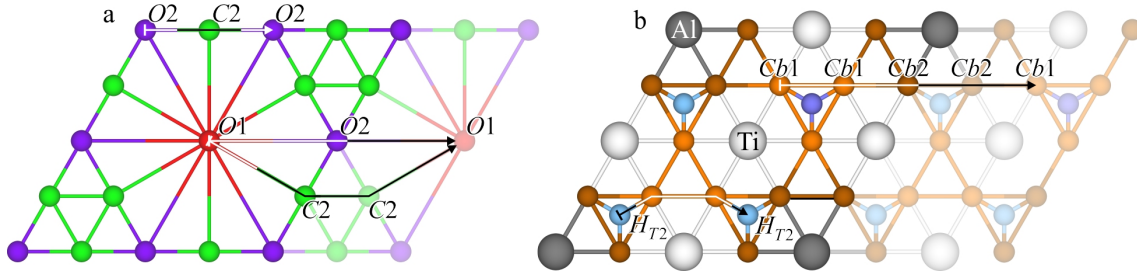


FIG. 10. Migration paths in the  $\alpha_2$ -Ti<sub>3</sub>Al alloy oriented along the  $(0001)$  plane and passing through octahedral sites (a) or bypassing them (b)

According to the statistical approach, the partial diffusion coefficient for a particular path  $i \rightarrow j$  has the following form:

$$D(i \rightarrow j) = F(i) \left( \frac{\mathbf{s} \cdot \mathbf{u}}{|\mathbf{u}|} \right)^2 \frac{P(i \rightarrow k_1)P(k_1 \rightarrow k_2) \dots P(k_n \rightarrow j)}{\tau(i \rightarrow k_1) + \tau(k_1 \rightarrow k_2) + \dots + \tau(k_n \rightarrow j)}, \quad (11)$$

where  $F(i)$  is the probability that the initial position is occupied by an impurity atom, calculated using the formula:

$$F(i) = \frac{n(i) \exp(E^f(i))}{\sum_k n(k) \exp(E^f(k))}, \quad (12)$$

where  $n(i)$  is the multiplicity of position  $i$  in the unit cell of the  $\alpha_2$ -Ti<sub>3</sub>Al alloy, the summation is over all stable interstitial positions;

$\mathbf{s}$  is the displacement vector,  $\mathbf{u}$  is an arbitrary vector along which the diffusion coefficient is calculated,  $P(i \rightarrow j)$  is the probability of jumping  $i \rightarrow j$  before all jumps from position  $i$ :

$$P(i \rightarrow j) = \frac{\Gamma(i \rightarrow j)}{\sum_k n(k) \Gamma(i \rightarrow k)}; \quad (13)$$

$\tau(i \rightarrow j)$  is the average time required for the jump  $i \rightarrow j$ , equal to

$$\tau(i \rightarrow j) = \frac{1}{\Gamma(i \rightarrow j)}. \quad (14)$$

The product and sum in the numerator and denominator of eq. (11) arise when diffusion is considered along a path consisting of several jumps. The resulting diffusion coefficient is the sum of all partial coefficients that contribute to

TABLE 4. Migration energies ( $E^m$ ), jump length ( $d$ ) and attempt frequency ( $\nu$ ) for all considered jumps of carbon in  $\alpha_2$ -Ti<sub>3</sub>Al. The values in parentheses are given for the reverse jump

| Path                             | $O1 \rightarrow O1 \parallel c$   | $O2 \rightarrow O2 \parallel c$   | $O1 \rightarrow Cb1 \parallel c$     | $O2 \rightarrow Cb1 \parallel c$     | $O2 \rightarrow Cb2 \parallel c$     |
|----------------------------------|-----------------------------------|-----------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| $E^m$ , eV                       | 3.01                              | 2.51                              | 2.50 (0.12)                          | 2.23 (1.03)                          | 1.58 (0.37)                          |
| $d$ , Å                          | 2.320                             | 2.320                             | 1.425                                | 1.425                                | 1.425                                |
| $\nu$ , $10^{12} \text{ s}^{-1}$ | 14.98                             | 13.69                             | 22.26 (5.01)                         | 20.99 (14.24)                        | 17.69 (8.56)                         |
| Path                             | $C2 \rightarrow Cb1 \parallel c$  | $C2 \rightarrow Cb2 \parallel c$  | $C2 \rightarrow H_{T1} \parallel c$  | $C2 \rightarrow H_{T2} \parallel c$  | –                                    |
| $E^m$ , eV                       | 0.95 (0.84)                       | 0.31 (0.19)                       | 1.21 (0.13)                          | 0.95 (0.55)                          | –                                    |
| $d$ , Å                          | 1.425                             | 1.425                             | 1.425                                | 1.425                                | –                                    |
| $\nu$ , $10^{12} \text{ s}^{-1}$ | 13.72 (12.89)                     | 7.88 (6.16)                       | 15.48 (5.07)                         | 13.71 (10.44)                        | –                                    |
| Path                             | $O1 \rightarrow O2 \parallel a$   | $O1 \rightarrow C2 \parallel a$   | $O2 \rightarrow C2 \parallel a$      | $C2 \rightarrow C2 \parallel a$      | $Cb1 \rightarrow Cb1 \parallel a$    |
| $E^m$ , eV                       | 3.14 (1.96)                       | 2.79 (0.52)                       | 1.20 (0.11)                          | 1.09                                 | 0.63                                 |
| $d$ , Å                          | 2.868                             | 2.484                             | 1.434                                | 1.434                                | 1.434                                |
| $\nu$ , $10^{12} \text{ s}^{-1}$ | 12.38 (9.78)                      | 13.48 (5.82)                      | 15.31 (4.63)                         | 14.59                                | 11.08                                |
| Path                             | $Cb2 \rightarrow Cb2 \parallel a$ | $Cb1 \rightarrow Cb2 \parallel a$ | $H_{T1} \rightarrow Cb1 \parallel a$ | $H_{T2} \rightarrow Cb1 \parallel a$ | $H_{T2} \rightarrow Cb2 \parallel a$ |
| $E^m$ , eV                       | 1.30                              | 0.31 (0.30)                       | 0.13 (1.10)                          | 0.02 (0.31)                          | 0.10 (0.38)                          |
| $d$ , Å                          | 1.434                             | 1.434                             | 0.828                                | 0.828                                | 0.828                                |
| $\nu$ , $10^{12} \text{ s}^{-1}$ | 15.92                             | 7.77 (7.64)                       | 8.66 (25.36)                         | 3.49 (13.45)                         | 7.67 (14.89)                         |

diffusion along the considered direction. It should be noted that the diffusion coefficient values were calculated for temperatures of 900–1500 K, after that these values were approximated using the Arrhenius law.

Calculations of partial diffusion coefficients for the above-mentioned paths showed that the main diffusion channels are  $O2 \rightarrow C2 \rightarrow O2$  along  $a$ -axis and  $O1 \rightarrow Cb1 \rightarrow O1$  along  $c$ -axis. As a result, the activation energies for the diffusion along  $a$  and  $c$  axes are approximately equal to the sum of the relative formation energy and the migration energy, i.e.  $E^f(O2) - E^f(O1) + E^m(O2 \rightarrow C2)$  and  $0 + E^m(O1 \rightarrow Cb1)$ , respectively, and the diffusion coefficient  $D_a$  and  $D_c$  can be written as follows:

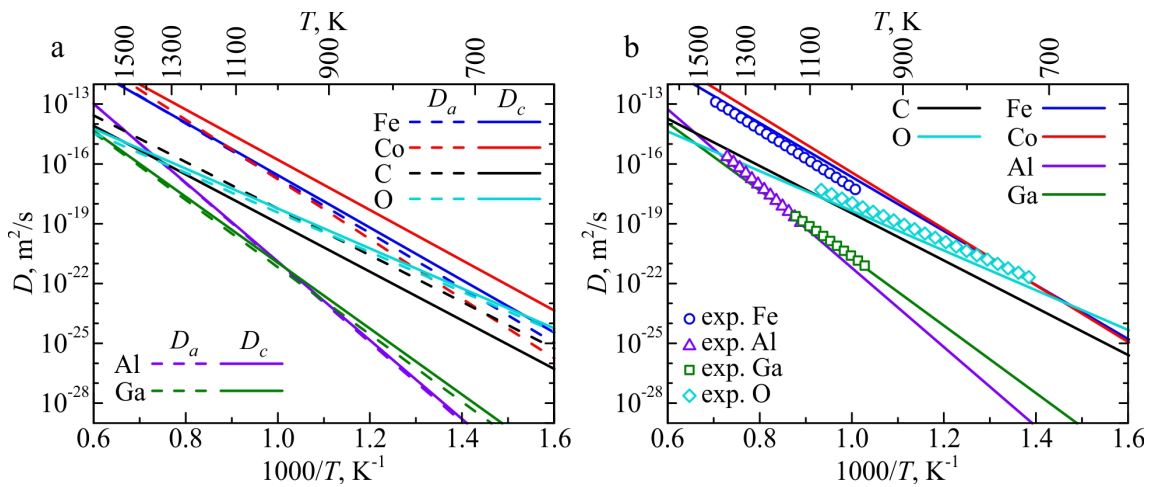


FIG. 11. Single-crystal (a) and polycrystalline (b) diffusion coefficients of carbon in  $\alpha_2$ -Ti<sub>3</sub>Al in comparison with our earlier calculations for Fe, Co, Al, Ga [16] and O [36] as well as experimental data for Fe [6], Al [7], Ga [8] and O [10]

$$\begin{aligned}
 D_a &= 2.79 \cdot 10^{-7} \exp\left(-\frac{2.32}{k_B T}\right) \text{ m}^2/\text{s}, \\
 D_c &= 1.68 \cdot 10^{-7} \exp\left(-\frac{2.42}{k_B T}\right) \text{ m}^2/\text{s}.
 \end{aligned}
 \tag{15}$$

The Arrhenius plot for the single-crystal diffusion coefficients of carbon in the  $\alpha_2$ -Ti<sub>3</sub>Al alloy in comparison with those for other impurities obtained previously in [16, 36] are shown in Fig. 11a. It is seen that carbon, like oxygen, is characterized by lower activation energies than that of metal impurities. At temperatures 700 to 1300 K both nonmetals diffuse faster than normal diffusers (Al, Ga) and slower than anomalous ones (Fe, Co). The carbon diffusion anisotropy ( $D_c/D_a$ ) is 0.17–0.27 for the temperatures of 900–1500 K. It is interesting that the ratio  $D_c/D_a < 1$  is valid only for carbon among the impurities shown in Fig. 11a and the same diffusion anisotropy was found for carbon in  $\alpha$ -Ti (Fig. 4b). To the best of our knowledge, there are no experimental or theoretical data on carbon diffusion in the  $\alpha_2$ -Ti<sub>3</sub>Al alloy; however, the polycrystalline diffusion coefficients of Fe, Al, Ga and O that we calculated earlier [16, 36] are in good agreement with the experimental data (Fig. 11b), which allows us to hope that the results obtained for carbon are correct. Finally, it should be noted that although the general trend in the diffusion coefficients of the above-mentioned elements in  $\alpha_2$ -Ti<sub>3</sub>Al is the same as in  $\alpha$ -Ti, the values are several orders of magnitude lower. This is consistent with experimental data and is explained by higher values of both the defect formation energy in the alloy and the migration barriers.

#### 4. Conclusion

In this work, a comparative *ab-initio* study of carbon diffusion in  $\alpha$ -Ti and  $\alpha_2$ -Ti<sub>3</sub>Al was performed using the combination of density functional theory and transition state theory. Octahedral interstitials were found to be the most energetically favored positions in both materials, mainly due to the mechanical (in  $\alpha$ -Ti) and chemical (in  $\alpha_2$ -Ti<sub>3</sub>Al) contributions to defect formation energy. Moreover, in the alloy carbon prefers the Ti local environment. The presence of Al significantly increases the interstitial defect formation energy, which is directly attributed to the higher rigidity of the alloy compared to pure titanium. This also induces higher migration barriers, slowing down the carbon diffusion in the alloy by several orders of magnitude. At the same time, in both materials carbon diffuses faster than normal diffusers (Al and Ga) and slower than anomalously fast *d*-metal impurities (Fe and Co) and  $D_c/D_a < 1$ . In the case of  $\alpha$ -Ti the calculated temperature-dependent diffusion coefficients demonstrate good agreement with available experimental and theoretical data. In general, the obtained results provide insight into the atomic diffusion of interstitial impurities, offering a theoretical basis for predicting the improvement of thermal stability of coatings and creep resistance of titanium aluminide-based aerospace materials.

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## Adiabatic conditions for non-stationary optical phase modulation: a non-degenerate case

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**ABSTRACT** This work examines a non-stationary phase-modulation process characterized by a time-dependent interaction coefficient, confined to the non-degenerate case. We derive an exact non-adiabatic solution to the time-dependent Schrödinger equation. We then establish the criterion under which adiabatic considerations become valid—specifically, the condition permitting a stationary-state solution to approximate the non-stationary problem. Our results hold for an arbitrary number of interacting modes and an arbitrary photon number.

**KEYWORDS** Phase modulation, non-stationary dynamics, quantum optics, Lie algebra.

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### 1. Introduction

Electro-optic phase modulation provides a coherent mechanism for coupling optical frequency modes through the linear electro-optic (Pockels) effect [1,2]. Under harmonic driving, an optical carrier is transformed into a discrete frequency comb consisting of sidebands separated by integer multiples of the modulation frequency [3]. From the perspective of quantum optics, this interaction implements a unitary transformation in the Hilbert space of optical frequency modes, enabling deterministic manipulation of high-dimensional photonic states and coherent engineering of multimode optical fields [4–10]. Accordingly, an electro-optic modulator may be viewed as a frequency-domain multiport interferometer whose applications span optical communications, quantum information processing, and precision metrology.

Electro-optic phase modulation is a well-studied process [1,2], especially when a modulation of an optical carrier by a harmonic voltage applied to a nonlinear crystal generates a frequency comb of sidebands offset by integer multiples of the driving signal [3]. This process, rooted in the Pockels effect, is not merely a spectral broadening tool but a fundamental operation for synthesizing arbitrary optical waveforms and engineering multimode quantum states, for instance [4–10]. In essence, the modulator acts as a controllable, lossless multiport interferometer, enabling deterministic transformations across a large number of frequency modes - a capability directly transferable to optical computing, metrology, and high-speed signal processing.

Beyond its well-known role in subcarrier wave quantum key distribution (SCW QKD) [11–15], the technique finds broad utility across diverse fields. In classical communications, it enables dense wavelength-division multiplexing and ultra-flat frequency comb generation for coherent transmission [16–20]. In quantum photonics, it serves as a building block for generating time-bin entanglement and frequency-bin qudits [17,21–25], while in metrology, it provides phase-stable references for optical frequency standards [1,26–29]. The ongoing push toward non-stationary operation - with modulation rates approaching and exceeding 100 GHz and switching times in the picosecond range - demands novel platform developments. Thin-film lithium niobate (TFLN) modulators [30–32] with traveling-wave electrodes now offer unprecedented bandwidth and reduced voltage-length products, while resonant cavity designs enhance efficiency at the cost of mode-count flexibility. These ultrafast regimes [33], however, invalidate adiabatic approximations, requiring time-dependent models that capture transient sideband dynamics. The central challenge thus shifts from mere generation to precise, real-time control of the spectral phase and amplitude under extreme temporal constraints.

This paper continues the work in [15], where a non-stationary phase-modulation process is considered within the framework of SCW QKD. However, the latter study examines modulation in an adiabatic regime. Here we dive deeply into non-adiabatic considerations and study the boundaries of its applicability. Also, here we do not limit ourselves only by QKD applications; current research may be implemented in a broad range of fields, discussed earlier in the introduction.

The article has the structure as follows. In Section 2 preliminaries and essential parts of the theoretical foundation are discussed. Section 3 is dedicated to derivation and studying the non-adiabatic solution of the non-stationary Schrödinger equation, where the interaction constant is dependent on time. In Section 4 analysis of the obtained solution is performed in order to define bounds of adiabatic approximation applicability. In Section 5 generalizations and extensions of the results are considered. Section 6 concludes the article.

## 2. Preliminaries

The foundation of current research is presented in [3], where a fully quantum description of modulation with alternating (harmonic) voltage applied to a nonlinear crystal was proposed. As we stated above, we are interested in a broadening of the theory by considering a non-stationary problem, where a modulation depth is changing, presumably rapidly, in time. At first, we recall the essential parts of the developed theory. Consider the non-periodic part of the Hamiltonian (quasi-energy operator) as follows:

$$Q(t) = m_{opt}\omega N + \omega J_0 + \frac{2\gamma(t)}{2S+1}(J_+e^{-i\varphi} + J_-e^{i\varphi}), \quad (1)$$

where  $m_{opt}$  stands for the mode number of this operational optical mode,  $\omega$  is a frequency mismatch of the optical and the microwave modes, the latter is defined by an applied to a crystal alternating voltage with phase  $\varphi$  that produces sidebands,  $2S+1$  is a number of interacting optical modes, and  $\gamma(t)$  is an interaction constant that is dependent on time, also

$$N = \sum_{j=-S}^S a_j^\dagger a_j, \quad J_0 = \sum_{j=-S}^S j a_j^\dagger a_j, \quad J_- = \sum_{j=-S}^{S-1} f_j a_{j+1}^\dagger a_j, \quad J_+ = (J_-)^\dagger, \quad f_j = \sqrt{(S+j+1)(S-j)}, \quad (2)$$

where  $a_j$  ( $a_j^\dagger$ ) is the annihilation (creation) operator for the  $j^{th}$  mode.

The operator  $Q(t)$  can be diagonalized, utilizing properties of the  $su(2)$  algebra; see App. A:

$$R[\varphi, \beta(t)] = e^{-i\varphi J_0} e^{-i\beta(t) J_y}, \quad R^\dagger[\varphi, \beta(t)] R[\varphi, \beta(t)] = I, \quad (3)$$

$$Q_d(t) = R^\dagger[\varphi, \beta(t)] Q(t) R[\varphi, \beta(t)] = m_{opt}\omega N + \Gamma(t) J_0 = \sum_{j=-S}^S (m_{opt}\omega + \Gamma(t)j) a_j^\dagger a_j, \quad (4)$$

$$\Gamma(t) = \sqrt{\omega^2 + \frac{16[\gamma(t)]^2}{(2S+1)^2}}, \quad \cos[\beta(t)] = \frac{\omega}{\Gamma(t)}. \quad (5)$$

Considering that the diagonalized operator,  $Q_d(t)$ , consists only of diagonal quadratic operators, it is convenient to assume its eigenvector as a basis vector in a Fock subspace,  $|\mathbf{v}_k\rangle = \bigotimes_j |v_j^{(k)}\rangle_j$ , where each mode  $j$  has  $v_j^{(k)}$  photons for a given basis vector with index  $k$ . Note that the range of the index  $k$  indicates the number of eigenvectors and eigenvalues and depends on the dimensions of the system. The latter, in turn, is defined by the total number of modes  $2S+1$  and a considered Fock subspace with a fixed total number of photons  $V = \sum_{j=-S}^S v_j^{(k)}$ , equal for all basis vectors in a given Fock subspace; the range then is defined as follows:

$$k \in \{1, 2, \dots, \binom{V+2S}{2S}\}, \quad (6)$$

where  $\binom{n}{k} = \frac{n!}{k!(n-k)!}$  is the binomial coefficient. Inferring from the above, we proceed with the following identities:

$$Q_d(t)|\mathbf{v}_k\rangle = \sum_{j=-S}^S (m_{opt}\omega + \Gamma(t)j) v_j^{(k)} |\mathbf{v}_k\rangle, \quad (7)$$

$$Q(t)R[\varphi, \beta(t)]|\mathbf{v}_k\rangle = \sum_{j=-S}^S (m_{opt}\omega + \Gamma(t)j) v_j^{(k)} R[\varphi, \beta(t)]|\mathbf{v}_k\rangle, \quad (8)$$

$$R[\varphi, \beta(t)]|\mathbf{v}_k\rangle \equiv |\phi_k(t)\rangle, \quad \sum_{j=-S}^S (m_{opt}\omega + \Gamma(t)j) v_j^{(k)} \equiv q_k(t). \quad (9)$$

Then Eq. (9) describes eigenvectors,  $|\phi_k(t)\rangle$ , and eigenvalues,  $q_k(t)$ , of the non-periodic part of the Hamiltonian  $Q(t)$ . It is essential for further analysis of a non-stationary and, presumably, non-adiabatic modulation process. Note, hereinafter we consider the non-degenerate case, characterized by  $q_k(\tau_0) \neq q_n(\tau_0)$  for arbitrary  $\tau_0$ .

### 3. Non-adiabatic solution

For a time-dependent non-periodic part of the Hamiltonian,  $Q(t)$ , the solution of the Schrödinger equation

$$i \frac{d}{dt} |\psi(t)\rangle = Q(t) |\psi(t)\rangle \quad (10)$$

has the following form:

$$|\psi(t)\rangle = \sum_k c_k(t) e^{-i \int_0^t q_k(t') dt'} |\phi_k(t)\rangle, \quad (11)$$

where the spectral problem solution for  $Q(t)$  is known:

$$Q(t) |\phi_k(t)\rangle = q_k(t) |\phi_k(t)\rangle. \quad (12)$$

Then, one needs to define coefficients  $c_k(t)$ . Substitution of Eq. (11) into Eq. (10) and multiplying both sides of the latter equation by  $\langle \phi_n(t) | e^{iq_n t}$  results in

$$\dot{c}_n(t) = - \sum_k c_k(t) \cdot e^{-i \int_0^t (q_k(t') - q_n(t')) dt'} \langle \phi_n(t) | \dot{\phi}_k(t) \rangle. \quad (13)$$

Also, notice that the latter expression can be rearranged by the following observation:

$$\dot{b}_n(t) = \dot{c}_n(t) e^{-i \int_0^t q_n(t') dt'} - i q_n(t) b_n(t), \quad b_n(t) = c_n(t) e^{-i \int_0^t q_n(t') dt'}, \quad (14)$$

that is

$$\dot{b}_n(t) = -i q_n(t) b_n(t) - \sum_k b_k(t) \langle \phi_n(t) | \dot{\phi}_k(t) \rangle. \quad (15)$$

In other words,

$$\dot{b}_n(t) = \sum_k \left( -i q_n(t) \delta_{n,k} - \langle \phi_n(t) | \dot{\phi}_k(t) \rangle \right) b_k(t) = \sum_k W_{nk}(t) \cdot b_k(t), \quad (16)$$

so the solution can be found by defining the matrix  $W$ .

We may use (12) in order to define  $\langle \phi_n(t) | \dot{\phi}_k(t) \rangle$  by taking the derivative and multiplying by  $\langle \phi_n(t) |$  as follows:

$$\langle \phi_n(t) | \dot{\phi}_k(t) \rangle = \frac{\langle \phi_n(t) | \dot{Q}(t) | \phi_k(t) \rangle}{q_k(t) - q_n(t)}, \quad n \neq k, \quad \langle \dot{\phi}_k(t) | \phi_k(t) \rangle = 0. \quad (17)$$

Then, see also App. A,

$$\dot{Q}(t) = \frac{2\dot{\gamma}(t)}{2S+1} (J_+ e^{-i\varphi} + J_- e^{i\varphi}), \quad (18)$$

$$R^\dagger[\varphi, \beta(t)] \dot{Q}(t) R[\varphi, \beta(t)] = \frac{4\dot{\gamma}(t)}{2S+1} e^{i\beta(t)J_y} J_x e^{-i\beta(t)J_y} = \frac{4\dot{\gamma}(t)}{2S+1} \left( \sin[\beta(t)] J_0 + \cos[\beta(t)] J_x \right). \quad (19)$$

In order to define  $\langle \phi_n(t) | \dot{Q}(t) | \phi_k(t) \rangle$ , it is essential to examine  $\langle \mathbf{v}_n | J_0 | \mathbf{v}_k \rangle$  and  $\langle \mathbf{v}_n | J_x | \mathbf{v}_k \rangle$  expressions. The action of the diagonal quadratic operator  $J_0$  on  $|\mathbf{v}_k\rangle$  does not change the state, and also  $|\mathbf{v}_k\rangle$  and  $|\mathbf{v}_n\rangle$  are orthogonal; so  $\langle \mathbf{v}_n | J_0 | \mathbf{v}_k \rangle$  only defines diagonal terms of a matrix. In turn, the action of  $J_x$  on  $|\mathbf{v}_k\rangle$  produces a linear combination of “adjacent” states. In other words,  $\langle \mathbf{v}_n | J_x | \mathbf{v}_k \rangle$  contributes to entries of secondary diagonals. Then, multiplying Eq. (19) by  $\langle \mathbf{v}_n |$  and  $|\mathbf{v}_k \rangle$ , we obtain the following expression:

$$\langle \phi_n(t) | \dot{Q}(t) | \phi_k(t) \rangle = \frac{2\dot{\gamma}(t)}{2S+1} \left( \sin[\beta(t)] \langle \mathbf{v}_n | J_0 | \mathbf{v}_k \rangle + \cos[\beta(t)] \langle \mathbf{v}_n | J_x | \mathbf{v}_k \rangle \right). \quad (20)$$

Note, the latter term enters the matrix  $W$  only if  $k \neq n$ , keeping in mind the discussion above, the latter expression results in

$$\langle \phi_n(t) | \dot{Q}(t) | \phi_k(t) \rangle = \frac{4\dot{\gamma}(t) \cos[\beta(t)] \langle \mathbf{v}_n | J_x | \mathbf{v}_k \rangle}{2S+1}. \quad (21)$$

Finally, the solution of time-dependent equation (10) can be expressed as follows in terms of time-ordered exponentiated matrix  $W$ :

$$|\psi(t)\rangle = \sum_k \left( e^{\int_0^t W(\tau) d\tau} \cdot \vec{b}(0) \right)_k |\phi_k(t)\rangle, \quad (22)$$

where

$$W_{nk}(t) = -i q_n(t) \delta_{n,k} - \frac{4\dot{\gamma}(t) \cos[\beta(t)] \langle \mathbf{v}_n | J_x | \mathbf{v}_k \rangle}{(2S+1)[q_k(t) - q_n(t)]} \delta_{n \neq k}, \quad (23)$$

where  $\delta_{n,k}$  and  $\delta_{n \neq k}$  indicate that a term is considered only if  $k = n$  or  $k \neq n$ , correspondingly.

