

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

Liyu Hou^{1,a}, Hongliang Li^{1,b}

¹Department of Mineral Processing Engineering, College of Mining Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China

^a3314869283@qq.com, ^blihongliang222@126.com

Corresponding author: Liyu Hou, 3314869283@qq.com

PACS 68.03.Cd, 68.43.Mn

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

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

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

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

1. Introduction

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

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

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

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

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

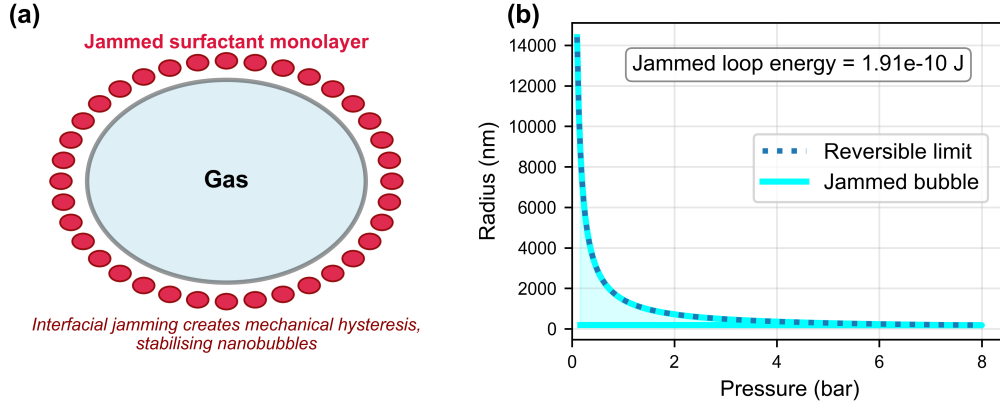


FIG. 1. (a) Schematic of a free nanobubble surrounded by a jammed surfactant monolayer. The central hypothesis is that interfacial jamming creates mechanical hysteresis and stabilises the bubble. (b) Jamming hysteresis signature. The blue dotted line is the reversible clean-water limit ($R = 2\gamma_0/P$).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