#### 4. Analysis

Here we consider a rather simple case, where  $S = 1$ ,  $V = 1$ ,  $j \in \{-1, 0, 1\}$ , and  $|\mathbf{v}_1\rangle = |1, 0, 0\rangle$ ,  $|\mathbf{v}_2\rangle = |0, 1, 0\rangle$ ,  $|\mathbf{v}_3\rangle = |0, 0, 1\rangle$ . Despite being simple, its analysis can be utilized as a tool to define bounds of (non-) adiabatic considerations' applicability as well as to study the potential for generalizations. It is considerably easier to analyze a close-to-adiabatic regime and explore whether it can not be considered so. In this case, the matrix  $W$  can be expressed as follows:

$$W(t) = \begin{pmatrix} -iq_{-1}(t) & \frac{w(t)}{\sqrt{2}} & 0 \\ -\frac{w(t)}{\sqrt{2}} & -iq_0(t) & \frac{w(t)}{\sqrt{2}} \\ 0 & -\frac{w(t)}{\sqrt{2}} & -iq_1(t) \end{pmatrix}, \quad (24)$$

$$-iq_j = -i[m_{opt}\omega + \Gamma(t)j], \quad w(t) = \frac{z\omega\dot{\gamma}(t)}{\Gamma(t)^2}, \quad z \equiv \frac{4}{2S+1} \quad (25)$$

Further, we investigate whether the absolute values of exponentiated matrix  $E = e^{\int_0^t W(\tau)d\tau}$  entries can be close to those of the identity matrix. If the latter is true, it indicates that the system is in an adiabatic regime, so we may consider the time-ordered exponential matrix  $E$  as the first-order approximation of the Magnus expansion [34], implying direct exponentiation of the following matrix:

$$\begin{aligned} \int_0^t W(\tau)d\tau &= \begin{pmatrix} -i[m_{opt}\omega t - g(t)] & \frac{a(t)}{\sqrt{2}} & 0 \\ -\frac{a(t)}{\sqrt{2}} & -i[m_{opt}\omega t] & \frac{a(t)}{\sqrt{2}} \\ 0 & -\frac{a(t)}{\sqrt{2}} & -i[m_{opt}\omega t + g(t)] \end{pmatrix} = \\ &= D \begin{pmatrix} -i[m_{opt}\omega t - b(t)] & 0 & 0 \\ 0 & -i[m_{opt}\omega t] & 0 \\ 0 & 0 & -i[m_{opt}\omega t + b(t)] \end{pmatrix} D^{-1}, \end{aligned} \quad (26)$$

$$D = \frac{1}{[a(t)]^2} \begin{pmatrix} -[a(t)]^2 - 2[g(t)]^2 - 2g(t)b(t) & [a(t)]^2 & -[a(t)]^2 - 2[g(t)]^2 + 2g(t)b(t) \\ -i\sqrt{2}a(t)[g(t) + b(t)] & -i\sqrt{2}a(t)g(t) & -i\sqrt{2}a(t)[g(t) - b(t)] \\ [a(t)]^2 & [a(t)]^2 & [a(t)]^2 \end{pmatrix}, \quad (27)$$

where

$$a(t) = \int_0^t w(\tau)d\tau, \quad g(t) = \int_0^t \Gamma(\tau)d\tau, \quad b(t) = \sqrt{[a(t)]^2 + [g(t)]^2}, \quad (28)$$

resulting in

$$E = e^{-im_{opt}\omega t} D \begin{pmatrix} e^{ib(t)} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-ib(t)} \end{pmatrix} D^{-1}. \quad (29)$$

Note that a closed-form solution for  $a(t)$  can be found as it is shown further. However, the same cannot be done for  $g(t)$ : it involves a general elliptic integral that does not have a closed-form solution (except for a few special cases). The latter fact significantly limits the direct analytical approach.

The absolute values of  $E$  entries (hereinafter we utilize notation  $|E|_{ij} \equiv |E_{ij}|$ ) are as follows:

$$|E| = I + \begin{pmatrix} -y & \sqrt{2}x\sqrt{1-y} & x^2 \\ \sqrt{2}x\sqrt{1-y} & -2x^2 & \sqrt{2}x\sqrt{1-y} \\ x^2 & \sqrt{2}x\sqrt{1-y} & -y \end{pmatrix}, \quad (30)$$

where

$$x = \frac{|a(t) \sin\left(\frac{b(t)}{2}\right)|}{b(t)}, \quad y = \frac{[a(t)]^2(1 - \cos[b(t)])}{2[b(t)]^2}. \quad (31)$$

In order to show closeness of  $|E|$  to the identity matrix, a case where non-adiabatic effects are negligible, one needs to demonstrate, that  $|a(t)| \ll b(t)$ . If  $|a(t)| \ll |g(t)|$ , then  $b(t) \approx |g(t)|$  and

$$\frac{|a(t)|}{b(t)} \approx \frac{|a(t)|}{|g(t)|} = r(t) \ll 1. \quad (32)$$

We consider a change of  $\gamma(t)$  between two times. Then  $\dot{\gamma}(t_1) = \dot{\gamma}(t_2) = 0$ ,  $\gamma_{\max} = \max_t[\gamma(t)] = \gamma(t_1)$  and  $\gamma_{\min} = \min_t[\gamma(t)] = \gamma(t_2)$  or vice versa. Note, we do not consider a degenerate case, where  $\gamma_{\min} = 0$  and  $\omega = 0$ ; this requires special methods; see a remark after Eq. (38). It is challenging to find in the general case the exact value of  $t_0$  analytically, where the latter is defined by  $\max_t[r(t)] = r(t_0)$  as well as precisely bounds the expression of interest as  $r(t) \leq r(t_0)$ . In order to do so, one should solve the following equation:

$$w(t) \int_0^t \Gamma(\tau) d\tau - \Gamma(t) \int_0^t w(\tau) d\tau = 0, \quad t \neq 0. \quad (33)$$

Note, however, this equation can be easily solved numerically. Then, we should find another approach to study the bounds of the (non-) adiabatic regime.

Observe that the maximal value of  $|a(t)|$  at some point  $t_0$  can be bounded from above as follows:

$$|a(t_0)| = \left| \int_0^{t_0} w(\tau) d\tau \right| = \left| \int_0^{t_0} \frac{z\omega\dot{\gamma}(\tau)}{\omega^2 + z^2[\gamma(\tau)]^2} d\tau \right| = \left| \frac{\omega}{z} \int_{\gamma(0)}^{\gamma(t_0)} \frac{d[\gamma(t)]}{\frac{\omega^2}{z^2} + [\gamma(t)]^2} \right| = \quad (34)$$

$$= \left| \arctan\left(\frac{z\gamma(t_0)}{\omega}\right) - \arctan\left(\frac{z\gamma(0)}{\omega}\right) \right| \leq \frac{\pi}{2}. \quad (35)$$

Since  $|g(t)|$  in  $r(t)$  is in the denominator, its value can be bounded from below as follows:

$$|g(t)| = \left| \int_0^t \sqrt{\omega^2 + z^2[\gamma(\tau)]^2} d\tau \right| \geq |t| \sqrt{\omega^2 + z^2\gamma_{\min}^2}. \quad (36)$$

The latter expression grows in time, so conservatively we may estimate the relation  $r(t)$  at  $t = 0$  as the following limit:

$$\lim_{t \rightarrow 0} r(t) = \left| \frac{\omega z \dot{\gamma}(0)}{[\Gamma(0)]^3} \right| = \left| \frac{z \dot{\gamma}(0) \cos[\beta(t)]}{[\Gamma(0)]^2} \right| \leq \left| \frac{z \dot{\gamma}(0)}{[\Gamma(0)]^2} \right|, \quad (37)$$

where we use identity (5). Due to an ambiguity of the initial time choice, we may bound the latter expression as follows:

$$r(0) \leq \left| \frac{z \dot{\gamma}(0)}{[\Gamma(0)]^2} \right| \leq \frac{z |\dot{\gamma}|_{\max}}{\Gamma_{\min}^2}, \quad (38)$$

where  $|\dot{\gamma}|_{\max} = \max_t(|\dot{\gamma}(t)|)$  and  $\Gamma_{\min} = \min_t[\Gamma(t)]$ . Here we assume that  $\Gamma_{\min} \neq 0$ , otherwise, it is a highly degenerate case (both  $\omega = 0$  and  $\gamma_{\min} = 0$ ), and another approach should be implemented right from the beginning (e.g. local algebraic geometry and singularity theory [35], generalized Wigner-Smith theory [36] or similar methods).

As a final remark, we consider a special case of resonant modulation. Note that if  $\omega \rightarrow 0$ , Eq. (33) has no solutions other than  $t_0 = 0$ ; it can be explicitly seen as follows by alternating the latter equation:

$$w(t) \int_0^t \Gamma(\tau) d\tau - \Gamma(t) \int_0^t w(\tau) d\tau = 0 \xrightarrow{\omega \rightarrow 0} 1 - \frac{\gamma(t)}{\gamma(0)} + \frac{\dot{\gamma}(t)}{\gamma(t)^2} \int_0^t \gamma(\tau) d\tau = 0. \quad (39)$$

Also  $\gamma(0) \neq 0$  and  $\dot{\gamma}(0) \neq 0$ , based on initial restrictions of  $\gamma(t)$ . Then, an alternative boundary is as follows:

$$\left| \frac{\omega z \dot{\gamma}(0)}{[\Gamma(0)]^3} \right| \leq \frac{\omega |\dot{\gamma}(0)|}{z^2 [\gamma(0)]^3} \xrightarrow{\omega \rightarrow 0} 0. \quad (40)$$

Then, if one considers resonant modulation (assuming  $\gamma_{\min} \neq 0$  and finite amount of interacting mode  $2S + 1$ , i.e.,  $z \neq 0$ , in order to avoid degeneracy), then the dynamics of a system can be treated as an adiabatic process regardless.

And for a general (non-degenerate) case, the restriction condition for adiabatic considerations is as follows based on Eq. (38):

$$|\dot{\gamma}|_{\max} \ll \left( \frac{\Gamma_{\min}}{2} \right)^2 (2S + 1). \quad (41)$$

The latter implies the utilization of a stationary solution for a non-stationary problem of interest; otherwise, a full non-adiabatic solution should be introduced, including consideration of higher orders of the Magnus expansion. Figure 1 shows time-dependent probabilities,  $p_j$  and  $p'_j$ , of observing a photon in  $j^{\text{th}}$  mode with  $E \equiv I$  and where  $E$  is expressed as in Eq. (29) correspondingly, where inequality (41) does not hold. The frequency of observed oscillatory deviation between  $p_j$  and  $p'_j$  is  $b(t)$ . So inequality (41) can be reformulated as a rule of thumb: oscillation frequency  $b(t)$  should be

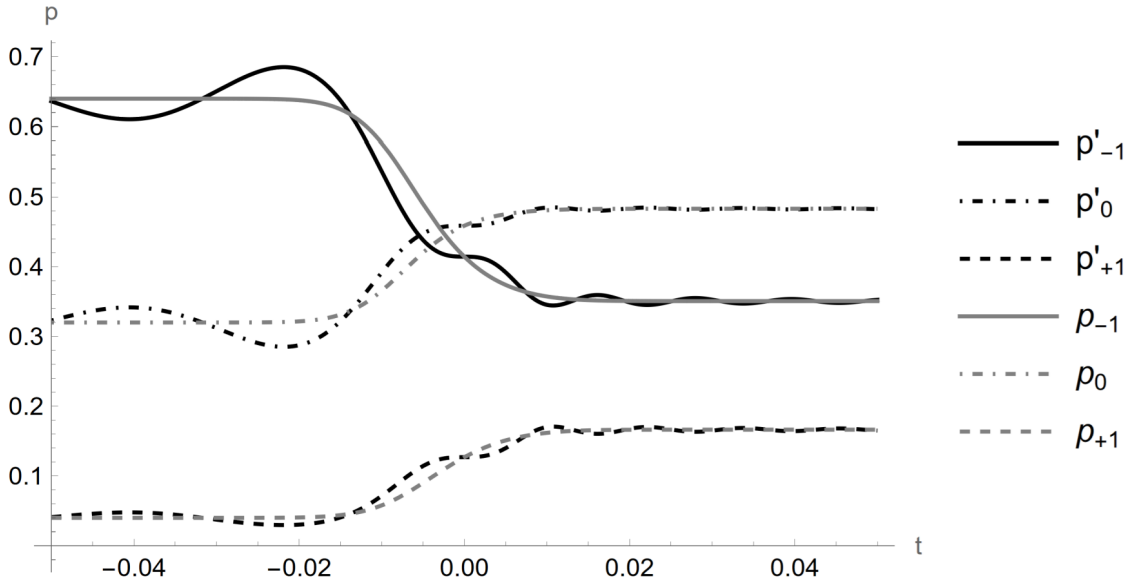


FIG. 1. Time-dependent probabilities,  $p_j$  and  $p'_j$ , of observing a photon in  $j^{th}$  mode with  $E \equiv I$  and where  $E$  is expressed as in Eq. (29) correspondingly. Here we consider  $\gamma(t) = \frac{1 + \text{erf}(t/s)}{2} |\gamma_1 - \gamma_2| + \min(\gamma_1, \gamma_2)$  with  $\gamma_1 = 400$ ,  $\gamma_2 = 100$ ,  $s = 0.01$ ,  $\omega = 100$ , and  $\vec{b}(0) = (1, 0, 0)$

higher than the “frequency” (inverse characteristic time) of transition between  $\gamma_1$  and  $\gamma_2$ . In order to specify dependencies, one should consider additional terms for Magnus expansion, which adds multiplicative frequencies of  $b(t)$ .

## 5. Generalizations and extensions

As we discussed earlier, the considered case, despite being simple, provides useful analytic transformation in regard to the bounds of (non-) adiabatic considerations’ applicability. In this section two extensions of the model are considered: we examine whether an increase of a number of interacting modes or a higher total number of photons in a Fock subspace may or may not change obtained estimations.

### 5.1. More interacting modes

Consider a larger amount of interacting modes, so  $S = 2$ ,  $V = 1$ ,  $j \in \{-2, -1, 0, 1, 2\}$ , and  $|\mathbf{v}_1\rangle = |1, 0, 0, 0, 0\rangle$ ,  $|\mathbf{v}_2\rangle = |0, 1, 0, 0, 0\rangle$ ,  $|\mathbf{v}_3\rangle = |0, 0, 1, 0, 0\rangle$ ,  $|\mathbf{v}_4\rangle = |0, 0, 0, 1, 0\rangle$ ,  $|\mathbf{v}_5\rangle = |0, 0, 0, 0, 1\rangle$ . In this case

$$\int_0^t W(\tau) d\tau = (-im_{opt}\omega t)I + \begin{pmatrix} 2ig(t) & a(t) & 0 & 0 & 0 \\ -a(t) & ig(t) & \sqrt{\frac{3}{2}}a(t) & 0 & 0 \\ 0 & -\sqrt{\frac{3}{2}}a(t) & 0 & \sqrt{\frac{3}{2}}a(t) & 0 \\ 0 & 0 & -\sqrt{\frac{3}{2}}a(t) & -ig(t) & a(t) \\ 0 & 0 & 0 & -a(t) & -2ig(t) \end{pmatrix}. \quad (42)$$

Applying the same procedure described above, we obtain

$$|E| = I + \mathcal{O}[r(t)], \quad (43)$$

and the deviation from the identity matrix in this case is proportional to  $r(t)$ . Thus, the same result as in Eq. (38) can be obtained. Considering the structure of matrix  $W$ , extension towards even more interacting modes implies the same proportionality of the deviation from the identity matrix to  $r(t)$ .

### 5.2. More photons

Consider a larger amount of photons in interacting modes associated with the corresponding Fock subspace, so  $S = 1$ ,  $V = 2$ ,  $j \in \{-1, 0, 1\}$ , and  $|\mathbf{v}_1\rangle = |0, 1, 1\rangle$ ,  $|\mathbf{v}_2\rangle = |1, 0, 1\rangle$ ,  $|\mathbf{v}_3\rangle = |1, 1, 0\rangle$ ,  $|\mathbf{v}_4\rangle = |2, 0, 0\rangle$ ,  $|\mathbf{v}_5\rangle = |0, 2, 0\rangle$ ,



$|\mathbf{v}_6\rangle = |0, 0, 2\rangle$ . In this case

$$\int_0^t W(\tau) d\tau = (-im_{opt}\omega t)I + \begin{pmatrix} ig(t) & -\frac{a(t)}{\sqrt{2}} & 0 & 0 & -a(t) & a(t) \\ \frac{a(t)}{\sqrt{2}} & 0 & -\frac{a(t)}{\sqrt{2}} & 0 & 0 & 0 \\ 0 & \frac{a(t)}{\sqrt{2}} & -ig(t) & -a(t) & a(t) & 0 \\ 0 & 0 & a(t) & 2ig(t) & 0 & 0 \\ a(t) & 0 & -a(t) & 0 & 0 & 0 \\ -a(t) & 0 & 0 & 0 & 0 & -2ig(t) \end{pmatrix}. \quad (44)$$

Applying the same procedure described above, we obtain

$$|E\rangle = I + \mathcal{O}[r(t)]. \quad (45)$$

Considering the structure of matrix  $W$ , extension towards even more photons in modes implies the same proportionality of the deviation from the identity matrix to  $r(t)$ .

## 6. Discussion and conclusion

A non-adiabatic solution for the non-stationary Schrödinger equation with the non-periodic part of the Hamiltonian (quasi-energy operator),  $Q(t)$ , see Eq. (1), which describes phase modulation, obtained by  $su(2)$  algebraic methods, see App. A, is considered in the article. Expressed in Eq. (9) eigenvectors and eigenvalues of  $Q(t)$  allows us constructing the non-stationary solution, described in Eq. (22), in terms of a time-ordered exponentiated matrix  $W$  (23).

As a rather simple case for initial analysis, in Section 4, we consider three interacting modes,  $S = 1$ , a Fock subspace with a single photon,  $V = 1$ , and only three eigenvectors. The condition that separates adiabatic and non-adiabatic considerations is derived in Eq. (32) and is specified in Eq. (41). An increase in the number of interacting modes,  $S > 1$  or a number of photons in the corresponding Fock subspace,  $V > 1$ , does not affect the condition that is shown in Section 5. At this point we conclude that the provided condition can be applied also for an arbitrary number of interacting modes and an arbitrary amount of photons in quantum optical states to be modulated.

In [3] it was shown that consideration of an infinite number of interacting modes restores classical phase modulation theory as the Wigner d-function transforms to a Bessel function of the first kind as a limiting case. A resonance,  $\omega \rightarrow 0$ , can also be considered for a stationary problem, providing significant simplifications. However, as it was shown, a non-stationary problem cannot be directly approached in this case; it requires rather sophisticated methods addressing high degeneracy. For now we left the degenerate case beyond the scope of the article for future research.

### A. Appendix: Diagonalization of $Q(t)$

Commutation relations of operators that form  $su(2)$  algebra are given by

$$[J_0, J_{\pm}] = \pm J_{\pm}, \quad [J_+, J_-] = 2J_0, \quad (46)$$

$$J_{\pm} = J_x \pm iJ_y, \quad J_y = \frac{J_+ - J_-}{2i}, \quad J_x = \frac{J_+ + J_-}{2}, \quad [J_y, J_0] = iJ_x, \quad [J_y, J_x] = -iJ_0. \quad (47)$$

And derived from the Baker-Campbell-Hausdorff formula, expressions for adjoint actions are as follows:

$$e^{aY} X e^{-aY} = X + a[Y, X] + \frac{a^2}{2}[Y, [Y, X]] + \dots, \quad (48)$$

$$e^{iaJ_0} J_{\pm} e^{-iaJ_0} = J_{\pm} e^{\pm ia}, \quad e^{i\varphi J_0} Q(t) e^{-i\varphi J_0} = m_{opt}\omega N + \omega J_0 + \frac{4\gamma(t)}{2S+1} J_x, \quad (49)$$

$$e^{iaJ_y} J_0 e^{-iaJ_y} = \cos(a)J_0 - \sin(a)J_x, \quad e^{iaJ_y} J_x e^{-iaJ_y} = \sin(a)J_0 + \cos(a)J_x, \quad (50)$$

$$e^{i\beta(t)J_y} e^{i\varphi J_0} Q(t) e^{-i\varphi J_0} e^{-i\beta(t)J_y} = m_{opt}\omega N + \Gamma(t)J_0, \quad (51)$$

$$\Gamma(t) = \sqrt{\omega^2 + \frac{16[\gamma(t)]^2}{(2S+1)^2}}, \quad \cos[\beta(t)] = \frac{\omega}{\Gamma(t)}. \quad (52)$$

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## Entropy for two weakly coupled quantum waveguides: asymptotic approach

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**ABSTRACT** Electron in a system of two plane quantum waveguides coupled through small window is considered. The method of matching the asymptotic expansions of the boundary problem solution is used. The dependence of entropy on the window width is described. for the case of small window in the framework of the asymptotic approach.

**KEYWORDS** quantum waveguides, entropy, asymptotics

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### 1. Introduction

A possibility of using coupled quantum (optical) waveguides for quantum computations (see, e.g., [1–4]) stimulates the interest to investigation of electron (photon) behaviour in the system. It can be useful for many quantum computing applications (see, e.g., [5–7]. An additional interest to the subject is inspired by widely discussed idea of topological quantum computations [8]. The study of spectral properties of waveguide systems with point defects and coupling apertures is one of the classical directions in mathematical physics and quantum microscopic. Bound states and resonances are of special interest [9, 10]. It was shown that small perturbation of the waveguide boundary (coupling window or deformation) can cause the appearance of the discrete spectrum (bound states) or resonances (quasibound states) (see, e.g., [11–16]). In the present paper, we consider the entropy of the electron bound state in a system of two 2D quantum waveguides coupled through small window.

### 2. Description of the system

We consider a system of two planar waveguides  $\Omega^+$  and  $\Omega^-$  with widths  $d_{\pm}$  ( $d_+ > d_-$ ), respectively, coupled through an aperture of small diameter  $2a$  (Fig. 1). The wave function satisfies the Helmholtz equation with the Dirichlet conditions on the external boundaries and the Neumann condition on the internal boundary:

$$\begin{aligned}\Delta\psi + k^2\psi &= 0, \\ \psi|_{x_2=-d_-, x_2=d_+} &= 0, \\ \frac{\partial\psi}{\partial x_2}|_{x_2=0} &= 0.\end{aligned}\tag{1}$$

It was previously proven in [11] that such a system has an eigenvalue  $k_a$  close to the spectral threshold. In [15, 16], the asymptotics (as  $a \rightarrow 0$ ) of this eigenvalue  $k_a$  were obtained, which can be conveniently written as

$$\gamma_a = \sqrt{\frac{\pi^2}{d_+^2} - k_a^2} = \frac{\pi^3}{d_+^3} a^2 + o(a^2).\tag{2}$$

Far from the aperture, the wave function is expressed through the normal derivative of Green's function (as  $a \rightarrow 0$ ):

$$\psi_a^{\pm}(x) = \mp\gamma_a \frac{\partial}{\partial n_y} G^{\pm}(x, 0, k) + o(1),\tag{3}$$

where the following expansion is known for the derivative of Green's function:

$$\frac{\partial G^{\pm}}{\partial n_y}(x, 0, k_a) = \sum_{n=1}^{\infty} \frac{\pi n}{d_{\pm}^2 \sqrt{\frac{\pi^2 n^2}{d_{\pm}^2} - k_a^2}} \sin\left(\frac{\pi n x_2}{d_{\pm}}\right) \exp\left(-|x_1| \sqrt{\frac{\pi^2 n^2}{d_{\pm}^2} - k_a^2}\right).\tag{4}$$

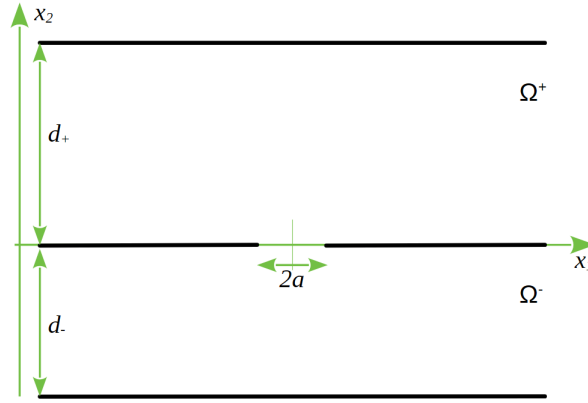


FIG. 1. The system of two planar waveguides

Extracting the first term and taking into account the known asymptotics, we obtain

$$\begin{aligned} -\psi_a^+(x) &\approx \frac{\pi}{d_+} \sin \frac{\pi x_2}{d_+} \exp \left( -\frac{\pi^3}{d_+^3} a^2 |x_1| \right) + \frac{\pi^3}{d_+^4} \sum_{n=2}^{\infty} \frac{n}{\sqrt{n^2-1}} \sin \left( \frac{\pi n x_2}{d_+} \right) \exp \left( -\frac{\pi}{d_+} \sqrt{n^2-1} |x_1| \right), \\ \psi_a^-(x) &\approx \frac{\pi^3}{d_+^3 d_-^2} a^3 \sum_{n=1}^{\infty} \frac{n}{\sqrt{\frac{n^2}{d_-^2} - \frac{1}{d_+^2}}} \sin \left( \frac{\pi n x_2}{d_-} \right) \exp \left( -\pi |x_1| \sqrt{\frac{n^2}{d_-^2} - \frac{1}{d_+^2}} \right). \end{aligned} \quad (5)$$

Note that for the symmetric system ( $d_+ = d_- = d$ ), the above formulas are not valid and need to be modified. Namely, instead of formulas (2) and (4), we have [15, 16]

$$\gamma_a = \sqrt{\frac{\pi^2}{d^2} - k_a^2} = \frac{2\pi^3}{d^3} a^2 + o(a^2), \quad (6)$$

$$\mp \psi_a^{\pm}(x) \approx \frac{\pi}{d} \sin \frac{\pi x_2}{d} \exp \left( -\frac{2\pi^3}{d^3} a^2 |x_1| \right) + \frac{2\pi^3}{d^4} \sum_{n=2}^{\infty} \frac{n}{\sqrt{n^2-1}} \sin \left( \frac{\pi n x_2}{d} \right) \exp \left( -\frac{2\pi}{d} \sqrt{n^2-1} |x_1| \right). \quad (7)$$

### 3. Results and discussion

We are interested in the Shannon entropy, which is defined by the following integral (see [17–19]):

$$S = - \int_{\Omega^+ \cup \Omega^-} |\psi|^2 \ln |\psi|^2 dx. \quad (8)$$

Figure 2 presents the results of numerical calculations for the entropy using formula (8) for the asymmetric system at various width ratios of the waveguides.

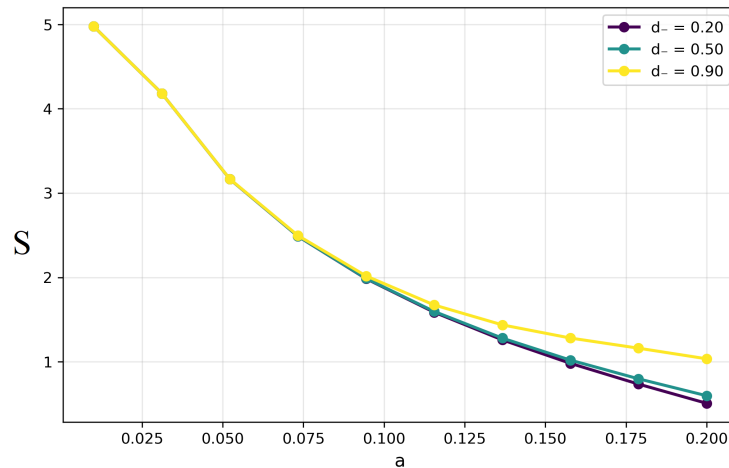


FIG. 2. Entropy of the system of waveguides of different widths ( $d_+ > d_-$ ) as a function of the aperture width,  $d_+ = 1$

Similar calculations were performed for the symmetric system. Fig. 3 shows the results of numerical calculations (blue line) and the results taken from the article [17] (red line).

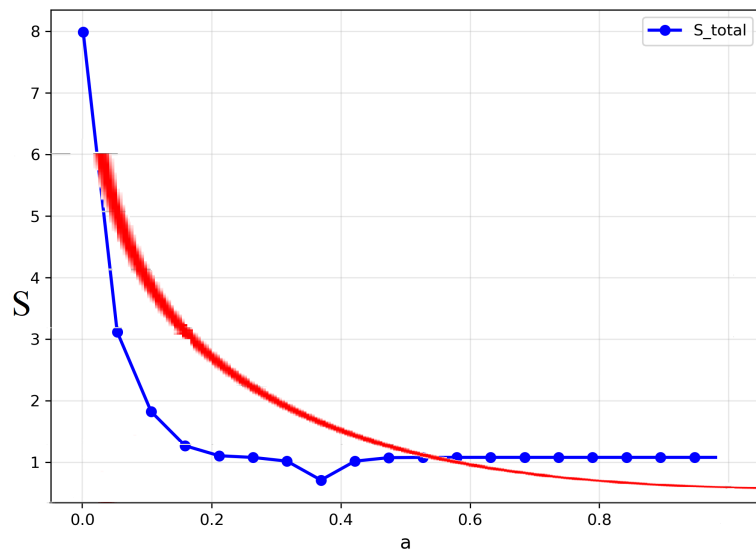


FIG. 3. Entropy of the system of waveguides of equal width ( $d_+ = d_- = 1$ ) as a function of the aperture width: red – from [17], blue – the present work

It should be mentioned that direct numerical approach [17] gives one good results for sufficiently large window and cannot describe the behaviour for  $a \rightarrow 0$  (see Fig. 2). As for our asymptotic result, it covers this gap - it presents good description for small window (see Fig. 2).

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## Magnetic fluid-assisted CoFeNi/NF bifunctional electrocatalyst for high-efficiency water splitting in alkaline medium

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**ABSTRACT** Developing efficient bifunctional electrocatalysts is vital for scalable hydrogen production via overall water splitting. Here, a magnetic-fluid-assisted CoFeNi–MF/NF catalyst was synthesized through a two-step hydrothermal process by integrating Fe<sub>3</sub>O<sub>4</sub>-based magnetic fluid into vertically aligned CoFeNi nanosheets on nickel foam. Structural analyses confirmed the formation of an FCC CoFeNi alloy coupled with spinel Fe<sub>3</sub>O<sub>4</sub>, creating an interconnected architecture with abundant active sites. Magnetic-fluid incorporation enhanced charge transfer, oxygen content, and electron/spin polarization, enabling faster catalytic kinetics. In 1.0 M KOH, CoFeNi–MF/NF delivered low overpotentials of 169 mV for HER and 199 mV for OER at 10 mA·cm<sup>−2</sup>, along with Tafel slopes of 133.09 and 91.41 mV·dec<sup>−1</sup>. The catalyst also showed low charge-transfer resistance and enlarged electrochemically active surface area. Durable operation at 100 mA·cm<sup>−2</sup> for 24 h further confirmed its stability. This work presents a promising strategy for designing magnetic-responsive, non-noble-metal electrocatalysts for alkaline water splitting.

**KEYWORDS** bifunctional electrocatalyst, alkaline water splitting, HER, OER

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### 1. Introduction

In recent years, environmental issues, particularly the greenhouse effect resulting from the combustion of fossil fuels, have garnered significant attention due to the intensification of ecological preservation [1]. Consequently, the global energy paradigm is shifting from non-renewable sources to clean and renewable energy types, including solar, wind, hydrogen, geothermal, and others. Among these, hydrogen energy stands out as a sustainable and environmentally safe energy carrier [2]. Fuel cells are one of the most efficient ways to utilize hydrogen, converting chemical energy directly into electricity with high efficiency and zero pollutant emissions throughout the process [3]. However, the high production cost of hydrogen remains one of the main barriers to the practical application of fuel cells [4, 5]. Therefore, identifying cost-effective and large-scale hydrogen production methods is crucial. Water electrolysis is considered as one of the most efficient solutions for hydrogen production, given the abundance of water resources on Earth [6, 7]. Furthermore, electricity generated by solar panels and wind turbines can be used to drive water electrolysis, thereby reducing the consumption of fossil fuels and minimizing CO<sub>2</sub> emissions [8–10]. Despite these advantages, additional voltage is required for water electrolysis, which must exceed the thermodynamic standard potential (1.23 V) due to interfacial resistance, concentration polarization, and other factors [11, 12]. Hence, the development and fabrication of efficient electrocatalysts to minimize this extra voltage have attracted considerable interest. Currently, alkaline water electrolysis has been commercialized and widely adopted due to several advantages. First, alkaline conditions allow operation at lower overpotentials at high current densities, thereby reducing energy consumption and extending the service life of electrolysis equipment [13]. Second, in contrast to acidic environments, alkaline conditions offer broader catalyst material selection, including many non-noble transition metals and their oxides, which lowers the cost of catalyst usage [14]. Third, electrolyzers designed for alkaline water splitting are simpler and more economical because they do not require expensive components like proton exchange membranes [15]. Nevertheless, recent attention is turning to neutral media for water electrolysis due to corrosion issues associated with alkaline conditions. Neutral electrolytes are attractive for their ease of preparation, lower hazards, and environmental compatibility [16]. However, challenges remain in this area, including low mass transfer rates,

reduced current densities, high overpotentials, limited durability and stability, and an insufficient understanding of reaction mechanisms and kinetics in neutral media [17]. In summary, developing more efficient, durable, and cost-effective electrocatalysts is of critical importance for advancing hydrogen production through water electrolysis, particularly under alkaline and neutral conditions [18]. In this context, modern research has demonstrated that incorporating magnetic fluid (MF) materials into electrocatalysts can significantly enhance their electrochemical activity [19–21]. Especially when MF, rich in ferromagnetic particles, is combined with CoFeNi-based catalysts, remarkable improvements in HER and OER performance have been observed. This is attributed to enhanced electron transport and mass transfer facilitated by the magnetic field [22, 23]. Magnetic fluids containing nanoparticles such as  $\text{Fe}_3\text{O}_4$  can align under an external magnetic field, contributing to the formation of new active catalytic centers on the electrode surface [24, 25]. Additionally, the synergistic interaction of Co, Fe, and Ni elements with the magnetic field improves electron density and reaction kinetics at the electrode/electrolyte interface [26, 27]. This reduces overpotential, improves Tafel slopes, and lowers energy consumption.

Several studies have shown that liquid-magnetic CoFeNi composites exhibit high current density, low onset potentials, and long-term durability under alkaline and neutral conditions [28–30]. Optimal distribution of magnetic particles activates the catalytic surface, accelerates hydrogen and oxygen evolution, and facilitates the detachment of gas bubbles from the electrode [31]. Furthermore, liquid magnetic electrocatalysts can be synthesized via simple hydrothermal or chemical routes, reducing production costs and increasing practical feasibility [32, 33]. CoFeNi-based nanocomposites demonstrate high activity for HER and OER due to synergistic effects among d-orbitals [34]. For example, the NFC@CNSs-700 catalyst developed by Yaseen et al. incorporates  $\text{CoFe}_2\text{O}_4$  and  $\text{FeNi}_3$  particles within a carbon nanosheet structure, achieving excellent stability and a Tafel slope of  $56.36 \text{ mV} \cdot \text{dec}^{-1}$  for OER and a capacitance of  $19.44 \text{ mF cm}^{-2}$  for HER [35]. Similarly, Liu et al. designed CoFeNi-LDH and CoP/FeNi<sub>2</sub>P heterojunctions tested at ampere-level current densities in 1.0 M KOH and alkaline seawater, demonstrating over 100 hours of stable operation [36]. These findings highlight the influence of magnetic field-assisted catalysis on electron configuration, spin polarization, and local magnetic heating, all of which improve HER/OER efficiency. Structural optimization, as seen in NiCoFe-Se@LDH/NF and FeNiMo-OOH catalysts, further enhances performance, demonstrating strong electron interactions and excellent stability [37].

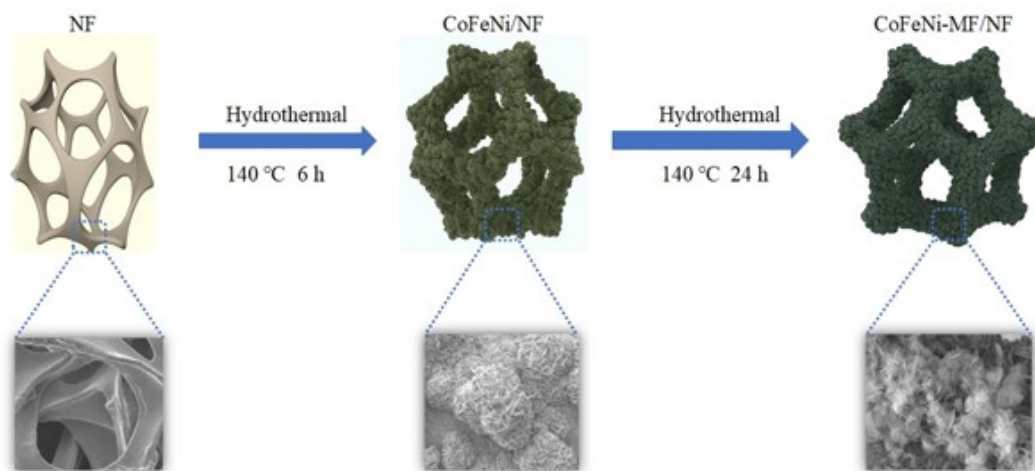


FIG. 1. Schematic illustration of the fabrication process for CoFeNi-MF/NF

In recent years, the development of highly active and durable bifunctional electrocatalysts for water splitting has attracted significant attention as a sustainable strategy for hydrogen production. Among transition metal-based systems, CoFeNi alloys have emerged as promising candidates due to their synergistic electronic interactions and cost-effectiveness. However, achieving efficient charge and mass transfer while maintaining long-term electrochemical stability remains a major challenge. To address this, a novel strategy was implemented in this study, where  $\text{Fe}_3\text{O}_4$ -based magnetic fluid (MF) was integrated into a CoFeNi/NF structure through a two-step hydrothermal synthesis. This hybrid approach facilitates enhanced electronic conductivity and accelerates charge transport, particularly under the influence of a magnetic field, leading to improved catalytic activity. The resulting CoFeNi-MF/NF nanocomposite demonstrates a dual-phase structure composed of FCC-type CoFeNi alloy and spinel-type  $\text{Fe}_3\text{O}_4$ . This architecture significantly increases the density of electrochemically active sites and exposes more surface area for reaction. As a result, the electrocatalyst exhibits outstanding performance toward both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Specifically, the overpotentials at a current density of  $10 \text{ mA} \cdot \text{cm}^{-2}$  were found to be 169 mV for HER and 241 mV for OER, indicating highly efficient reaction kinetics. Corresponding Tafel slopes of  $86 \text{ mV} \cdot \text{dec}^{-1}$  (HER) and  $74 \text{ mV} \cdot \text{dec}^{-1}$  (OER) further confirm the rapid reaction pathways. Electrochemical double-layer capacitance ( $C_{dl}$ ) measurements suggest a notably enhanced

electrochemically active surface area (ECSA) in the CoFeNi–MF/NF system compared to the pristine CoFeNi/NF. In addition, the catalyst maintains excellent stability, showing negligible degradation after long-term chronopotentiometry and cyclic voltammetry tests. These results demonstrate the potential of CoFeNi–MF/NF as a robust and efficient bifunctional electrocatalyst for overall water splitting, offering a scalable pathway toward clean hydrogen energy technologies.

## 2. Materials and methods

### 2.1. Materials and chemicals

The following chemicals were used in this study: Iron(III) nitrate nonahydrate  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Sigma-Aldrich, 99 %), Nickel(II) nitrate hexahydrate  $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ , Alfa Aesar, 98 %), Cobalt(II) nitrate hexahydrate  $(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ , Sigma-Aldrich, 98 %), Ammonium fluoride  $(\text{NH}_4\text{F})$ , Merck, 99.5 %), Urea  $(\text{CO}(\text{NH}_2)_2)$ , Sigma-Aldrich, 99 %), Iron(III) chloride hexahydrate  $(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$ , Sigma-Aldrich, 98 %), Polyethylene glycol (PEG, Mw = 4000, Alfa Aesar, 99 %), Hydrazine hydrate  $(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O})$ , Sigma-Aldrich, 98 %), Ethanol  $(\text{C}_2\text{H}_5\text{OH})$ , Merck, 99.9 %), and deionized water (prepared in the lab). Nickel foam (NF,  $3 \times 3 \text{ cm}^2$ , 0.3 mm thick, 95 %) from Delving Metal Technology Co., Ltd. (China) was used as the substrate. All reagents were used as received without further purification.

### 2.2. Synthesis of CoFeNi/NF

CoFeNi/NF was synthesized using a hydrothermal method. Specifically, 0.45 mmol  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 0.9 mmol  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.45 mmol  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 3 mmol  $\text{NH}_4\text{F}$ , and 6 mmol urea were dissolved in 80 mL deionized water and stirred for 30 minutes. The resulting solution and a  $3 \times 3 \text{ cm}^2$  piece of nickel foam were transferred to a 100 mL Teflon-lined autoclave. The hydrothermal reaction was conducted at  $140^\circ\text{C}$  for 6 hours. After cooling to room temperature, the sample was washed multiple times with ethanol and distilled water, dried at  $70^\circ\text{C}$  for 4 hours, and then annealed at  $350^\circ\text{C}$ .

### 2.3. Synthesis of magnetic fluid (MF)

The magnetic fluid was prepared hydrothermally. 0.28 mmol  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.3 mmol PEG were dissolved in 30 mL deionized water, followed by dropwise addition of 3 mL hydrazine hydrate  $(\text{N}_2\text{H}_4)$ . A reddish precipitate formed immediately. The mixture was transferred to a Teflon-lined autoclave and heated at  $140^\circ\text{C}$  for 4 hours. After cooling, the product was magnetically separated and washed several times with ethanol and water.

### 2.4. Integration of MF with CoFeNi/NF

10 mg of MF was dispersed in a 1:1 mixture of ethanol and deionized water (50 mL total) using ultrasonication for 30 minutes. The dispersion and a pre-prepared CoFeNi/NF electrode were placed in a 100 mL Teflon-lined autoclave and subjected to a second hydrothermal treatment at  $140^\circ\text{C}$  for 24 hours. The resulting sample was washed with distilled water and ethanol, dried at  $70^\circ\text{C}$  for 4 hours, and annealed at  $400^\circ\text{C}$  for 2 hours.

### 2.5. Physical characterization

X-ray diffraction (XRD, PANalytical X'Pert PRO) and scanning electron microscopy (SEM, JEOL JSM-IT510) were employed to analyze the structural and morphological properties. XRD measurements were performed using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). SEM images were used to evaluate the uniformity and morphology of the nanostructured surfaces.

### 2.6. Electrochemical measurements

Electrochemical tests were conducted using a Corrtest CS310X (Wuhan, China) workstation in a standard three-electrode setup. A Pt electrode served as the counter electrode,  $\text{Hg/HgO}$  as the reference electrode, and the synthesized electrocatalysts as the working electrodes. All tests were performed in 1.0 M KOH electrolyte.

Electrode potentials were converted to the reversible hydrogen electrode (RHE) scale using the formula:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098V + 0.059 \times \text{pH}.$$

Overpotentials ( $\eta$ ) were calculated using:

$$\eta = E_{\text{RHE}} - 1.23V.$$

Linear sweep voltammetry (LSV) measurements were recorded at a scan rate of  $20 \text{ mV}\cdot\text{s}^{-1}$  with iR compensation. Cyclic voltammetry (CV) was carried out at scan rates ranging from  $1.0$  to  $5.0 \text{ mV}\cdot\text{s}^{-1}$ . Electrochemical impedance spectroscopy (EIS) was performed over the frequency range 0.01 to 100 Hz. In order to approximate the empirical data of EIS, Randleselectrical circuit was used.

### 3. Results and discussion

The surface morphology of the pristine Ni foam (NF) substrate, the CoFeNi/NF, and CoFeNi-MF/NF nanocomposites synthesized upon it was thoroughly examined using scanning electron microscopy (SEM) to understand the structural evolution and its implications for electrocatalytic performance. Fig. 2(a–c) illustrates the top-view SEM images of these samples. As shown in Fig. 2(a), the pristine NF substrate exhibits a smooth, open, and interconnected 3D porous structure composed of metallic ligaments. This architecture not only ensures low internal resistance and high electrical conductivity but also facilitates easy electrolyte access and gas diffusion during electrochemical reactions. Additionally, the NF substrate possesses excellent mechanical stability, making it a widely employed support material for direct catalyst deposition in water electrolysis systems. Upon hydrothermal synthesis of the CoFeNi nanocomposite onto the NF substrate, significant morphological changes occur. In Fig. 2(b), it is evident that vertically aligned, sharp-edged nanosheets are densely and uniformly grown on the surface of the Ni foam. These nanosheet structures create a hierarchical morphology characterized by a large specific surface area, which is known to be beneficial for maximizing the density of catalytically active sites. The ordered and homogeneous coverage of the nanosheets also indicates strong interaction and good adhesion between the CoFeNi precursor and the NF framework. Moreover, such nanosheet arrays can promote efficient ion and electron transport pathways due to the reduced diffusion length, ultimately contributing to improved electrocatalytic kinetics. The morphology undergoes further transformation after the introduction of magnetic fluid (MF) into the CoFeNi/NF system. As depicted in Fig. 2(c), the surface of the CoFeNi-MF/NF sample becomes more compact and fully covered with overlapping, plate-like structures. These layers are believed to form due to the effective interaction between the MF (rich in  $\text{Fe}_3\text{O}_4$  nanoparticles) and the preformed CoFeNi nanosheets, resulting in a secondary surface modification. The presence of MF induces additional texturing and increases the surface roughness, which can further enhance the number of exposed catalytic sites. Simultaneously, the coating with MF may improve the overall electrical conductivity by contributing conductive and magnetic nanostructures, potentially facilitating charge carrier transport within the catalyst film. This multilayered and interconnected architecture plays a crucial role in electrochemical performance. Firstly, the high-aspect-ratio nanosheets ensure a large electrochemical surface area (ECSA), which is directly correlated with the number of redox-active sites available for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Secondly, the hierarchical structure, including both nanosheet growth and MF coating, facilitates rapid mass and charge transport. The open macroporous network of the NF backbone promotes fast gas bubble detachment and minimizes mass transport limitations. Meanwhile, the nanosheet/MF composite layer ensures short diffusion distances for electrolyte ions and efficient electron transport to the active sites. Furthermore, the intimate contact between the catalyst layer and the NF scaffold reduces interfacial resistance and improves long-term operational stability. The morphological characteristics observed via SEM are consistent with the desired properties of an efficient bifunctional electrocatalyst. The synergistic combination of the NF substrate's porous conductivity, the CoFeNi nanosheets' high surface area, and the MF-derived modification layer results in a structurally robust and electrochemically favorable electrode. These features are expected to enhance not only the intrinsic catalytic activity of the material but also its stability under prolonged electrolysis conditions in an alkaline environment.

To evaluate the elemental composition and spatial distribution of the constituent elements in the synthesized electrocatalysts, energy-dispersive X-ray spectroscopy (EDS) analysis was conducted, including both elemental mapping and point spectrum measurements (Fig. 3(a–g)). This characterization is crucial for confirming the successful incorporation and uniform dispersion of the key metallic components (Ni, Fe, and Co), as well as oxygen, which collectively contribute to the electrochemical performance of the material. For the CoFeNi/NF sample, the EDS spectrum (Fig. 3(f)) reveals the presence of nickel (Ni), iron (Fe), cobalt (Co), and oxygen (O) with corresponding weight percentages of 63.2, 8.6, 8.6, and 19.6 %, respectively. The high content of Ni reflects its predominance as both a substrate and active phase component, while Fe and Co are successfully integrated in comparable proportions, forming a homogeneous trimetallic oxide system. The oxygen content confirms the partial oxidation of the metallic components, resulting in the formation of mixed metal oxides (MMOs), which are well-known for their enhanced electrocatalytic activity in both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) processes. In contrast, the CoFeNi-MF/NF sample exhibits a notable shift in elemental composition, with Ni reduced to 50.6 %, Fe increased to 11.9 %, Co slightly decreased to 6.3 %, and O significantly increased to 31.2 % (Fig. 2(g)). This variation is attributed to the introduction of the magnetic fluid (MF), which primarily contains  $\text{Fe}_3\text{O}_4$  nanoparticles. The elevated Fe content indicates the successful incorporation of MF-derived iron oxide, while the sharp increase in oxygen content is indicative not only of  $\text{Fe}_3\text{O}_4$  inclusion but also of additional surface oxidation processes occurring during or after synthesis. Such oxidation may result in the formation of amorphous or hydrated oxide phases, which can further enhance electrocatalytic activity by increasing surface defect density and active site exposure. The elemental mapping images (Fig. 3(a–d)) for the CoFeNi-MF/NF sample corroborate the uniform distribution of Ni, Fe, Co, and O across the catalyst surface. Homogeneous dispersion of these elements is critical to ensure consistent catalytic behavior across the electrode, preventing localized performance degradation or instability. This uniformity also suggests that the synthesis route employed facilitates even nucleation and growth of the active components across the porous substrate, a key factor in achieving high and reproducible electrochemical efficiency.



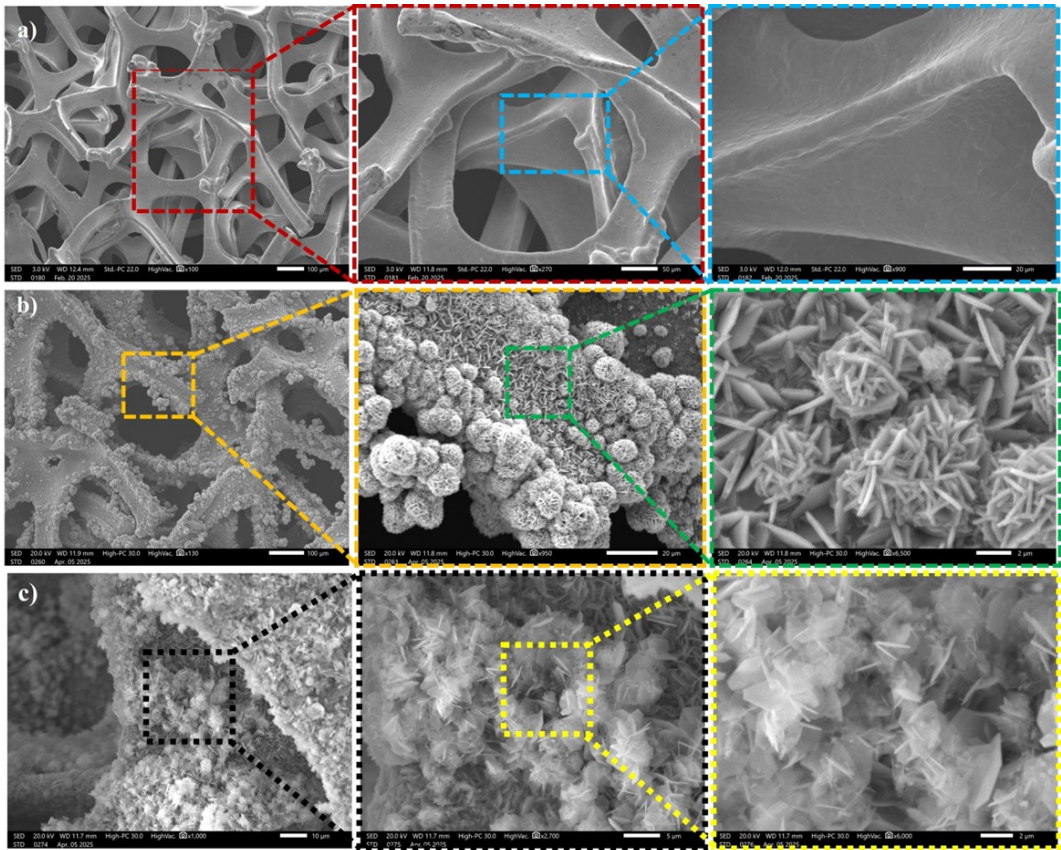


FIG. 2. SEM images of a) NF, b) CoFeNi/NF, c) CoFeNi–MF/NF

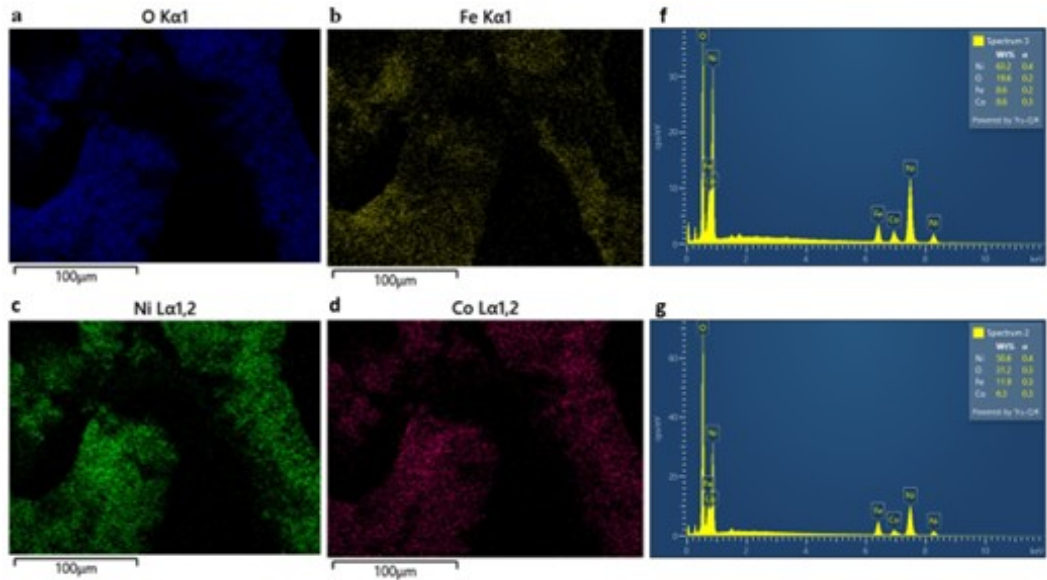


FIG. 3. a-d) EDS elemental mapping of f) EDS spectrum of CoFeNi/NF and g) EDS spectrum of CoFeNi–MF/NF

The increased Fe content in the CoFeNi–MF/NF confirms successful MF integration and magnetic nanoparticle loading. Crystallinity and phase identification were examined via XRD patterns (Fig. 4(a)). For CoFeNi/NF, three main peaks were observed at  $2\theta \approx 44.5^\circ$ ,  $51.8^\circ$ , and  $76.4^\circ$ , corresponding to the (111), (200), and (220) planes of the face-centered cubic (FCC) structure, characteristic of Ni–Co–Fe alloys. Upon addition of MF, additional weak diffraction peaks appeared near  $2\theta \approx 30.1^\circ$ ,  $31.5^\circ$ , and  $39.2^\circ$ , which can be indexed to (220), (100), and (111) planes of  $\text{Fe}_3\text{O}_4$  (magnetite). Although the characteristic peaks are weak, likely due to the relatively low content or amorphous nature of MF nanoparticles, their presence supports the partial incorporation of  $\text{Fe}_3\text{O}_4$  into the composite structure. The average crystallite size was estimated using the Scherrer formula, where the broadening of the FCC peaks indicated size variation. For CoFeNi/NF, the crystallite size was calculated to be approximately 18.2 nm, whereas for CoFeNi–MF/NF, it slightly decreased to 16.3 nm, suggesting that MF addition leads to finer nanostructures. This reduction enhances the surface-to-volume ratio, which is beneficial for electrocatalytic activity. In summary, the combined SEM, EDS, and XRD results confirm the successful formation of a uniform, high-surface-area, and crystalline CoFeNi–MF/NF electrode. The structural features – nanosheet morphology, MF coating, and increased oxygen content collectively enhance active site density, electrical conductivity, and catalytic efficiency for HER and OER processes.

The chemical structure and bonding environment of the CoFeNi/NF electrocatalyst were further investigated through Fourier-transform infrared (FTIR) spectroscopy (Fig. 4(b)). The FTIR spectrum exhibits several characteristic vibrational bands corresponding to oxygen-containing surface groups, residual solvent species, and metal-oxygen lattice modes, confirming the successful formation of a multimetal oxide/hydroxide network on the substrate. A broad absorption band centered at  $3378\text{ cm}^{-1}$  is attributed to the stretching vibrations of surface hydroxyl groups (O–H). Such a broad O–H mode is typical for metal hydroxides and physically adsorbed water molecules, indicating that the catalyst surface is rich in hydroxyl terminations. In alkaline electrocatalysis, the presence of abundant O–H groups plays an essential role in accelerating water dissociation during the Volmer step of HER and contributes to the formation of MOOH intermediates during OER, thereby enhancing both catalytic pathways. A weaker band observed near  $2357\text{ cm}^{-1}$  corresponds to physically adsorbed  $\text{CO}_2$  species, which are commonly detected on metal oxide surfaces exposed to air. The small vibrational feature around  $2181\text{ cm}^{-1}$  is associated with  $\text{C}\equiv\text{N}$  or  $\text{–CN}$  stretching, likely originating from residual urea-derived intermediates from the hydrothermal synthesis. The presence of such organic residuals is minimal and does not affect the structural or catalytic properties of the final material. The band located at  $1635\text{ cm}^{-1}$  is assigned to the bending vibration of molecular water (H–O–H), confirming the presence of adsorbed water molecules trapped within the porous nanosheet framework. The peak at  $1356\text{ cm}^{-1}$  corresponds to C–O stretching vibrations, which originate from surface carbonate or adsorbed organic groups, often introduced during washing or drying. Most importantly, the low-wavenumber region ( $500\text{--}800\text{ cm}^{-1}$ ) provides direct structural evidence for the formation of mixed metal-oxygen frameworks. A pronounced absorption peak at  $693\text{ cm}^{-1}$  is characteristic of Co–O stretching vibrations, confirming the presence of cobalt oxide/hydroxide phases such as  $\text{Co}(\text{OH})_2$  or  $\text{CoOOH}$ -related species. The absorption at  $603\text{ cm}^{-1}$  corresponds to the Fe–O vibrational mode, demonstrating the incorporation of iron oxides/hydroxides such as  $\text{FeOOH}$  or  $\text{Fe}_2\text{O}_3$  into the catalyst lattice. Additionally, the peak at  $545\text{ cm}^{-1}$  is assigned to the Ni–O stretching mode, confirming the presence of nickel-based oxide/hydroxide species (likely  $\text{Ni}(\text{OH})_2$  or  $\text{NiOOH}$ ). The simultaneous appearance of Co–O, Fe–O, and Ni–O bands demonstrates the formation of a trimetallic oxide/hydroxide network, which aligns closely with the XPS findings showing multivalent  $\text{Co}^{2+}/\text{Co}^{3+}$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , and  $\text{Ni}^{2+}/\text{Ni}^{3+}$  species. The presence of multiple metal-oxygen vibrational bands suggests strong electronic interactions among the three metals, which can modulate the local electronic environment, enhance charge-transfer processes, and facilitate the formation of high-valence oxyhydroxide intermediates under OER conditions. Collectively, the FTIR analysis supports the successful synthesis of a multimetal oxide/hydroxide framework on the NF substrate, characterized by abundant hydroxyl groups, adsorbed water, and well-defined M–O lattice modes for Co, Fe, and Ni. These structural features are directly relevant to the electrocatalytic performance of the material. The hydroxyl-rich surface promotes water adsorption and dissociation during HER, whereas the presence of strong M–O stretching vibrations confirms the existence of catalytically active Co–O, Fe–O, and Ni–O units that undergo in situ transformation into high-valent MOOH phases during OER. These structural characteristics synergistically contribute to the experimentally observed low overpotentials and efficient bifunctional activity of the CoFeNi/NF catalyst.

The surface chemical composition and electronic structure of the CoFeNi/NF electrocatalyst were comprehensively investigated through X-ray photoelectron spectroscopy (XPS). The wide-scan spectrum confirms the presence of Co, Fe, Ni, O, and C elements, indicating the successful formation of a trimetallic hydroxide/oxide layer on the nickel foam substrate. Distinct Co 2p, Fe 2p, and Ni 2p signatures demonstrate that all three metals exist in mixed-valence states, which is a crucial electronic feature governing the bifunctional electrocatalytic behavior of multimetallic catalysts in alkaline media. The Co 2p high-resolution region reveals two main spin–orbit doublets centered at 780.6 eV (Co  $2p_{3/2}$ ) and 796.1 eV (Co  $2p_{1/2}$ ), accompanied by satellite peaks located near 786.1 and 802.3 eV. Deconvolution identifies the coexistence of  $\text{Co}^{2+}$  (780.4 eV) and  $\text{Co}^{3+}$  (781.6 eV) components, along with a minor metallic  $\text{Co}^0$  (778.2 eV) contribution. The mixed  $\text{Co}^{2+}/\text{Co}^{3+}$  states suggest that the catalyst surface is partially oxidized, enabling rapid  $\text{Co}^{2+} \leftrightarrow \text{Co}^{3+}$  redox cycling during the oxygen evolution reaction (OER). The presence of  $\text{Co}^{3+}$  is strongly associated with the formation of  $\text{CoOOH}$  intermediates, known to serve as highly active OER centers, whereas  $\text{Co}^{2+}$  species contribute to hydrogen adsorption/desorption during the hydrogen evolution reaction (HER). The metallic  $\text{Co}^0$  fraction further enhances electrical conductivity, thereby

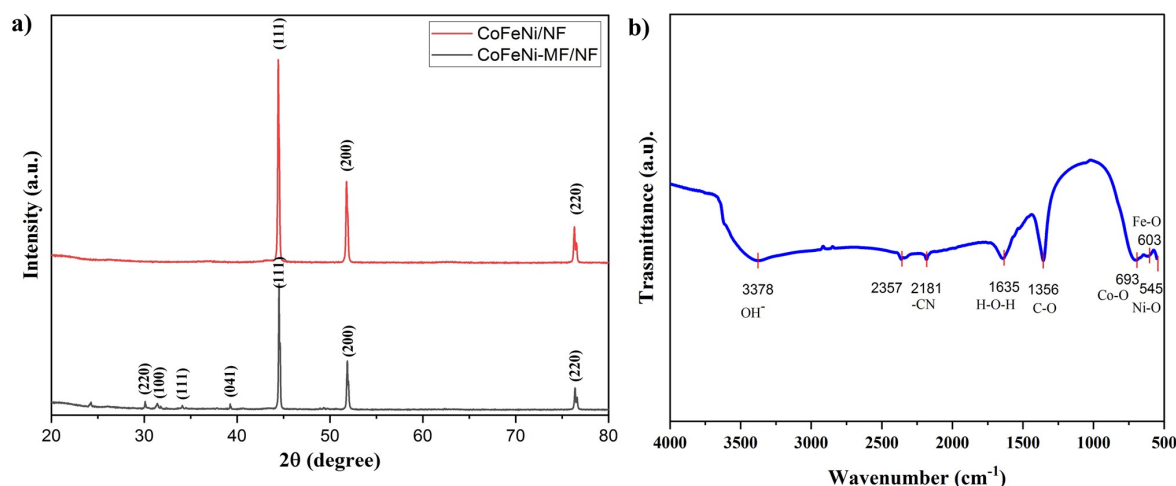


FIG. 4. a) XRD analysis of synthesized CoFeNi/NF and CoFeNi-MF/NF b) FT-IR spectra of CoFeNi MF/NF

promoting charge mobility across the electrode-electrolyte interface. The Fe 2p spectrum displays characteristic peaks at 710.8 eV (Fe 2p<sub>3/2</sub>) and 724.9 eV (Fe 2p<sub>1/2</sub>), with satellite features positioned at 717.2 eV, indicating the presence of oxidized iron species. Peak deconvolution identifies Fe<sup>2+</sup> (710.4 eV), Fe<sup>3+</sup> (712.0 eV), and a weak Fe<sup>0</sup> (707.3 eV) component. The Fe<sup>2+</sup>/Fe<sup>3+</sup> redox couple plays a significant role in tuning the electronic configuration of the adjacent Co and Ni sites. Numerous studies have shown that Fe incorporation into Co- or Ni-based systems facilitates lattice oxygen activation and enhances OER kinetics through the formation of FeOOH motifs. The strong intensity of Fe<sup>3+</sup> indicates that the catalyst surface possesses high-valence iron sites capable of participating in proton-electron-coupled steps that are essential for O–O bond formation. The Ni 2p spectrum shows two main peaks at 855.8 eV (Ni 2p<sub>3/2</sub>) and 873.3 eV (Ni 2p<sub>1/2</sub>), along with pronounced satellite features located near 861.4 and 879.2 eV. Deconvolution confirms the presence of Ni<sup>2+</sup> (855.4 eV) and Ni<sup>3+</sup> (856.5 eV) species. The existence of Ni<sup>3+</sup> indicates that the catalyst surface readily transforms into NiOOH under anodic polarization, which is recognized as a primary active phase for OER. The Ni<sup>2+</sup>/Ni<sup>3+</sup> couple is also indicative of facile electronic reconstruction, enabling fast electron exchange during reaction cycles. The significant proportion of Ni<sup>3+</sup> species correlates well with the experimentally observed low OER overpotential and favorable Tafel slope, demonstrating that Ni plays a key role in accelerating reaction kinetics. The O 1s spectrum consists of two major components: lattice oxygen (M–O) at 529.7–530.1 eV and hydroxyl/adsorbed oxygen species (M–OH, O<sub>ads</sub>) at 531.4–531.9 eV. The dominant M–OH contribution implies that the catalyst surface is rich in hydroxyl terminations – an essential characteristic for alkaline electrocatalysis. During HER, surface hydroxyl groups facilitate rapid water dissociation (Volmer step), lowering the activation barrier for H<sup>\*</sup> formation. During OER, these hydroxyl groups participate in generating MOOH intermediates, which function as catalytically active sites for O–O coupling. The C 1s peak at 284.6 eV (C–C/C–H) and 286.2 eV (C–O) originates from surface adventitious carbon and the underlying substrate. Overall, the XPS results demonstrate that the CoFeNi/NF catalyst possesses a highly modulated electronic environment characterized by mixed-valence Co<sup>2+</sup>/Co<sup>3+</sup>, Fe<sup>2+</sup>/Fe<sup>3+</sup>, and Ni<sup>2+</sup>/Ni<sup>3+</sup> species, combined with partially metallic Co<sup>0</sup>, Fe<sup>0</sup>, and Ni<sup>0</sup> domains. This multivalence is a hallmark of highly active multimetal catalysts, as it enhances the density of redox-active centers, facilitates rapid electron transfer, and enables dynamic surface reconstruction under electrochemical conditions. The strong electronic coupling among Co, Fe, and Ni likely alters the local density of states near the Fermi level, optimizing adsorption energies for reaction intermediates and reducing overall reaction barriers. These electronic features are fully consistent with the catalyst's superior HER and OER behavior. In alkaline HER, the presence of metallic sites (Co<sup>0</sup>/Ni<sup>0</sup>), moderate-strength hydrogen-binding centers (Co<sup>2+</sup>, Ni<sup>2+</sup>), and hydroxyl-rich surfaces work synergistically to improve water dissociation and hydrogen release kinetics, resulting in a low HER overpotential. In OER, the abundance of high-valence Co<sup>3+</sup>, Fe<sup>3+</sup>, and Ni<sup>3+</sup> species strongly favors the formation of active oxyhydroxide intermediates (CoOOH, FeOOH, NiOOH), which accelerate the proton-electron transfer steps necessary for oxygen evolution. The observed catalytic performance therefore directly originates from the unique electronic structure revealed by XPS, confirming that the hydrothermal synthesis strategy successfully produces a highly active, electronically optimized trimetallic electrocatalyst.

### 3.1. Electrochemical measurement for OER

To determine the electrochemical activity of the synthesized electrocatalyst samples in 1.0 M KOH alkaline electrolyte, a conventional three-electrode setup was used. LSV polarization curves were collected to assess catalytic activity and oxidation-reduction/catalytic indicators for HER and OER. The results for OER showed that the CoFeNi-MF/NF catalyst achieved maximum activity. For comparison, CoFeNi/NF, MF/NF, and NF were analyzed under the same conditions. As shown in Fig. 6(a), CoFeNi-MF/NF exhibited higher OER efficiency compared to other catalysts. The OER



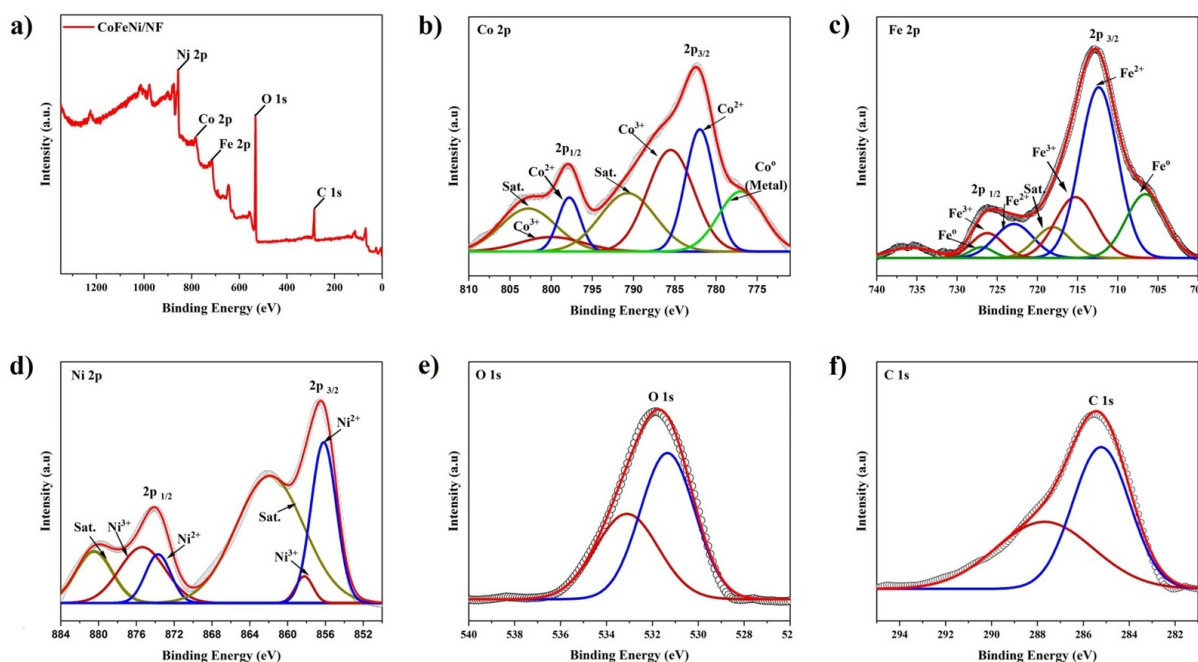


FIG. 5. X-ray photoelectron spectrum of CoFeNi-NF: a) survey spectrum, b) Co 2p, c) Fe 2p, d) Ni 2p, e) O 1s and f) C 1s

overpotential was only 199 mV at  $10 \text{ mA} \cdot \text{cm}^{-2}$ . However, CoFeNi/NF and MF/NF required higher overpotentials of 310 and 217 mV at a current density of  $10 \text{ mA} \cdot \text{cm}^{-2}$ , respectively. All catalysts contain NF, and to demonstrate the catalytic activity of NF, we compared the catalytic performance of bare NF. The results showed that NF had an overpotential of 470 mV at  $10 \text{ mA} \cdot \text{cm}^{-2}$ . This proves that adding MF during the synthesis process can improve the catalytic effect. LSV tests with different catalysts are shown in detail in Fig. 6(a), which confirms the superior performance of CoFeNi-MF/NF for OER among these catalysts. It was determined that the thermodynamic efficiency of the process for the CoFeNi-MF/NF electrode under standard conditions is 86 %, while for CoFeNi/NF, MF/NF, and NF electrodes it is 80, 85, and 72 %, respectively, which indicates the ratio of useful energy output to total energy input. This efficiency value reflects how effectively the system can convert the supplied energy under these controlled conditions into the required chemical or electrical energy. Achieving high thermodynamic efficiency is crucial as it directly affects the overall energy efficiency and stability of the system. Additionally, the kinetics and mechanism of the OER reaction were assessed by measuring the corresponding Tafel slope. It is known that OER exhibits slow kinetics and presents a barrier in the water splitting process due to its multi-electron pathway. The results showed that the Tafel slope of CoFeNi-MF/NF ( $91.41 \text{ mV} \cdot \text{dec}^{-1}$ ) is significantly lower than that of CoFeNi/NF ( $81.69 \text{ mV} \cdot \text{dec}^{-1}$ ), MF/NF ( $236.76 \text{ mV} \cdot \text{dec}^{-1}$ ), and NF ( $150.68 \text{ mV} \cdot \text{dec}^{-1}$ ), as seen in Fig. 6(b). This indicates that the reaction kinetics in CoFeNi-MF/NF are optimal. The low Tafel slope of the CoFeNi-MF/NF catalyst implies a rapid dynamic reaction rate, which significantly enhances the catalyst's efficiency. Fig. 6(c) presents the electrochemical impedance spectroscopy (EIS) results for CoFeNi-MF/NF, conducted in the frequency range of 0.01 – 100 Hz at 1.5 V versus RHE. The figure includes the impedance spectrum and its equivalent circuit. As evident from Fig. 6(c), the charge transfer resistance ( $R_{ct}$ ) of CoFeNi-MF/NF was determined to be  $1.0 \Omega$ . This low value indicates good electrical conductivity rapid surface charge transfer. The electrochemically active surface area (ECSA) is a key parameter of electrocatalysts, representing the portion of the electrode surface that actively participates in electrochemical reactions. Unlike the geometric surface area, which only considers the physical dimensions of the electrode, ECSA reflects the actual number of accessible catalytic sites available for charge transfer. Higher ECSA typically enhances electrocatalytic efficiency by increasing the number of available reaction sites for key processes such as OER and HER. Double-layer capacitance,  $C_{dl}$ , is a parameter representing the capacitance of the electrical double layer formed at the interface between the electrode surface and the electrolyte solution. When a potential is applied to the electrode, ions from the electrolyte are attracted to the surface, forming a double layer with a capacitance that depends on the electrode's surface area. To determine the electrochemical surface area (ECSA), the double-layer capacitance ( $C_{dl}$ ) is initially obtained from cyclic voltammetry (CV) measurements in the non-Faradaic region. This is achieved by plotting the average current density against the scan rate, where the resulting slope corresponds to the  $C_{dl}$  value. Fig. 6(d) shows the cyclic voltammetry (CV) curves for the CoFeNi-MF/NF electrode, recorded at different scan rates (1, 2, 3, 4, and 5 mV/s). These curves demonstrate the capacitive behavior of the electrode in the non-Faradaic region, confirming the formation of an electrochemical double layer. A gradual increase in current density with increasing scan rate indicates improved charge storage capabilities and surface area influence. The linear fit of  $\Delta i/2$  versus scan rate

to estimate  $C_{dl}$  yields a capacitance value of  $32.84 \text{ mF}\cdot\text{cm}^{-2}$  for OER, as shown in Fig. 6(e). This relatively high  $C_{dl}$  suggests that the CoFeNi-MF/NF composite possesses a large active surface area, which facilitates charge accumulation and enhances reaction kinetics during water oxidation. To better understand the origin of the enhanced OER activity, the electrochemically active surface area (ECSA) of the electrodes was evaluated based on the double-layer capacitance ( $C_{dl}$ ). In alkaline media, a specific capacitance ( $C_s$ ) value of  $0.04 \text{ mF cm}^{-2}$  was used to estimate the ECSA,

$$ECSA = \frac{C_{dl}}{C_s}.$$

As presented in Fig. 6(e), the  $C_{dl}$  values increase progressively from NF to CoFeNi-MF/NF, suggesting that the surface becomes more electrochemically accessible after each modification step. The calculated ECSA values are 280, 631, 631, and  $821 \text{ cm}^2$  for NF, MF/NF, CoFeNi/NF, and CoFeNi-MF/NF, respectively. Among them, CoFeNi-MF/NF shows the highest  $C_{dl}$  ( $32.84 \text{ mF cm}^{-2}$ ), indicating that more active sites are exposed to the electrolyte. This increase is likely related to the formation of a more open and rough nanosheet structure after the incorporation of magnetic fluid. A larger ECSA generally means that more reaction sites are available, which helps explain the improved OER performance. Therefore, the enhanced catalytic behavior of CoFeNi-MF/NF can be reasonably attributed, at least in part, to its increased electrochemically active surface area.

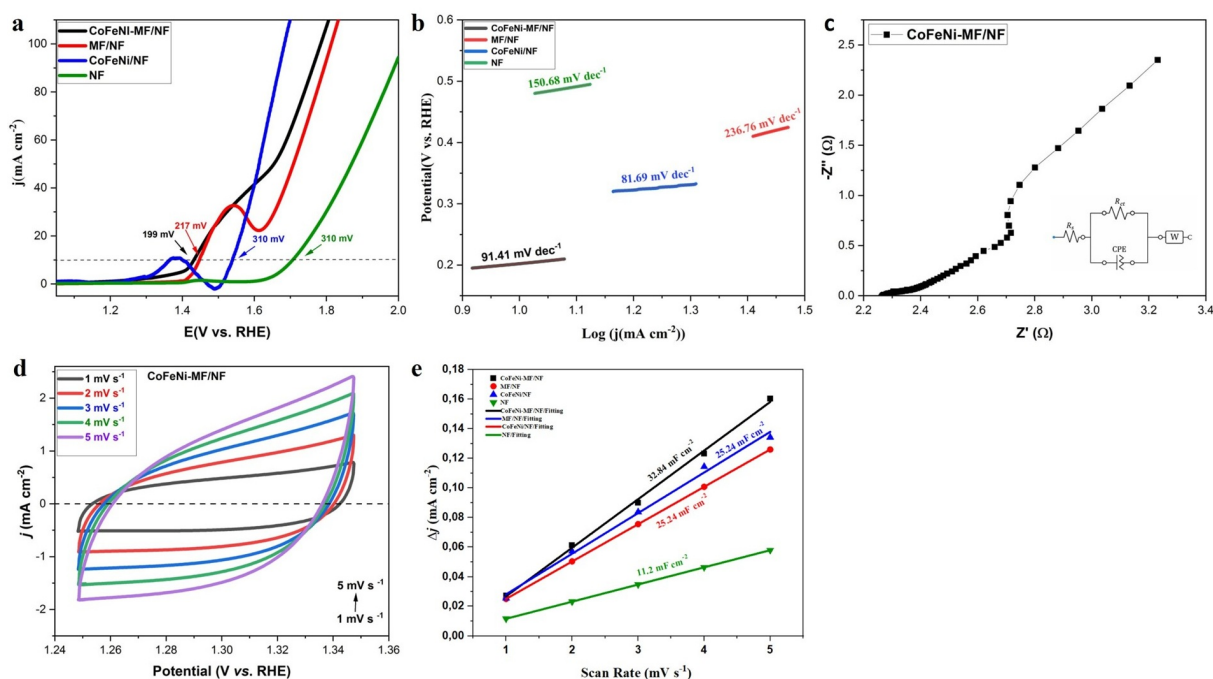


FIG. 6. OER performance under 1 M KOH: a) LSV polarization curves of asprepared catalysts for OER; b) Corresponding Tafel plots; c) Nyquist plot over the frequency range d) CV of CoFeNi-MF/NF catalyst at different scan rates; e) The differences in current density variation ( $\Delta j = j_a - j_c$ ) plotted against scan rate fitted to a linear regression for  $C_{dl}$  estimation

### 3.2. Electrochemical measurement for HER

The performance of the synthesized catalysts for HER was studied. Among these catalysts, CoFeNi-MF/NF in 1 M KOH medium requires the lowest overpotential of 169 mV to achieve a current density of  $10 \text{ mA}\cdot\text{cm}^{-2}$ , as shown in Fig. 7(a). Similarly, the HER performance of CoFeNi/NF, MF/NF, and NF under 1 M KOH was compared. CoFeNi/NF requires overpotentials of 284, 185, and 304 mV to drive a catalytic current density of  $10 \text{ mA}\cdot\text{cm}^{-2}$  for HER. This demonstrates a significant difference compared to CoFeNi-MF/NF, further highlighting the efficiency advantage of CoFeNi-MF/NF in electrocatalysis. Additionally, Fig. 7(b) shows the Tafel slope values of CoFeNi-MF/NF ( $133.09 \text{ mV}\cdot\text{dec}^{-1}$ ), CoFeNi/NF ( $240.08 \text{ mV}\cdot\text{dec}^{-1}$ ), MF/NF ( $174.26 \text{ mV}\cdot\text{dec}^{-1}$ ), and NF ( $169.54 \text{ mV}\cdot\text{dec}^{-1}$ ). The mechanisms of HER and OER reactions are believed to be based on several factors, such as Tafel slope, electrolyte, and others. Generally, the Volmer reaction involves electron adsorption and proton discharge in the first stage, followed by electrodesorption and the Heyrovsky reaction. The results showed that the CoFeNi-MF/NF catalyst exhibits a Tafel slope of  $133.09 \text{ mV}\cdot\text{dec}^{-1}$ , suggesting Volmer–Heyrovsky pathways with adsorption as the rate-limiting step.

The kinetics and charge transfer properties of the synthesized CoFeNi-MF/NF catalysts were studied using electrochemical impedance spectroscopy (EIS). In the low-frequency range, the small semicircle in the impedance data arises

from the faradaic resistance due to charge transfer at the electrode/electrolyte interface. The CoFeNi–MF/NF catalyst showed an  $R_{ct}$  value of  $7.0 \Omega$ , as seen in Fig. 7(c). The study revealed that a low  $R_{ct}$  at the electrode/electrolyte interface can enhance the electron transport properties of nanostructured materials, thereby increasing catalytic efficiency. The  $C_{dl}$  method was used to calculate the ECSA value of the prepared catalysts. CV measurements were performed at various scan rates of  $1 - 5 \text{ mV} \cdot \text{s}^{-1}$  in the non-faradaic region in a  $1.0 \text{ M KOH}$  medium. As shown in Fig. 7(d–e), the CoFeNi–MF/NF catalyst exhibits a significant  $C_{dl}$  value of  $58.2 \text{ mF cm}^{-2}$ . Such a surface area provides more contact points between the electrolyte and the catalytic surface. A similar analysis was performed for the HER process to further clarify the relationship between the electrochemically active surface area and catalytic performance. The ECSA values were estimated from the  $C_{dl}$  using the same method described above. As shown in Fig. 7(e), the  $C_{dl}$  values differ significantly among the samples, indicating noticeable changes in the accessible surface area after each modification step. The corresponding ECSA values were calculated to be  $240 \text{ cm}^2$  for NF,  $585 \text{ cm}^2$  for MF/NF,  $1102 \text{ cm}^2$  for CoFeNi/NF, and  $1455 \text{ cm}^2$  for CoFeNi–MF/NF. Among all the electrodes, CoFeNi–MF/NF exhibits the highest  $C_{dl}$  value ( $58.2 \text{ mF cm}^{-2}$ ), which corresponds to the largest ECSA. This suggests that the combined introduction of CoFeNi and magnetic fluid leads to a substantial increase in the number of exposed active sites. As a result, faster reaction kinetics can be achieved, which is consistent with the improved HER activity observed in the polarization curves. Overall, the superior HER performance of CoFeNi–MF/NF can be attributed, at least in part, to its significantly enlarged active surface area, although the contribution of intrinsic catalytic activity should also be considered. Fig. 7(f) shows a chronoamperometric stability test of the CoFeNi–MF/NF electrode at  $100 \text{ mA} \cdot \text{cm}^{-2}$ , where the stability potential over 24 hours demonstrates robust structural integrity and excellent long-term durability, which are necessary for the practical application of electrocatalysts.

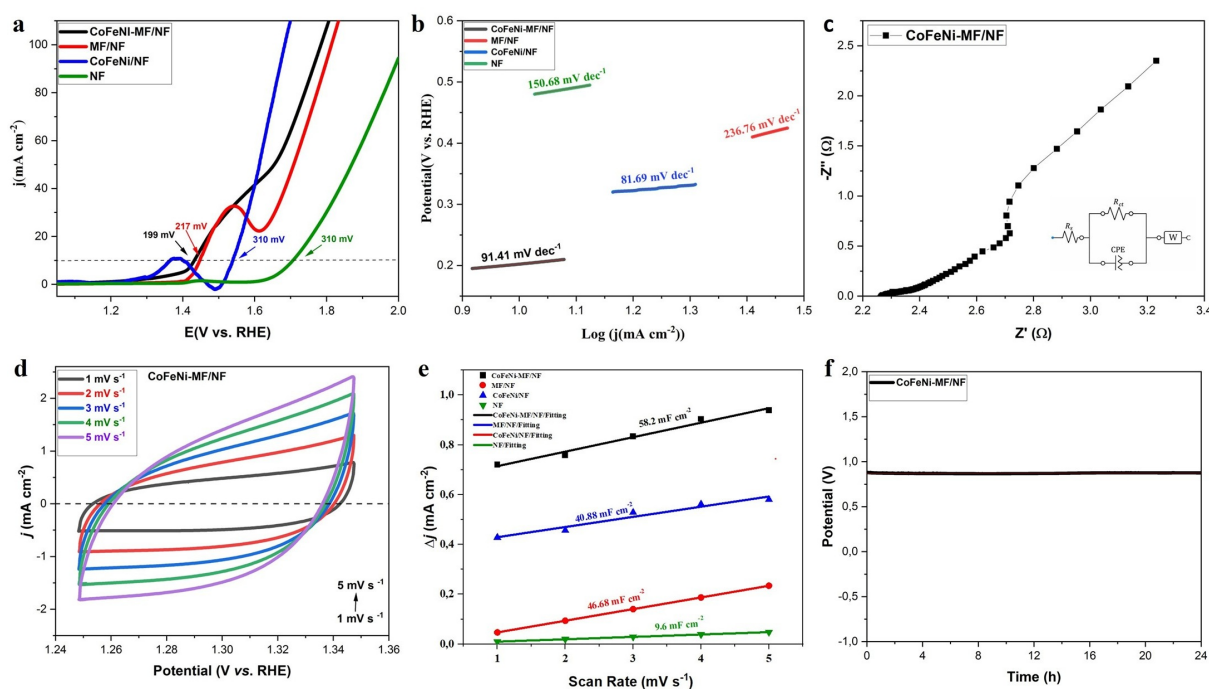


FIG. 7. HER performance under 1 M KOH: a) LSV polarization curves of asprepared catalysts for HER; b) Corresponding Tafel plots; c) Nyquist plot over the frequency range d) CV of CoFeNi–MF/NF catalyst at different scan rates; e) The differences in current density variation ( $\Delta j=j_a-j_c$ ) plotted against scan rate fitted to a linear regression for  $C_{dl}$  estimation; and f) Chronoamperometry test at a current density of  $100 \text{ mA} \cdot \text{cm}^{-2}$  for

The comparison of this research with other similar works is shown in the Table 1. The unique nanomassive morphology based on CoFeNi–MF/NF provided a significantly active surface for OER and HER, contributing to competitive overvoltage at  $10 \text{ mA} \cdot \text{cm}^{-2}$  and Tafel slopes. CoFeNi–MF/NF is a promising choice for water electrolysis.

#### 4. Conclusion

In this study, a highly efficient bifunctional electrocatalyst, CoFeNi–MF/NF, was rationally designed and synthesized through a two-step hydrothermal approach involving the integration of  $\text{Fe}_3\text{O}_4$ -based magnetic fluid into a CoFeNi nanosheet framework. Structural characterizations including XRD, SEM, EDS, FTIR, and XPS collectively confirm that the incorporation of MF introduces a dual-phase composition composed of FCC-type CoFeNi alloy and spinel  $\text{Fe}_3\text{O}_4$ , accompanied by the formation of vertically aligned nanosheets with significantly enhanced surface roughness

TABLE 1. Comparative analysis of this study with other similar works

| Electrocatalyst                                                 | Current density<br>(mA·cm <sup>-2</sup> ) | Overpotential |     | Tafel slopes mV·dec <sup>-1</sup> |       | Reference |
|-----------------------------------------------------------------|-------------------------------------------|---------------|-----|-----------------------------------|-------|-----------|
|                                                                 |                                           | HER           | OER | HER                               | OER   |           |
| Co <sub>0.45</sub> Fe <sub>0.45</sub> Ni <sub>0.9</sub> -MOF/NF | 50                                        | 225           | 244 | 91.6                              | 127   | [19]      |
| NFC@CNSs-700                                                    | 10                                        | 213           | 256 | 21.95                             | 61.29 | [24]      |
| CoFeNi-MF/NF                                                    | 10                                        | 169           | 199 | 91                                | 91.41 | This work |
| CoFeNi-/NF                                                      | 10                                        | 270           | 310 | 92                                | 81.69 | This work |

and defect density. The uniform dispersion of Co, Fe, Ni, and O, as revealed by elemental mapping, highlights the successful construction of a chemically and electronically interconnected multimetallic architecture. The introduction of Fe<sub>3</sub>O<sub>4</sub> nanoparticles via magnetic fluid not only increases the Fe and O content in the composite but also establishes stronger electronic coupling and magnetic-field-induced polarization effects among the Co-Fe-Ni centers. These synergistic interactions promote improved charge transfer, optimized adsorption/desorption energetics, and accelerated formation of active MOOH species under alkaline conditions. FTIR spectra further confirm the presence of abundant hydroxyl groups and well-defined M-O vibrational modes, while XPS analysis reveals the coexistence of mixed-valence states (Co<sup>2+</sup>/Co<sup>3+</sup>, Fe<sup>2+</sup>/Fe<sup>3+</sup>, Ni<sup>2+</sup>/Ni<sup>3+</sup>) and partially metallic domains, which collectively play a crucial role in enhancing reaction kinetics. Electrochemical measurements demonstrate that CoFeNi-MF/NF exhibits remarkable bifunctional activity toward both HER and OER in 1.0 M KOH. The catalyst requires low overpotentials of 169 mV (HER) and 199 mV (OER) at 10 mA·cm<sup>-2</sup>, significantly outperforming pristine CoFeNi/NF and MF/NF. Corresponding Tafel slopes of 133.09 mV·dec<sup>-1</sup> (HER) and 91.41 mV·dec<sup>-1</sup> (OER) further confirm rapid reaction kinetics facilitated by the magnetic-fluid-assisted architecture. The exceptionally low charge-transfer resistances – 7.0 Ω for HER and 1.0 Ω for OER-combined with the high double-layer capacitance values (58.2 mF cm<sup>-2</sup> for HER, 32.84 mF cm<sup>-2</sup> for OER) attest to the expanded electrochemically active surface area and superior intrinsic conductivity of the hybrid catalyst. The electrochemically active surface area (ECSA) analysis further confirms the superior catalytic performance of the CoFeNi-MF/NF electrode. For OER, the CoFeNi-MF/NF catalyst exhibits the highest ECSA value of 821 cm<sup>2</sup>, while for HER, it reaches 1455 cm<sup>2</sup>, both significantly higher than those of the reference samples. This increase in ECSA indicates a larger number of accessible active sites, which contributes to enhanced reaction kinetics in both HER and OER processes. These findings demonstrate that the improved electrocatalytic activity of CoFeNi-MF/NF is closely related to its enlarged active surface area. Long-term chronopotentiometry at 100 mA·cm<sup>-2</sup> for 24 hours demonstrates outstanding structural and electrochemical durability, validating the robustness of the CoFeNi-MF/NF system under practical operating conditions. These results collectively reveal that magnetic-fluid-induced modifications profoundly enhance both catalytic performance and stability by optimizing electron/spin transport, strengthening interfacial interactions, and enabling efficient gas evolution dynamics. Overall, the CoFeNi-MF/NF nanocomposite developed in this work represents a promising, cost-effective, and scalable electrocatalyst for overall water splitting. The proposed design strategy-combining trimetallic alloys with magnetic-fluid-assisted surface engineering-offers a versatile platform for future development of advanced magnetic-field-responsive catalysts for industrial hydrogen production under alkaline and potentially neutral media.

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*Data availability*

Data associated with this study are available from the corresponding author upon request.

## Role of electronic structure of vanadium oxide cluster in methanol oxidation

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**ABSTRACT** To reveal the catalytic activity of neutral vanadium oxide nanoclusters in methanol (CH<sub>3</sub>OH) oxidation, quantum chemical simulation of methanol adsorption on V<sub>4</sub>O<sub>10</sub> cluster and further oxidation to formaldehyde (CH<sub>2</sub>O) is performed at DFT PBE level. According to calculation, the cluster has a tetrahedral cage structure with four terminal V=O(t) and six bridging V–O(b)–V fragments. The reaction of methanol and V<sub>4</sub>O<sub>10</sub> occurs through association and two abstraction stages sequentially. The role of the two oxygens O(t) and O(b) in these processes is shown to be different. Analysis of atomic charges and electron density in V<sub>4</sub>O<sub>10</sub> allowed to explain the observed patterns and predict the reduction of the activation barrier of rate-determining step of (CH<sub>2</sub>O)V<sub>4</sub>O<sub>10</sub>H<sub>2</sub> formation when the V<sub>4</sub>O<sub>10</sub> has positive charge or titanium is introduced into the cluster's structure.

**KEYWORDS** transition metal oxide cluster, methanol oxidation, V<sub>2</sub>O<sub>5</sub>, mechanism, oxygen radical, activation energy, transition state

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### 1. Introduction

Transition metal oxide nanoclusters are used in various fields of science including catalysis, materials science, and medicine [1–3]. These small clusters contain low-coordinated metal atom, large surface area, oxygen radicals and vacancies which is responsible for their unique properties [4]. They are a common model of active sites in nanostructured catalysts for studying the mechanisms of heterogeneous catalytic reactions [5, 6]. Fundamental information on the mechanism of catalytic reactions and the structure of active sites is necessary for the targeted design of effective catalysts, which is important for the development of technologies that comply with the principles of energy conservation and green chemistry.

Various experimental and theoretical methods are commonly employed to determine the structure of metal oxide clusters. Significant progress in structure clarification was achieved through beam methods and quantum chemical methods. For instance, V<sub>m</sub>O<sub>n</sub><sup>+</sup> ( $m = 1 \div 4$ ,  $n = 1 \div 11$ ) were synthesized [7], the composition and growth dynamics of vanadium oxide clusters were recorded [8]. The structures of V<sub>m</sub>O<sub>n</sub> and V<sub>m</sub>O<sub>n</sub><sup>+</sup> ( $m = 2 \div 4$ ,  $n = 2 \div 10$ ) were calculated by different quantum-chemical methods including UHF, B3LYP and BP86 [9–12]. The authors considered various isomers including chain, cyclic, and fragments of vanadium oxide crystal lattice, and demonstrated that for V<sub>4</sub>O<sub>10</sub> the tetrahedral structure with pronounced closed-cage character is the most energetically stable. In addition to V<sub>m</sub>O<sub>n</sub> structures, the reaction of vanadium oxide clusters with stable molecules (such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CCl<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>) was also studied [13–16]. For instance, it was demonstrated that tetranuclear V<sub>4</sub>O<sub>10</sub><sup>+</sup> can activate C–H bond in methane with low activation energy (37 kJ/mol) and catalyzes methane oxidation to CH<sub>3</sub>OH [13]. Further oxidation of methanol on vanadium oxide clusters appears promising for further investigation.

Vanadium oxide-based materials catalyze methanol oxidation to produce useful chemical products, such as formaldehyde (CH<sub>2</sub>O), dimethoxymethane (CH<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>), methyl formate (HCOOCH<sub>3</sub>), dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>), formic acid (HCOOH) with high selectivity [17, 18]. The reaction, also known as methanol oxidative dehydrogenation, has been studied on vanadium oxide [19–23]. The Mars-van Krevelen redox cycle is accepted as the reaction mechanism, where the rate-determining step is the C–H bond cleavage in the methoxide intermediate leading to the formation of adsorbed CH<sub>2</sub>O [20, 21]. This step is determined by many factors including the structure and charge of the V<sub>2</sub>O<sub>5</sub> active site. The surface of the catalysts is not uniform. Different forms of vanadium oxide were observed on the support including isolated VO<sub>x</sub> samples, polymeric (VO<sub>x</sub>)<sub>n</sub> species and 3D particles such as clusters or crystallites [22, 23]. The most active catalysts in methanol oxidation were V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> with monomeric and polymer particles, as opposed to V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub>, in which all the vanadium was in the bulk phase. An inverse correlation between catalytic activity and the



content of the bulk phase was observed. It can be assumed that small vanadium oxide clusters, i.e. model  $V_4O_{10}$ , will act as an active site and catalyze the oxidation of methanol.

To test this hypothesis, a quantum chemical simulation of methanol oxidation to formaldehyde on model  $V_4O_{10}$  was performed at DFT PBE level. To elucidate the catalytic activity of the cluster, structure, energy changes and activation energy at each step of methanol oxidation were calculated including C–H bond cleavage in the methoxide intermediate. Particular attention is paid to the influence of electronic effects on the stability of the formed intermediates and the activation energy.

## 2. Calculation details

To simulate methanol oxidation on  $V_4O_{10}$ , structures of the clusters,  $CH_3OH$ , and all intermediates were fully optimized and the energies were calculated using the spin-polarised DFT method with PBE functional [24]. The Dirac–Coulomb–Breit Hamiltonian with separate spin-free and spin-dependent components was applied [25]. The energy-optimized extended Gaussian basis set of triple-polarized quality of the large component, and the corresponding kinetically balanced basis for the small component was used [26]: V [26s23p16d5f/7s6p4d1f], O [10s7p3d/3s2p1d], C [10s7p3d/3s2p1d], and H [6s2p/2s1p].

The reaction pathways were preliminarily analyzed by scanning the potential energy surface along the reaction coordinate. The exact transition state (TS) structure was determined by eigenvector following using the Berny algorithm [27]. To confirm the TS structure, intrinsic reaction coordinate (IRC) calculations [28] were performed by following the single imaginary mode. Atomic charges were calculated using overlap populations analysis (Mulliken scheme, MS) and analysis of atomic partitions of the density (Hirshfeld scheme, HS). All calculations were performed by the Priroda software package [29]. The method was successfully applied in the theoretical study of the structure and simulation of catalytic properties of metal nanoclusters [30–32].

## 3. Results and discussion

The  $V_4O_{10}$  cluster is considered as a model of the active site of a heterogeneous catalyst containing vanadium oxide for methanol oxidation. According to previous calculations [10, 33], it has a tetrahedral cage structure with four terminal  $V=O(t)$  and six bridging  $V-O(b)-V$  fragments. Molecular geometry calculated by our method is shown in Fig. 1. The structure and interatomic distances agree with both the recent calculation of  $V_4O_{10}$  at B3LYP/TZVP level [12] and with previously theoretical study at B3LYP/6-31G\* level [11]. The minimum-energy structure has a singlet electronic state and closed electron shells. Atomic charge calculation for  $V_4O_{10}$  using both MS and HS approaches reveals that all vanadium atoms have the same positive charge. The O(t) and O(b) differ in charge: all bridging oxygen atoms possess higher negative charge (–0.500 MS and –0.232 HS) than terminal oxygens (–0.288 MS and –0.203 HS). The O(t) and O(b) differ in interatomic V–O distances: V–O distances in terminal fragments are 1.60 Å; calculated V–O distances in bridging fragments are 1.81 Å. Analysis of molecular orbitals of  $V_4O_{10}$  demonstrates that the isosurfaces of HOMO are localized on two oxygen atoms. Both oxygen O(t) and O(b) sites are likely to be active in hydrogen binding as a result of oxidative dehydrogenation of methanol.

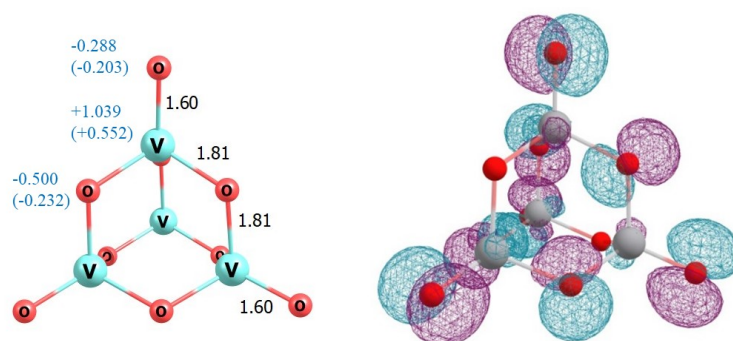


FIG. 1. Left picture: optimized structure with calculated interatomic distances (colored by black), MS and HS atomic charges (colored by blue). Right picture: HOMO of  $V_4O_{10}$

The  $CH_3OH$  oxidation to  $CH_2O$  on neutral  $V_4O_{10}$  cluster is simulated. The process occurs through several steps involving association of methanol with cluster (1), abstraction of the first hydrogen from –O–H group (2) and abstraction of the second hydrogen atom from – $CH_3$  group (3) to form product  $CH_2O$ :  $CH_3OH + V_4O_{10} \rightarrow (CH_3OH)V_4O_{10} \rightarrow (CH_3O)V_4O_9OH \rightarrow (CH_2O)V_4O_8(OH)_2$

The structures of the optimized complexes formed in steps 1, 2 and 3, as well as the transition state of step 3 are shown in Fig. 2. The thermodynamic and kinetic parameters of each stage including energy changes and activation energies are

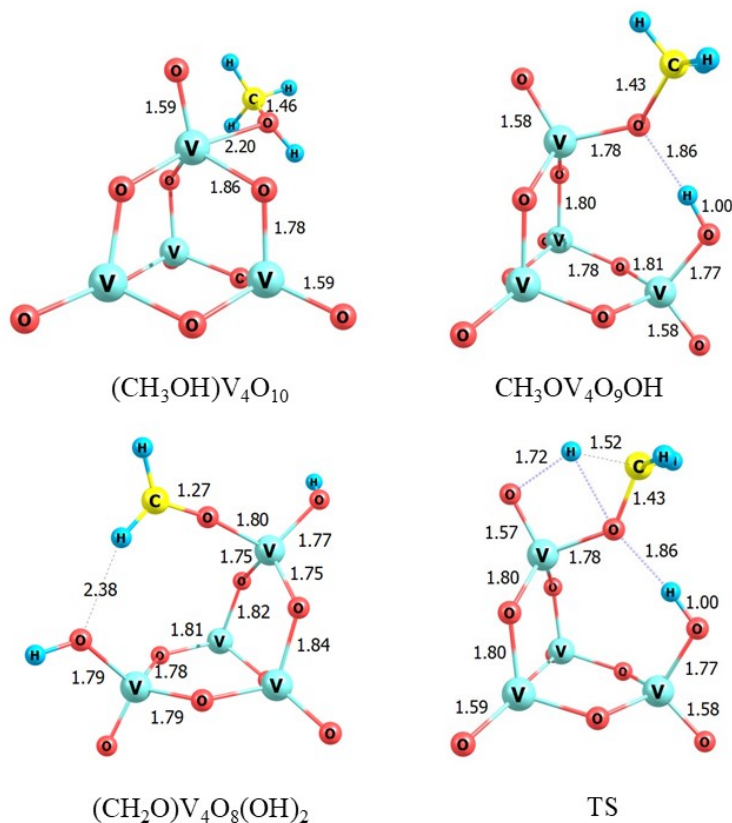


FIG. 2. Optimized structures and calculated interatomic distances in complexes and transition state of the steps 1–3 in  $CH_3OH$  oxidation to  $CH_2O$  on neutral  $V_4O_{10}$  cluster

considered below. Association product  $(CH_3OH)V_4O_{10}$  is formed spontaneously on V site via  $-OH$  coordination with an energy gain of  $-59.3$  kJ/mol.

This coordination of the alcohol molecule is due to a positive charge on the vanadium ion. The second step of methanol oxidation involves the abstraction of the first hydrogen. The dissociative adsorption of  $CH_3OH$  on the clusters occurs through O–H bond cleavage in hydroxyl group and breaking the V–O–V fragment. The formation of  $(CH_3O)V_4O_9OH$  complex is energetically favorable by 55.4 kJ/mol compared to association product  $(CH_3OH)V_4O_{10}$  and 114.7 kJ/mol compared to an isolated gas-phase cluster and methanol. A proton in  $(CH_3O)V_4O_9OH$  is attached to the oxygen, while the methoxy group is coordinated to the vanadium atom. A similar mechanism of the dissociative addition of methanol on vanadium surface with the saving of the valence of the vanadium atom was predicted previously [33]. Further abstraction of the second hydrogen atom from  $CH_3-$  group to form product  $(CH_2O)V_4O_{10}H_2$  occurs on terminal O(t) site increasing total energy on 130 kJ/mol in relative to energy of  $(CH_3O)V_4O_9OH$ . Calculated activation barrier is high (189 kJ/mol) due to the need to destroy the strong cage structure of the cluster. High activation energy, 147 kJ/mol, of the step  $CH_3-O- \rightarrow CH_2-O- + H-$  was also predicted previously on vanadium oxide monolayer [33].

It seems interesting to analyze the atomic charges on the key atoms V(1), O<sub>b</sub>(2), O<sub>t</sub>(3), O(4) and C(5) in the complexes involved in the stages 1–3 (Fig. 3). Compared to the original  $V_4O_{10}$  cluster, vanadium in the complexes is in a reduced state throughout the oxidation process. This is consistent with experimental studies of the methanol oxidation mechanism [22], according to which vanadium is reduced from  $V^{+5}$  to  $V^{+4}$  at the stage of alcohol adsorption. In this case, the carbon atom is oxidized, which corresponds to the general idea of its state in formaldehyde. Both the terminal and bridging oxygen of the cluster are converted into a hydroxy group, which is confirmed by the equalization of their charges.

According to simulation,  $CH_3OH$  oxidation to  $CH_2O$  on neutral  $V_4O_{10}$  cluster requires the presence of different sites including V, O(b), O(t). The role of the two oxygens O(t) and O(b) is shown to be different. Bridging oxygen V–O–V is active in O–H bond cleavage, while terminal V=O is necessary for C–H bond cleavage in  $CH_3-$ . The methanol oxidation on the cluster is accompanied by a change in the electronic state of vanadium and two oxygen sites of the cluster, which causes high activation energy of the C–H bond cleavage. So, methanol oxidation on a model neutral  $V_4O_{10}$  cluster is expected to occur only at elevated temperatures.

The potential applications and possible ways to improve  $V_4O_{10}$  reactivity can be explored. Based on the ideas described in the review [4], the properties of transition metal oxide clusters are determined by the presence of mono-nuclear oxygen-centred radical species  $O^{-*}$  in their composition. To have oxygen-centred radical  $O^{-*}$ , the composition

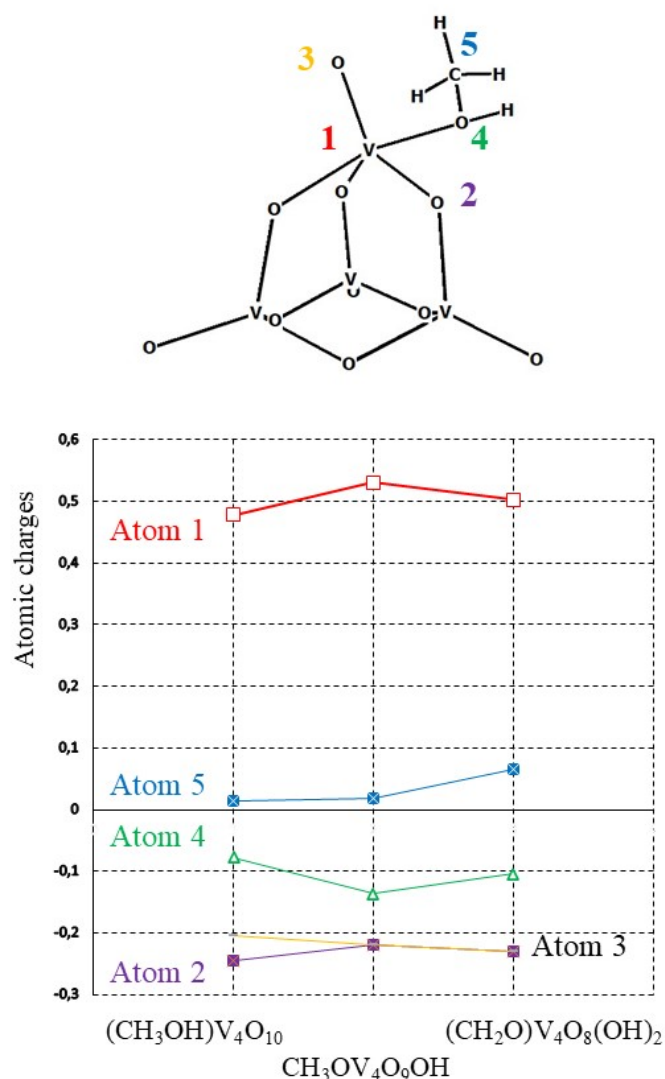


FIG. 3. Calculated atomic charges in the complexes involved in methanol oxidation on  $V_4O_{10}$

of the oxide cluster  $M_xO_y^q$  must satisfy the following formula:

$$\Delta = 2y - nx + q = 1,$$

in which  $n$  is the number of valence electrons of element  $M$  that can be oxidized by oxygen to  $+n$  oxidation state. The  $\Delta$  is called as *extent of cluster over-oxidation*. Substituting the charge and composition of our neutral  $V_4O_{10}$  into this formula leads to  $\Delta = 0$ :

$$\Delta = 2 \cdot 10 - 5 \cdot 4 + 0 = 0.$$

Thus, neutral  $V_4O_{10}$  does not contain oxygen radical species  $O^{-*}$ ; therefore, it is unreactive to oxidation. The situation can be corrected by changing the cluster's charge with saving atomic composition. When the charge is  $+1$ , the calculated extent of cluster over-oxidation is 1. So, cationic  $V_4O_{10}^+$  contains an active oxygen radical, and it is expected to exhibit higher activity in the oxidation of methanol. Based on such reasoning, the catalytic properties of the cationic  $V_4O_{10}^+$  cluster are tested in methanol oxidation. Anion  $V_4O_{10}^-$  cluster is also considered for comparison.

Optimization of the structure of  $V_4O_{10}^+$  and  $V_4O_{10}^-$  estimated that, in general, they retain the structure of a neutral cluster with complete preservation of key distances in the case of an anionic cluster, and a slight reduction in the  $V=O$  distance to 1.59 Å and an increase in the  $V-O$  distance to 1.80 Å in the cationic one. Atomic charges in the charged clusters were calculated. The loss of one electron from a neutral cluster results in a decrease in charge on all atoms: V atom is  $MS=1.1627$  or  $HS=0.6304$ ; O(t) atoms are  $MS=-0.2072$  or  $HS=-0.0996$ ; O(b)\* atoms are  $MS=-0.4622$  or  $HS=-0.1744$ ; O(b) atoms are  $MS=-0.4745$  or  $HS=-0.1939$ . The spin density has the shape of a p orbital and is mainly localized at O(t) atom. A small amount of the spin density is also delocalized over the two closest O(b)\* atom. For the anionic cluster, an alternative distribution of charge and electron density is observed: V atom is  $MS=0.8959$  or  $HS=0.4508$ ; O(t) atoms

are  $MS = -0.3662$  or  $HS = -0.2966$ ; O(b) atoms are  $MS = -0.5097$  or  $HS = -0.2650$ . The spin density has the shape of a d orbital and is mainly localized at V atom.

Let us consider how the difference in the electronic structure of  $V_4O_{10}^+$  and  $V_4O_{10}^-$  will affect their reactivity in methanol oxidation. The structures and energies of the charged complexes involved in the stages of methanol oxidation to formaldehyde, which were determined for the neutral  $V_4O_{10}$ , were calculated and the energy changes in stages 1, 2 and 3 was estimated (Table 1). The anionic cluster activates methanol very poorly in the associative step. In the first stage, a  $(CH_3OH)V_4O_{10}$  complex is formed with a binding energy lower than that of a neutral cluster. The cleavage of the O-H bond in the alcohol molecule is also less favorable than for neutral cluster. Thus, the  $V_4O_{10}^-$  exhibits poor activity in preactivating even the O-H bond in methanol. Therefore, there is no point in studying its properties in C-H bond cleavage; its thermodynamic and kinetic properties in this case are obviously poor. In contrast, for the cationic  $V_4O_{10}^+$ , an increase in energy change is observed even at the first associative stage. Further O-H bond breaking (stage 2) is also energetically favorable. The largest energy change is calculated for C-H bond cleavage (stage 3) in the  $CH_3$ -O-intermediate and the formation of formaldehyde.

TABLE 1. Calculated energy changes (kJ/mol) in stages 1, 2 and 3 of methanol oxidation on  $V_4O_{10}$ ,  $V_4O_{10}^+$ ,  $V_4O_{10}^-$

| Charge | $\Delta E_1$ | $\Delta E_2$ | $\Delta E_3$ |
|--------|--------------|--------------|--------------|
| 0      | -59.3        | -55.4        | +130.0       |
| +1     | -142.4       | -38.8        | -112.8       |
| -1     | -30.0        | -24.8        | —            |

As noted earlier, stage 3 is the rate-determining step in methanol oxidation on vanadium oxide. To test its rate on the cationic  $V_4O_{10}^+$  cluster, the transition state is found and the activation energy is calculated. The transition state structure is shown in Fig. 4. The calculated activation energy is 42.1 kJ/mol, indicating that formaldehyde forms on the cationic cluster at low temperature. Two possible reasons for the decrease in activation energy can be identified. The first is the presence of an oxygen radical within the cluster, which facilitates methanol activation. The second reason is the loosening of the stable tetrahedral structure due to the loss of one electron. This leads to the easy opening of the cage, which is necessary for the transition state of the third stage, leading to the cleavage of the C-H bond in the  $CH_3$ -O intermediate.

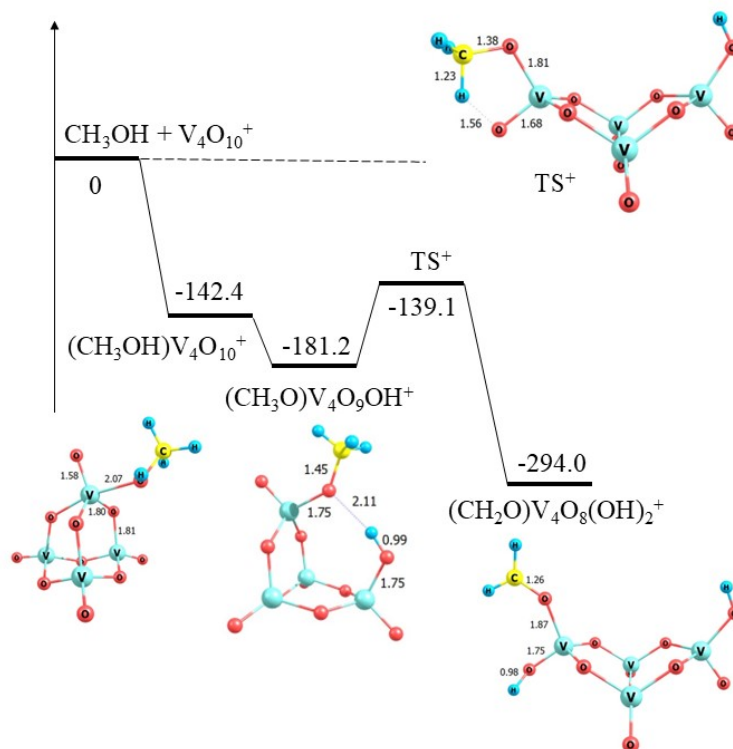


FIG. 4. An energy diagram illustrating the change in energy at the stages of methanol oxidation on  $V_4O_{10}^+$  relative to the total energy of the cluster and methanol (energies are given in kJ/mol)

Can cationic clusters form on the surface of a heterogeneous catalyst? It is known that the support used to stabilize transition metal oxide nanoparticles can generate positively or negatively charged sites. Among the vanadium oxide catalysts considered in methanol oxidation, the most active one is  $\text{V}_2\text{O}_5/\text{TiO}_2$  [22]. It can be assumed that titanium oxide creates cationic vanadium oxide. Alternatively, titanium itself can be part of the active site forming an active oxygen radical. Calculation of the expected composition of the bimetallic cluster according to the formula proposed in the review [4] leads to  $\text{TiV}_3\text{O}_{10}$ . Simulation of methanol oxidation on a mixed vanadium-titanium oxide cluster requires further investigation and will be addressed in the future work.

#### 4. Conclusions

The present study provides a detailed quantum chemical analysis of methanol oxidation to formaldehyde on the model  $\text{V}_4\text{O}_{10}$  cluster using DFT methods. The results demonstrate that the reaction proceeds via a multistep mechanism involving methanol adsorption, O–H bond cleavage, and subsequent C–H bond activation, with the latter identified as the rate-determining step. It has been shown that the catalytic activity of the neutral  $\text{V}_4\text{O}_{10}$  cluster is limited by a high activation barrier for C–H bond cleavage, which restricts the reaction to elevated temperatures. The analysis of electronic structure and atomic charge redistribution reveals that both terminal and bridging oxygen atoms play distinct and essential roles in the reaction mechanism, with bridging oxygen sites facilitating O–H bond cleavage and terminal oxygen atoms participating in C–H activation.

A key finding of this work is the pronounced effect of cluster charge on catalytic performance. The introduction of a positive charge leads to the formation of oxygen radical species and significantly enhances catalytic activity. In particular, the cationic  $\text{V}_4\text{O}_{10}^+$  cluster exhibits a substantially reduced activation energy for the rate-determining step, enabling methanol oxidation under milder conditions. In contrast, the anionic  $\text{V}_4\text{O}_{10}^-$  cluster demonstrates poor reactivity, particularly at the initial activation stages.

These results highlight the importance of electronic structure tuning in transition metal oxide nanoclusters and suggest that cationic species may represent the true active sites in supported vanadium oxide catalysts. The findings also provide a theoretical basis for the design of more efficient catalytic systems, including mixed-metal oxide clusters such as Ti–V–O systems, which may further enhance reactivity through electronic and structural modification. Overall, this study contributes to a deeper understanding of the relationship between charge state, electronic structure, and catalytic activity in vanadium oxide nanoclusters, offering valuable insights for the rational design of catalysts for selective methanol oxidation.

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## Alternating field magneto-optical response of hard magnetic nanoplate dispersions

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**ABSTRACT** Here we provide an analysis of alternating field magneto-optical (AFMO) response for concentrated dispersions of hard magnetic nanoplates. Dynamics of hexaferrite 50×5 nm nanoplates in 0.3–30 g/L magnetic fluids was traced with amplitude and phase shift of transmission AFMO response in the frequency range of 1 Hz – 10 kHz and magnetic fields up to 50 Oe. AFMO signal was used for reconstructing fast magnetization susceptibility dependence on the applied field depending on concentration of nanoplates. The two modes of platelets reorientation were revealed with AC field frequency and amplitude variation. High-frequency mode, characterized by magnetization phase lag, increasing with the excitation field frequency, corresponds to incomplete orientation of platelets after the field. Contrary, the low-frequency mode with magnetization phase lag, increasing reciprocally to the excitation field frequency, reveals AC coercivity of ferrofluid. The last is addressed to the self-stabilization of particles orientations by magnetic momenta of constituent particles.

**KEYWORDS** Hexaferrite, ferrofluid, magneto-optics, magnetization dynamics.

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### 1. Introduction

In the recent years, magnetic fluids of hard magnetic nanoparticles with anisotropic shape have attracted considerable attention [1]. Compared to conventional magnetic fluids, built from soft magnetic nanospheres nanoparticles, ferrofluids comprising of hard magnetic wires or platelets enables both stabilization of magnetic momenta within the particles with magnetocrystalline anisotropy and stabilization of particles orientation within the liquid with drag momenta [2]. These properties make these ferrofluids extremely attractive for many technological applications, including reconfigurable magnets, bistable solenoids, tunable friction pairs and bearings, magnetorheological systems, magnetic lubrication, viscous dampers, triboelectric generators etc [3–5].

Nanoscale dynamics in ferrofluids is considered a most important factor, affecting their technological applicability. The dynamic behavior of magnetic particles in a viscous medium is determined by the interplay of Brownian motion, viscous drag, external magnetic field strength and interparticle interactions [2, 6]. In common magnetic fluids, the relaxation of the magnetization of the system proceeds by two distinct mechanisms: Néel and Brownian relaxation [7, 8]. Soft superparamagnetic particles predominantly exhibit Néel relaxation, whereas hard magnetic particles are dominated by Brownian mechanism. In hard magnetic materials magnetocrystalline anisotropy barrier strongly suppresses internal moment rotation and demagnetization proceeds by physical rotation of particles [1, 9, 10]. The dynamics of this process is governed by solvent viscosity and particle shape [9]. While spherical particles possess lowest drag momenta for rotational movement, dominated by viscous friction, nanorods and nanoplates experience additional drag due to the necessity of fluid displacement [11]. The largest drag momentum is attained for disc-shaped particles, which makes them most attractive for hydrodynamic and magnetorheological applications.



Among the few hard magnetic materials capable of forming stable colloidal solutions of anisotropic particles, M-type hexaferrites stand out due to their high thermodynamic and chemical stability, unique magnetic structure and strong structural anisotropy [12–15]. These materials exhibit a pronounced uniaxial magnetocrystalline anisotropy with a magnetic easy axis aligned along the crystallographic *c*-axis. Owing to the superexchange interactions of  $\text{Fe}^{3+}$  ions occupying five inequivalent lattice sites, a ferrimagnetic order is established, with the moment rigidly fixed perpendicular to the basal plane of nanoplates [14, 16]. Consequently, even at extremely small dimensions, these particles possess a substantial intrinsic magnetic moment and high coercivity. The combination of high magnetocrystalline anisotropy and platelet morphology enables complex rotational dynamics of hexaferrite hard magnetic nanoplates under an alternating magnetic field. Furthermore, due to the significant difference in the depolarization factors of nanoplates and dielectric ellipsoid components of hexaferrite phase along *a* and *c* crystallographic axis [9, 17], the colloidal solutions of such particles exhibit strong magneto-optical response upon particle reorientation [14]. These effects form the physical basis for the magneto-optical response of hexaferrite ferrofluids and allow optical tracking of the rotational dynamics of the nanoplates.

Based on the above principles, our group recently used strontium hexaferrite nanoplates as nanorotor viscosity sensors [18]. Through a combination of experiments and theoretical modeling, the rotational dynamics of the nanoplates under an alternating magnetic field was systematically investigated. A relation of drag force, phase lag tangent and the viscosity of the medium was established, enabling fast, in-situ evaluation of liquid viscosity over a range of 0.5–1000 mPa·s. Furthermore, a spatial resolution down to 4  $\mu\text{m}$  was demonstrated, allowing viscosity visualization in microchannels with micrometer resolution.

The detailed studies of dynamic behavior of colloid nanoparticles under rotating magnetic field showed the presence of two distinct regimes of particles precession: synchronous and asynchronous modes [19, 20]. Romodina et al. [19] showed that Brownian torque induces the flattening of the breakdown transition between the synchronous and asynchronous modes. The results of Brownian dynamics simulations agree with the experimental data, confirming the essential role of thermal fluctuations in field-driven rotation. Honecker et al. have demonstrated [20] that, as the frequency of a rotating magnetic field increases, the motion of hematite nanospindle (length 374 nm, diameter 51.5 nm) evolves from coherent precession involving rotation about the minor axis to synchronized spinning about the principal axis with spindles tending to collinea alignment perpendicular to the rotation field plane. In contrast to rotating magnetic field, an alternating magnetic field causes periodic reversal of the magnetic torque [18], leading to the observation of three distinct regimes of particle rotation with increasing frequency: synchronous rotation, synchronous oscillation, and asynchronous response.

Despite of rather a significant progress made in the recent years in the field, the information on particles dynamics in ferrofluid remains rather scarce. To the best of our knowledge no information on the collective effects on nanoplates dynamics in ferrofluids has been reported yet. Thus, in the present study we provide a comprehensive investigation of the dispersions of hexaferrite hard magnetic nanoplates over a concentration range of 0.3–30 g/L with earlier developed alternating field magneto-optical (AFMO) method [18]. This study enabled to reveal the dynamics of reorientation of platelets in the dispersion depending on concentration. Using the AFMO signal, we reconstructed the dependence of the magnetic susceptibility on the applied magnetic field for magnetic fluids at different concentrations. Additional information on the structure of dispersions is gained with the analysis of AC coercivity on excitation frequency, enabling to propose self-stabilization of particles orientations by the magnetic moment of the platelets.

## 2. Experimental

Plate-like strontium hexaferrite nanoparticles were synthesized via the glass-ceramic route [14, 21]. The precursor glass with the nominal composition  $4\text{Na}_2\text{O} \times 9\text{SrO} \times 5.5\text{Fe}_2\text{O}_3 \times 4.5\text{Al}_2\text{O}_3 \times 4\text{B}_2\text{O}_3$  was prepared by rapid melt quenching. To induce crystallization, the glass was subjected to isothermal heat treatment at 700°C for 2 hours, followed by air quenching. The resulting glass-ceramic was treated with 3% aqueous hydrochloric acid to dissolve borate matrix. The residual particles were washed with deionized water and redispersed in acidic aqueous media with pH = 4, obtaining a stable colloidal solution with concentration of  $\sim 0.3$  g/L. The concentrated dispersions of approximately 30 g/L were obtained by centrifugation at 10,000 rpm (11,000 g) for 30 minutes followed by 1 day separation in gradient magnetic field. Condensed phase was extracted from the bottom of the vial.

Magnetic measurements of field-frozen colloid particles were performed using a Faraday balance type magnetometer with magnetic fields of up to 18 kOe at 77 K. The magnetic moment measurement accuracy was 3%, and the applied magnetic field accuracy was  $\pm 100$  Oe. Magnetic properties of colloidal solution were measured at room temperature (298 K) using a Quantum Design SQUID MPMS-7XL magnetometer. Particle sizes and shape were analyzed using transmission electron microscopy (Zeiss Libra 200 and Jeol JEM-2100).

The AC magneto-optical (AFMO) measurements were performed in a originally developed setup (Fig. 2a) similar to previously reported in [18]. Perpendicular geometry of laser beam (532 nm) and magnetic field was used to maximize the magneto-optical response. To avoid polarization induced artifacts, the laser beam first passed through a polarizer, then through the cuvette (standard 10 mm quartz cuvette for diluted dispersion and 50  $\mu\text{m}$  thick microcuvette for concentrated solution) containing the investigated dispersion. Fast BPW21R photodiode (Vishay Semiconductors) was used for light intensity detection. Microfocus experiments were conducted using Renishaw Invia system. The magnetic field in the micro-cuvette was generated by specially designed Helmholtz coils. A sinusoidal alternating current with a frequency

range from 2 Hz to 5 kHz was supplied by a digital oscilloscope with a built-in signal generator (Velleman Instruments PCSGU250). The signal was amplified using CREST AUDIO VS1500 to provide AC field magnitude of 2–50 Oe. Synchronization of the optical signal with the magnetic field was achieved by simultaneous registration of the Hall sensor (rigidly fixed on the coils) response.

AFMO signal analysis and hysteresis-like loop reconstruction was performed according to the following routine. To extract the positions of maxima and minima of AFMO signal, the experimental field-time dependency was converted into half-period fraction  $T$  values (varying in  $-\pi/2$  to  $\pi/2$  range) by maximum field normalization as momentary field was directly evaluated from Hall sensor response:

$$T = \arcsin\left(\frac{H(t)}{H_{\max}}\right), \quad (1)$$

where  $H_{\max}$  is maximum applied field and  $H(t)$  is momentary field value at time  $t$ . This allowed one to build AFMO- $T$  curve which was fitted with 5-th order polynomial function around extreme values in the range of  $0.15\pi$  of oscillating field half-period. The corresponding key point time lag and AFMO amplitude values were extracted from the fit curves. Demagnetization and magnetization phase lag (normalized to 0–1 range) values were evaluated as:

$$\varphi_{\text{dem}} = 2 \cdot \text{abs}(T_{\min})/\pi, \quad (2)$$

$$\varphi_{\text{mag}} = 2 \cdot (1 - \text{abs}(T_{\max}))/\pi, \quad (3)$$

where  $T_{\min}$  represents the period lag to minimal AFMO signal within the half-period and  $T_{\max}$  represents the period lag to maximal AFMO signal within the half-period as extracted from experimental data. Phase lag data were averaged over at least 5 sampling periods.

As AFMO minima positions correspond to the most disordered state, minimal AFMO voltage was considered zero magnetization level. AFMO minima were used as reference key points for inverting AFMO signal and obtaining hysteresis-like form of AFMO magnetic susceptibility. This hysteresis-like form was further used to extract full AFMO amplitude, AC coercive fields and visualize the positions of the maximum field response.

### 3. Results and discussion

Prior to spectroscopic investigation, the morphology and phase composition of hexaferrite nanoplates was examined with common solid-state methods including XRD, transmission electron microscopy and magnetic measurements (Fig. 1). The plates represent hexaferrite phase  $\text{SrFe}_{11.5}\text{Al}_{0.5}\text{O}_{19}$  having average lateral size of  $50 \pm 20$  nm and the thickness of  $5 \pm 1$  nm. The concentration of particles in the dilute colloid as determined by both gravimetry and magnetometry equals to  $0.3 \pm 0.1$  g/L. Combined centrifugation and magnetic separation concentration processes allows one to increase the dispersed phase concentration to  $30 \pm 5$  g/L. Magnetic properties of ferrofluids were analyzed for both field-frozen (at  $\sim 18$  kOe) concentrated dispersion of nanoplates and liquid ferrofluid. While oriented frozen particles reveal high coercivity of  $\sim 5$  kOe (Fig. 1b), the liquid colloidal solution demonstrates soft magnetic behavior with nearly undetectable coercive force (Fig. 1c). Importantly, conventional magnetometry equipment (especially SQUID) have very long measurement duration, which makes impossible investigations of fast particles dynamics. On contrary fast alternating field magneto-optical response allows to follow reorientation of nanoplates enabling development of alternative powerful and fast approach (Fig. 2).

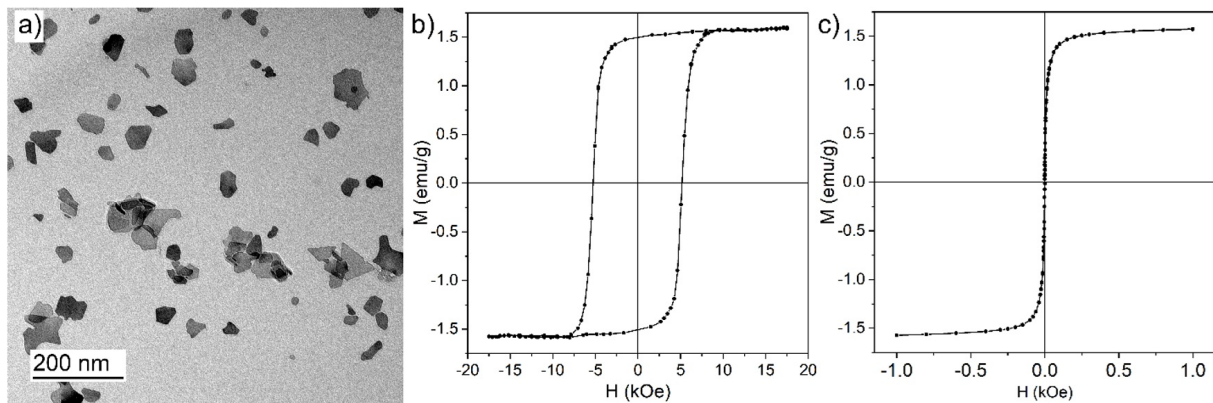


FIG. 1. Transmission electron micrograph of hexaferrite  $50 \times 5$  nm nanoplates (a) and magnetic hysteresis loops for field-frozen dispersion of nanoplates at 77 K (b) and liquid ferrofluid at 298 K (c)

The optical properties of hexaferrite nanoplates dispersions are determined by both the anisotropic scattering and the absorbance of as reported in previous study [18]. Scattering anisotropy effect improves slightly with diminishing the wavelength all over the range of 800–300 nm (Fig. 2b), while absorbance anisotropy has a wide maximum around

700 nm [18]. As a result, the most pronounced optical effect is achieved for the transmission geometry at the low wavelengths. However as hexaferrite is a semiconductor with a band gap of  $\sim 2$  eV with optical absorption increasing strongly below 500 nm, further magneto-optical measurements were conducted at the wavelength of 532 nm.

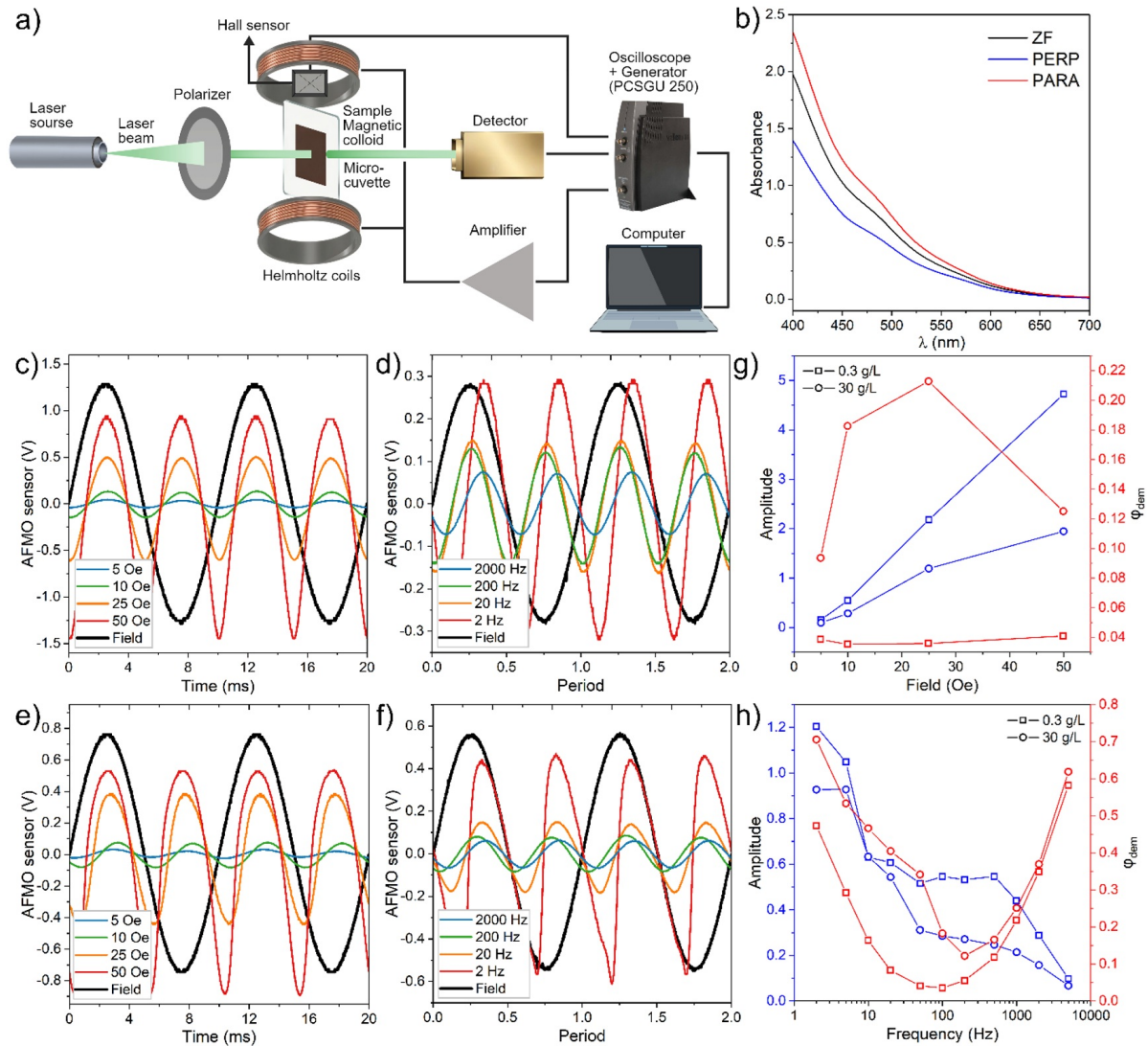


FIG. 2. Optical scheme for evaluation of alternating field magneto-optical (t-AFMO) response (a). Transmission spectra of nanoplate dispersions aligned along and perpendicular to the field direction (b). Example AFMO response for diluted (0.3 g/L, c–d) and concentrated (30 g/L, e–f) hexaferrite nanoplate dispersions depending on field amplitude at 100 Hz (c, e) and frequency at 10 Oe (d, f). Field (g) and frequency (h) amplitude and phase angle dependencies for diluted and concentrated colloid. Note the 200x difference in the optical path for diluted and concentrated dispersions during data acquisition.

The alternating field magneto-optical (AFMO) response was registered with an optical scheme depicted in Fig. 2a in a wide range of frequencies from 2 Hz to 5 kHz and magnetic field amplitudes up to 50 Oe (RMS). As detector voltage is linearly proportional to illumination intensity, AFMO should be considered as transmission-like response with minima, corresponding to the disordered state of dispersion, and maxima, reflecting maximum orientational order in ferrofluid.

Generally, the amplitude of magneto-optical response grows proportionally with AC field amplitude and starts to saturate for concentrated ferrofluid at the fields above 50 Oe (Fig. 2g). AFMO amplitude also generally decreases with increasing excitation field frequency (Fig. 2h). Contrary, both field and frequency effect on phase lag is far from being monotonic (Fig. 2d, f, h). That is addressed to nonlinear variation of a phase angle between the excitation field and magneto-optical response. According to experimental results, the phase angle diminishes at low frequencies but grows at high frequencies with the frequency of excitation field (Fig. 2h). For better understanding of underlying processes complete field-frequency maps for AFMO signal amplitude and phase shifts were assembled for further analysis (Fig. 3).

Importantly, one can notice an asymmetry in AFMO waves at high fields and low frequencies (Fig. 2e,f). Such signal form obviously arises from the difference in the dynamics of magnetization and relaxation processes. According to earlier

study, magnetization is driven by magnetic and Brownian torque (thus strongly dependent on field strength), while the surrounding medium slows down particle rotation with drag forces [18]. On the contrary, demagnetization relies only on Brownian relaxation, being also affected by the medium drag. These processes are described with magnetization and demagnetization relaxation times defined with:

$$\tau_{r,magn} = \frac{3\eta\pi^3 R^3}{2\mu_0\mu H + ok_B T}, \quad (4)$$

$$\tau_{r,demagn} = \frac{3\eta\pi^2 R^3}{k_B T}, \quad (5)$$

where  $\eta$  is media viscosity,  $R$  is the particle radius,  $\mu_0$  is the vacuum magnetic permeability,  $\mu$  is the magnetic moment of the particle,  $H$  is the applied field, coefficient  $o$  depicting orientational distribution (averaged number of available degrees of freedom),  $k_B$  is the Boltzmann constant and  $T$  is the temperature.

According to (4),(5), synchronization of the magnetic field and AFMO signal occurs at equality of field-induced and drag momenta of platelets rotation, while the torque values for magnetization and relaxation processes can appear to be quite different, especially at high fields. Moreover field-driven structural transformations in ferrofluid can also significantly affect relaxation times. Thus, extreme magnetization and demagnetization phase shifts were extracted separately from AFMO data. Maximum AFMO signal was ascribed to a magnetized state and characterized with  $\varphi_{mag}$  magnetization process phase shift term, while  $\varphi_{dem}$  term (minimal AFMO signal) was used for disordered state phase shift characterization.

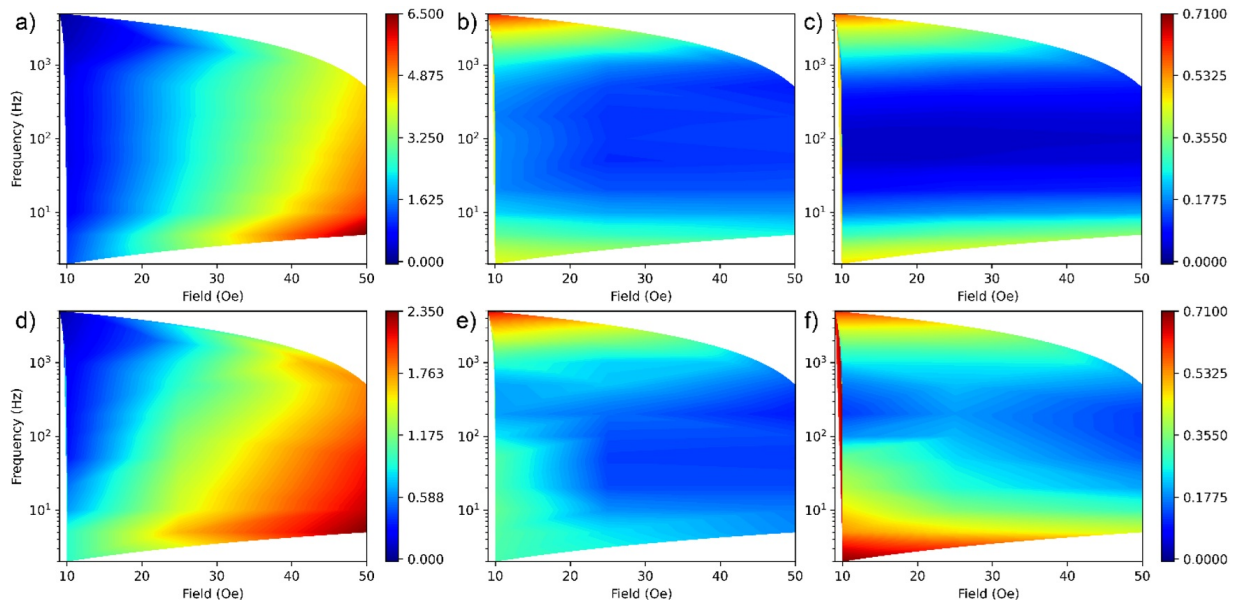


FIG. 3. Transmission AFMO maps for signal amplitude and phases for diluted (0.3 g/L, a–c) and concentrated (30 g/L, d–f) hexaferrite nanoplate dispersions. Due to asymmetry in magnetization and demagnetization processes, the phase maps are provided for AFMO maxima  $\varphi_{mag}$  (corresponding to utmost alignment of nanoplates, b, e) and AFMO minima  $\varphi_{dem}$  (corresponding to the disordered state, c, f)

In high frequency region (above 100 Hz) phase angle comes in agreement with previously reported AC magnetometry data for both diluted and concentrated colloids as magneto-optical response in this case arises from single particle reorientation (Fig. 3b,c,e,f). Fig. 3a, d illustrate decline in AFMO amplitude with frequency and its rise with field intensity as indented by “paramagnetic gas” model. Thus, one can conclude on domination of individual particle response and uncorrelated rotation of platelets in either diluted or concentrated ferrofluids at high frequencies.

Low frequency region demonstrates odd behavior for dilute and concentrated dispersions. The major difference appears in both magnetization and demagnetization phase maps at low field/low frequency region. Obviously, it should be ascribed to the difference in the collective behavior of nanoplates. It is known, that the internal structure of concentrated ferrofluid (30 g/L) contains large thread-like dynamic aggregates [22, 23]. Field-driven assembly and relaxation of these threads should occur at much higher relaxation times, as it requires movement of large volumes in the dispersion. It gives rise to magnetization and relaxation phase lags at low frequencies in concentrated nanoplate dispersions (Fig. 3e,f). Notably, a strong enhancement of  $\varphi_{dem}$  compared to  $\varphi_{mag}$  in concentrated ferrofluid suggests stabilization of its magnetized state. We consider this effect to arise due to internal field provided by the oriented constituent particles. With



disorientation process slowed down by both the internal field and drag forces, one can expect an appearance of remanent magnetization and AC coercive force, rising at lower frequencies due to larger threads formation.

In order to give one common representation for this statement, we have reconstructed hysteresis-like field dependencies of vectorized orientational order of nanoplates from time-resolved AFMO data (Fig. 4). Those can be considered a direct analog to fast magnetic susceptibility measurements.

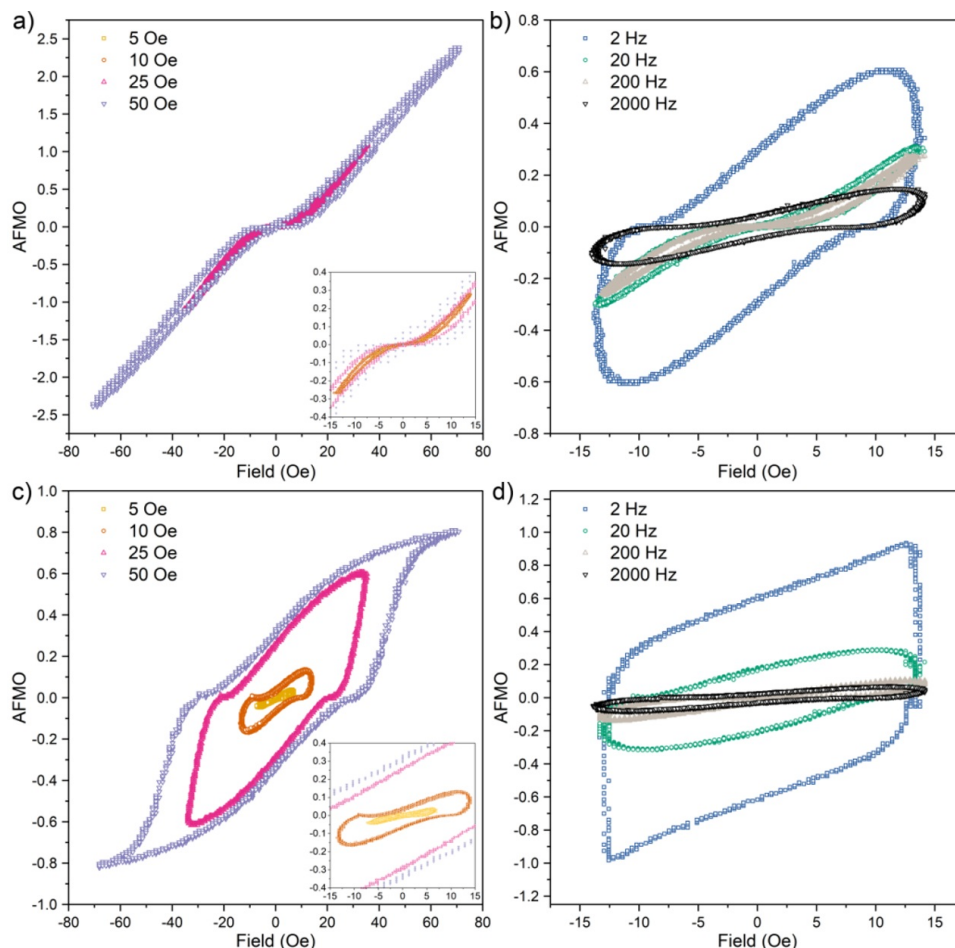


FIG. 4. Sample magnetic hysteresis loops reconstructed with t-AFMO signal for diluted (0.3 g/L, a,b) and concentrated (30 g/L, c,d) hexaferrite nanoplate dispersions depending on AC field amplitude (a, c) and frequency (b, d)

For the diluted colloid at high and intermediate frequency region of  $> 100$  Hz, AFMO magnetization shows closely a linear field dependence without any significant remanence, as expected for freely rotating magnetic particles in the colloid (Fig. 4a). However decreasing field frequency induces hysteresis like response (Fig. 4b). While high frequency irreversibility can be ascribed to particle rotation phase lag due to domination of drag momentum, appearance of hysteresis at low frequency remains of unknown nature. Analysis of concentrated phase AFMO curves can provide necessary insight to unravel reasons for such behavior.

Concentrated magnetic fluid demonstrates strong hysteresis in both field and frequency dependencies (Fig. 4c,d) with maximum detectable value of AC coercive force of about 40 Oe at low frequencies (below 100 Hz). Moreover, this coercivity is proportional to the applied field amplitude with appearance of saturation above 60 Oe. which points out ferromagnetic nature of concentrated colloid. Low frequency hysteresis has a quasi-rectangular shape, indicating very slow relaxation of threads orientational order even at high opposite fields. While such stabilization expected for concentrated liquid due to presence of large dynamic aggregates the same behavior for 0.3 g/L suspensions cannot be addressed using a common “paramagnetic gas” interpretation.

It is known from previous experiments that diluted state is prone to condensation under external field [23]. Formation of dynamic aggregates consisting of several platelets under applied field can lead to significant increase of the drag momentum. Therefore, presence of high coercive force in this case indicates slow assembly of similar to concentrated phase dynamic aggregates, which also can reorient under external magnetic field without thread disruption.

Therefore, the magnetic fluids, consisting of hard magnetic nanoplates combine both the properties of classical magnetic fluids (such as fluidity and ability of particles reorientation) and solid-state magnets (like coercivity and slow relaxation dynamics). Importantly, the typical relaxation times of 0.1 s achieved in concentrated dispersions, strongly exceed Brownian relaxation of  $\sim 0.5$  ms for single particles, revealing the principal possibility of attaining stable magnetization in nanoplate ferrofluids. These specific features make this material highly prospective for the development of new magnetorheological systems including tunable friction pairs and bearings, magnetic lubrication, shielding materials, viscous dampers, triboelectric generators etc.

#### 4. Conclusions

The proposed methodology of alternating field transmission magneto-optical (t-AFMO) measurements have been successfully applied for investigation of fast dynamics of hard magnetic hexaferrite  $50 \times 5$  nm nanoplate dispersions. It provides fast and efficient pathway for investigation of the particles reorientation and field-driven assembly in ferrofluids.

The studies reveal a strong dependence of both AFMO phase shift and amplitude on the external field frequency in concentrated dispersions of nanoplates. The phase shift has non-monotonic dependence on frequency, exposing the peculiarities of magnetic nanoplatelets dynamics. Synchronization of the magnetic field and AC magnetization occurs at equality of field-induced and drag momenta of platelets rotation. At high frequencies, magnetization lags the AC field and the phase lag increases proportionally to the excitation field frequency, revealing an incomplete orientation of platelets after the applied field. Contrary, at low frequencies, the magnetization phase lag increases reciprocally to the excitation field frequency. The effect is addressed to stabilization of platelets orientation with an internal magnetic field, produced by the dispersed particles. This self-stabilizing field leads to an appearance of high AC coercivity in a magnetic fluid, proportional to the applied field amplitude. Described peculiarities of the dynamics in the magnetic fluid, consisting of hard magnetic nanoplates illustrate a pivotal role of interparticle interactions in ferrofluids and their great potential for development of new magnetorheological systems.

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## Paper abstracts in Russian / Аннотации статей

### Полная геометрическая классификация спектральных конфигураций для двухчастичного оператора Шредингера на $\mathbb{Z}$ с взаимодействием ранга три

Лакаев С.Н., Ахмадова М.О., Ахматова Ш.Б.

Мы изучаем семейство решеточных операторов Шредингера  $H_\mu(K)$ , описывающих два одинаковых бозона на одномерной решетке  $\mathbb{Z}$ , где  $K \in \mathbb{T}$  – квазиимпульс. Взаимодействие описывается вектором связи  $\mu = (\mu_1, \mu_2, \mu_3)$ , где  $\mu_1$  действует в начале координат, а  $\mu_2, \mu_3$  в узлах  $|x| = 1, 2$ . В статье мы фокусируемся на нулевом слое квазиимомента  $H_\mu(0)$ , где существенным спектром является отрезок  $[0, 8]$ , в то время как дискретные собственные значения могут быть больше 8 и ниже 0.

Используя определитель Фредгольма, мы выводим точный полином, чье нулевое множество:  $\Gamma^\pm := \{\mu \in \mathbb{R}^3 : C^\pm(\mu) = 0\}$  определяет три критические поверхности в  $\mathbb{R}^3$ . Эти поверхности разбивают пространство параметров на области с постоянным количеством собственных значений и определяют значения параметров, при которых собственные значения входят или выходят из границ 0 и 8.

Основной результат работы – полная геометрическая классификация множества спектральных конфигураций  $\mathcal{S} = (n_-, n_+)$ . Мы показываем, что  $(\mu_2, \mu_3)$ -плоскость разделяется на области  $D_j^\pm$ , которые строго управляют областью значений спектральной функции. Мы доказываем, что параметр  $\mu_3$  действует как глобальный фазовый контроллер: критические значения  $\mu_3 = \pm 2$  разделяют качественно разные спектральные режимы, определяя множество всех возможных конфигураций при общем ограничении на ранг, равный 3.

В заключение мы расширяем результаты на  $K \neq 0$  и демонстрируем, что дискретный спектр сохраняется для всех квазиимоментов при  $|\mu_3| > 2$ .

**Ключевые слова:** двухчастичный решеточный оператор Шредингера, дискретный спектр, возмущение ранга три, детерминант Фредгольма, уравнение Липпмана–Швингера, пороговая асимптотика, критическая поверхность, спектральная классификация.

### О собственных значениях дискретного оператора Шрёдингера на лестнице $d$ -мерной квадратной решётки

Муминов М.И., Садуллаева М.С.

Рассматривается дискретный оператор Шрёдингера  $H$  на лестнице  $d$ -мерных квадратных решёток с самосопряжённым матричнозначным потенциалом, элементами которого являются скаляры  $\lambda$  и  $\mu$ . Исследуются условия существования собственных значений и описывается их точное расположение в зависимости от параметров  $\lambda$  и  $\mu$  для случаев  $d = 1$  и  $d = 2$ .

**Ключевые слова:** дискретный оператор Шрёдингера, собственные значения, дискретный спектр.

### Двухфазная модель наночастицы типа «ядро–оболочка»

Рехвиашвили С.

Предложена двухфазная модель плавления наночастицы типа «ядро–оболочка», в которой твердое ядро окружено квазжидкой оболочкой. Модель позволяет получить самосогласованные аналитические выражения для температуры плавления и эффективного поверхностного натя-

жения, зависящих от размера наночастицы, а также кинетические уравнения, описывающие временную эволюцию сокращающегося при нагреве твердого ядра. Анализ выявляет различные режимы плавления, в том числе выраженное ускорение на заключительной стадии, обусловленное понижением температуры плавления вследствие кривизны поверхности. Численные оценки для наночастиц серебра и меди показывают, что размерные эффекты способны существенно сократить время плавления. Полученные результаты дают простые и физически наглядные соотношения, позволяющие лучше понять процесс плавления на наноуровне, дают простую интерпретацию длины Толмена и объясняют перегрев, часто наблюдаемый при моделировании методом молекулярной динамики.

**Ключевые слова:** наночастицы, двухфазная модель, кинетика плавления, термодинамическое равновесие, поверхностные эффекты, размерные зависимости, фазовый переход.

## **Структура, механические и фильтрационные свойства графиновых соединений автоинтеркалированного типа**

Грешняков В.А., Павлик В.В.

Выполнено исследование группы гибридных углеродных соединений на основе графиновых слоев с автоинтеркалированным типом кристаллической решетки в рамках *ab initio* расчетов. Установлено, что упорядоченную кристаллическую структуру могут иметь соединения только на основе  $\alpha$ -графина-1 и  $\beta$ 1-графина-2. Расчеты показали, что наиболее устойчивой фазой  $\alpha$ -типа является тетрагональный ( $I/4mcm$ ) автоинтеркалированный  $\alpha$ -графин-1 с плотностью  $1.28 \text{ г/см}^3$ , объемным модулем 31 ГПа, модулем Юнга от 3 до 107 ГПа, который характеризуется минимальной отрицательной линейной сжимаемостью  $-11.7 \text{ ТПа}^{-1}$  вдоль оси [001], из-за чего материалы на его основе могут найти широкое практическое применение при создании датчиков давления. Кроме того,  $I/4mcm$  фаза может быть использована в качестве селективного фильтра для молекул водорода, пропускную способность которой можно увеличивать при одноосном сжатии или растяжении перпендикулярно кристаллографической оси [001]. Изученные наноструктурированные фазы можно однозначно идентифицировать по рассчитанным порошковым рентгенограммам.

**Ключевые слова:** наноструктурированные материалы, графин, механические характеристики, фильтрационные свойства, порошковые рентгенограммы, первопринципные расчеты.

## **Теоретическое исследование влияния изменения вязкости, моментного напряжения и скорости скольжения на пленочную смазку пористых конических подшипников**

Кашинат Бирадар, Адинатха С. Упадхья

В данном исследовании изучается влияние изменения вязкости и скольжения скорости на характеристики пористых конических подшипников, смазываемых жидкостью с учетом моментных напряжений. Закон Дарси используется для описания течения жидкости через пористую среду, а теория моментных напряжений Стокса учитывает микроструктуру смазки. Разработано модифицированное уравнение Рейнольдса с учетом изменения вязкости и эффектов скольжения. Численные результаты иллюстрируют влияние моментных напряжений, скорости скольжения, проницаемости и изменения вязкости на распределение давления, несущую способность и время сжатой пленки. Наблюдается, что увеличение параметра моментных напряжений повышает давление и несущую способность, в то время как более высокая проницаемость, как правило,

снижает несущую способность подшипника. Наличие скольжения на границе изменяет поведение потока и способствует улучшению характеристик смазки. Совместное воздействие пористой структуры и скольжения приводит к улучшению общих характеристик, а использование жидкостей с учетом моментных напряжений значительно повышает эффективность смазки и эксплуатационную надежность.

**Ключевые слова:** жидкость с учетом парных напряжений, изменение вязкости, проскальзывание скорости, пористый конический подшипник.

## **Влияние геометрии шероховатости и температуры на адсорбцию потока аргона в наноканалах: подход молекулярной динамики**

Арман Салехи, Самранд Раш-Ахмади

Наноканалы имеют шероховатость поверхности из-за своей неидеальной формы. Эта шероховатость на поверхности наноканалов оказывает важное влияние на поведение потока атомов аргона. В данном исследовании с помощью моделирования методом молекулярной динамики изучался поток аргона в наноканалах при различных геометрических параметрах шероховатости. Кроме того, исследователи исследовали скорость адсорбции, плотность и диффузию атомов аргона при различных температурах и высоте шероховатости в наноканалах. Результаты показали, что наноканалы с цилиндрической шероховатостью демонстрируют более высокие уровни энергии взаимодействия (адсорбции) ( $-149$  ккал/моль) и плотности ( $144$  г/см<sup>3</sup>) по сравнению с наноканалами с квадратной и конической шероховатостью. Более того, с увеличением высоты шероховатости наноканалов (от  $11$  до  $20$  Å) количество адсорбции (энергия взаимодействия) и плотность также возрастают. Сравнивая диаграмму среднеквадратичного смещения (MSD) наноканалов, можно заметить, что наноканалы с наибольшей диффузией атомов аргона имеют коническую шероховатость в отличие от квадратных и цилиндрических наноканалов.

**Ключевые слова:** адсорбция, коэффициент диффузии, геометрия шероховатости, аргон, наноканалы.

## **О корректности сведения трёхмерной модели планарного сцепления Фурнье-Галатолы к двумерной модели для полимерно-дисперсных нематических жидких кристаллов**

Чимытов Т.

Аналитически и численно исследована корректность прямого сведения трехмерной модели планарного сцепления Фурнье-Галатолы к двумерным нематическим системам. Для сравнения предложена альтернативная двумерная формулировка, основанная на непосредственном задании целевого поверхностного  $Q$ -тензора. Аналитические расчеты показывают, что редуцированный функционал Фурнье-Галатолы приводит к кубическому восстанавливающему моменту на полюсах эллиптической капли, тогда как модель с непосредственным заданием целевого тензора сохраняет линейный отклик вдоль всей границы. Влияние этого различия на релаксацию ориентационной структуры исследовано с использованием модели Ландау-де Жена для мезоскопических эллиптических капель нематика 5ЦБ. Показано, что редуцированная модель Фурнье-Галатолы приводит к повышенной подвижности буджумов, изменяет конечную ориентацию биполярной структуры при умеренных значениях отношения полуосей и систематически предсказывает более низкие равновесные значения свободной энергии. Полученные результаты свидетельствуют о том, что непосредственное проекционное сведение может приводить к каче-

ственно различным сценариям релаксации в двумерных моделях нематиков.

**Ключевые слова:** биполярная структура, планарное сцепление,  $Q$ -тензор, буджумы, мезоскопические нематические капли.

## Диффузия углерода в $\alpha$ -Ti и $\alpha_2$ -Ti<sub>3</sub>Al

Горев Н.Д., Бакулин А.В., Кулькова С.Е.

Методом проекционных присоединенных волн рассчитаны энергии образования дефектов внедрения углерода в различных междоузлиях, заселенности кристаллических орбиталей Гамильтона, функция локализации электронов, объемы Вороного и другие характеристики  $\alpha$ -Ti и  $\alpha_2$ -Ti<sub>3</sub>Al. Для оценки барьеров миграции вдоль путей между стабильными позициями внедрения использовался метод подталкивающих упругих связей с восходящим изображением. Температурно-зависимые коэффициенты диффузии углерода были оценены вдоль двух неэквивалентных кристаллографических направлений ( $a$  и  $c$ ) в  $\alpha$ -Ti и, впервые, в  $\alpha_2$ -Ti<sub>3</sub>Al. Энергетически предпочтительной позицией как в  $\alpha$ -Ti, так и в  $\alpha_2$ -Ti<sub>3</sub>Al является октаэдрическая, локальное окружение которой содержит только атомы Ti. Эта предпочтительность зависит от материала и в первую очередь обусловлена низким механическим вкладом в энергию образования дефектов в  $\alpha$ -Ti и химическим вкладом в случае сплава. Присутствие Al приводит к увеличению энергии образования дефектов в сплаве. В случае  $\alpha$ -Ti полученные коэффициенты диффузии хорошо согласуются с экспериментом. Присутствие алюминия в сплаве приводит к замедлению диффузии углерода из-за более высоких энергий как образования дефектов, так и миграции.

**Ключевые слова:** титан, алюминид титана, диффузия углерода, первопринципные расчеты.

## Адиабатические условия для нестационарной оптической фазовой модуляции: невырожденный случай

Гайдаш А.А., Мемех Э.Е., Мирошниченко Г.П., Козубов А.В.

В данной работе исследуется нестационарный процесс фазовой модуляции, характеризующийся зависящим от времени коэффициентом взаимодействия, ограниченный невырожденным случаем. Мы выводим точное неадиабатическое решение зависящего от времени уравнения Шрёдингера. Затем мы устанавливаем критерий, при котором адиабатические соображения становятся справедливыми, а именно, условие, позволяющее стационарному решению аппроксимировать нестационарную задачу. Наши результаты справедливы для произвольного числа взаимодействующих мод и произвольного числа фотонов.

**Ключевые слова:** фазовая модуляция, нестационарная динамика, квантовая оптика, алгебры Ли.

## Энтропия для двух слабо связанных квантовых волноводов: асимптотический подход

Трифанова Е. С., Юрова Т.С., Блинова И.В., Попов И.Ю.

Рассматривается электрон в системе из двух плоских квантовых волноводов, связанных через малое окно. Используется метод согласования асимптотических разложений решения краевой задачи. Описывается зависимость энтропии от ширины окна для случая малого окна в рамках

асимптотического подхода.

**Ключевые слова:** квантовые волноводы, энтропия, асимптотика.

## Магнитожидкостный бифункциональный электрокатализатор CoFeNi-MF/NF для высокоэффективного расщепления воды в щелочной среде

Хошимов Ф., Бутанов Х., Маматкулов Ш., Рузимурадов О.

Разработка эффективных бифункциональных электрокатализаторов имеет ключевое значение для масштабируемого производства водорода методом полного расщепления воды. В данной работе катализатор CoFeNi-MF/NF, модифицированный магнитной жидкостью, был синтезирован двухстадийным гидротермальным методом путем интеграции магнитной жидкости на основе  $\text{Fe}_3\text{O}_4$  в вертикально ориентированные наноллисты CoFeNi, выращенные на никелевой пене. Структурный анализ подтвердил формирование сплава CoFeNi с гранецентрированной кубической решеткой (FCC) в сочетании со шпинельной фазой  $\text{Fe}_3\text{O}_4$ , образующих взаимосвязанную архитектуру с большим количеством активных центров. Введение магнитной жидкости способствовало улучшению переноса заряда, увеличению содержания кислорода, а также усилению электронной и спиновой поляризации, что обеспечило ускоренную кинетику электрокаталитических реакций. В растворе 1,0 М КОН катализатор CoFeNi-MF/NF продемонстрировал низкие перенапряжения 169 мВ для реакции выделения водорода (HER) и 199 мВ для реакции выделения кислорода (OER) при плотности тока  $10 \text{ mA} \cdot \text{cm}^{-2}$ . Значения наклонов Тафеля составили 133,09 и  $91,41 \text{ mV} \cdot \text{dec}^{-1}$  соответственно. Кроме того, катализатор характеризовался низким сопротивлением переносу заряда и увеличенной электрохимически активной площадью поверхности. Испытания на стабильность при плотности тока  $100 \text{ mA} \cdot \text{cm}^{-2}$  в течение 24 часов подтвердили его высокую долговечность. Полученные результаты демонстрируют перспективность предложенного подхода для создания магниточувствительных бездрагоценных электрокатализаторов, предназначенных для эффективного щелочного электролиза воды.

**Ключевые слова:** бифункциональный электрокатализатор, щелочное расщепление воды, выделение водорода (HER), выделение кислорода (OER), магнитная жидкость, CoFeNi, электролиз воды.

## Роль электронной структуры оксидного кластера ванадия на окисление метанола

Пичугина Д.А., Романовская Ю.А., Бандурист П.С.

Для объяснения каталитической активности нейтральных оксидных кластеров ванадия в окислении метанола ( $\text{CH}_3\text{OH}$ ) проведено квантово-химическое моделирование адсорбции метанола на кластере  $\text{V}_4\text{O}_{10}$  и его дальнейшее окисление до формальдегида ( $\text{CH}_2\text{O}$ ) методом функционала плотности и функционалом PBE. Согласно проведенным расчетам, кластер имеет тетраэдрическую «клеточную» структуру с четырьмя терминальными  $\text{V}=\text{O}(\text{t})$  и шестью мостиковыми  $\text{V}-\text{O}(\text{b})-\text{V}$  фрагментами. Реакция метанола и  $\text{V}_4\text{O}_{10}$  проходит по сложному механизму, включающему последовательные стадии ассоциации и дегидрирования. Показана различная роль в процессе двух кислородов  $\text{O}(\text{t})$  и  $\text{O}(\text{b})$ . Анализ атомных зарядов и электронной плотности в  $\text{V}_4\text{O}_{10}$  позволил нам объяснить полученные закономерности и предсказать снижение активационного барьера лимитирующей стадии образования  $(\text{CH}_2\text{O})\text{V}_4\text{O}_{10}\text{H}_2$  при наличии положительного заряда на кластере  $\text{V}_4\text{O}_{10}$  или при введении в структуру кластера титана.

**Ключевые слова:** оксидные кластеры переходных металлов, окисление метанола,  $\text{V}_2\text{O}_5$ , меха-

низм, радикал кислорода, энергия активации, переходное состояние.

### **Магнитооптический отклик дисперсий магнитотвердых нанопластин в переменном поле**

Елисеев А.А., Цзытянь Ся, Лукашин А.В., Казин П.Е., Елисеев А.А

В настоящей работе представлен анализ магнитооптического отклика переменного поля для концентрированных дисперсий магнитотвердых нанопластин. Динамика наночастиц гексаферрита с размерами  $50 \times 5$  нм в магнитных жидкостях с концентрацией 0,3–30 г/л отслеживалась по амплитуде и фазовому сдвигу магнитооптического отклика в диапазоне частот 1 Гц – 10 кГц и магнитных полях амплитудой до 50 Э. Магнитооптический сигнал использовался для реконструкции зависимости мгновенной намагниченности от приложенного поля в зависимости от концентрации нанопластинок. Были выявлены два режима переориентации наночастиц в зависимости от частоты и амплитуды приложенного переменного поля. Высокочастотный режим характеризуется фазовым сдвигом процесса намагничивания, который увеличивается с частотой возбуждающего поля и соответствует неполной ориентации пластинок в результате последнего. Напротив, в низкочастотном режиме сдвиг фазы увеличивается обратно пропорционально частоте возбуждающего поля, что позволяет выявить наличие «коэрцитивной силы переменного поля». Последний эффект связан со стабилизацией ориентации пластинок магнитными моментами составляющих феррожидкость наночастиц.

**Ключевые слова:** Гексаферрит, феррожидкость, магнитооптика, динамика намагничивания.



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