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

2. Model and computational methods

2.1. Adsorption isotherm and surface equation of state

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

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

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

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

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

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

2.2. Jamming criterion and elastic shell constitutive law

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

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

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

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

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

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

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

2.3. Mechanical equilibrium

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

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

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

2.4. Kinetic equation for the mean coverage

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

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

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

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

2.5. Hysteresis energy

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

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

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

2.6. Parameter space and computational campaigns

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

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

TABLE 2. Summary of key quantitative findings

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

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

2.7. Limitations

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

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

3. Results and discussion

3.1. Jamming phase diagram

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

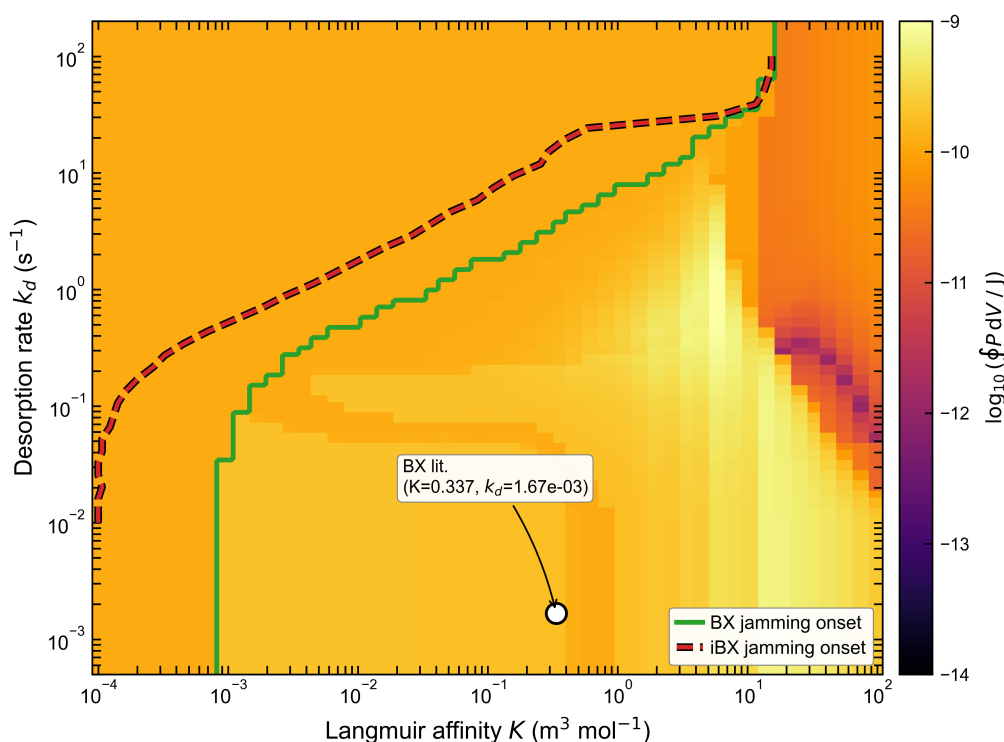


FIG. 2. Jamming phase diagram. Colour map: $\log_{10}$ hysteresis energy, ranging from -14 (dark, unjammed) to -9 (bright, strongly jammed). Solid green line: BX jamming onset. Dashed crimson line: iBX jamming onset. White circle: literature BX point ($K = 0.337 \text{ m}^3 \text{ mol}^{-1}$, $k_d =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

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

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

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

3.2. Hysteresis loops and coverage evolution

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

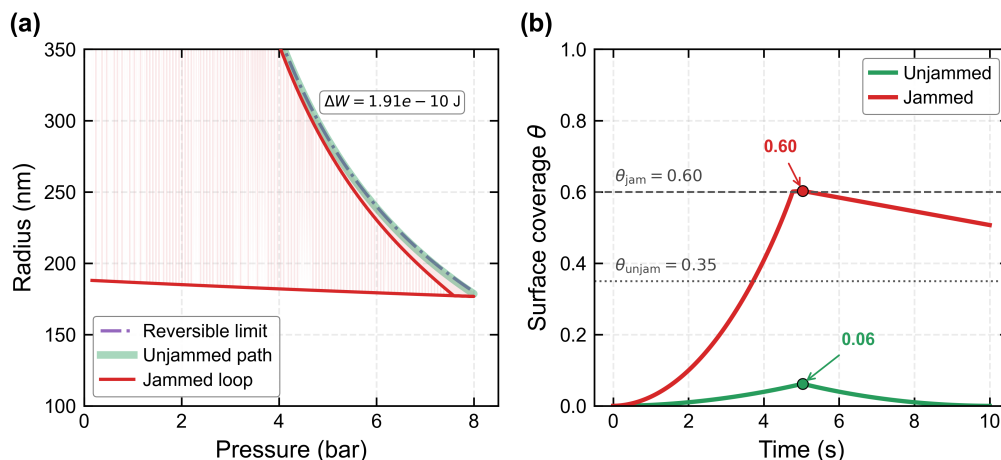


FIG. 3. (a) Pressure-radius hysteresis loops. Purple dash-dot: reversible clean-water limit. Semi-transparent green: unjammed trajectory ($K = 1.0 \cdot 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, $k_d = 1.0 \cdot 10^{-2} \text{ s}^{-1}$). Solid crimson: jammed trajectory ($K = 0.337 \text{ m}^3 \text{ mol}^{-1}$,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

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

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

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

3.3. Monte-Carlo uncertainty propagation

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

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

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

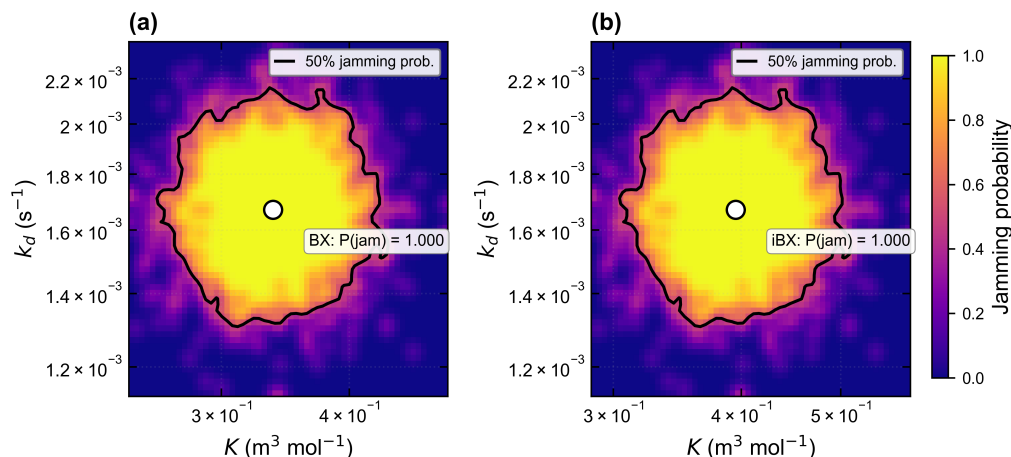


FIG. 4. Monte-Carlo jamming-probability clouds for (a) BX and (b) iBX. Colour map: jamming probability from 5000 samples. Black contour: 50 % probability. White circle: literature point; annotation reports the probability at that location

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

3.4. Critical collector dosage

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

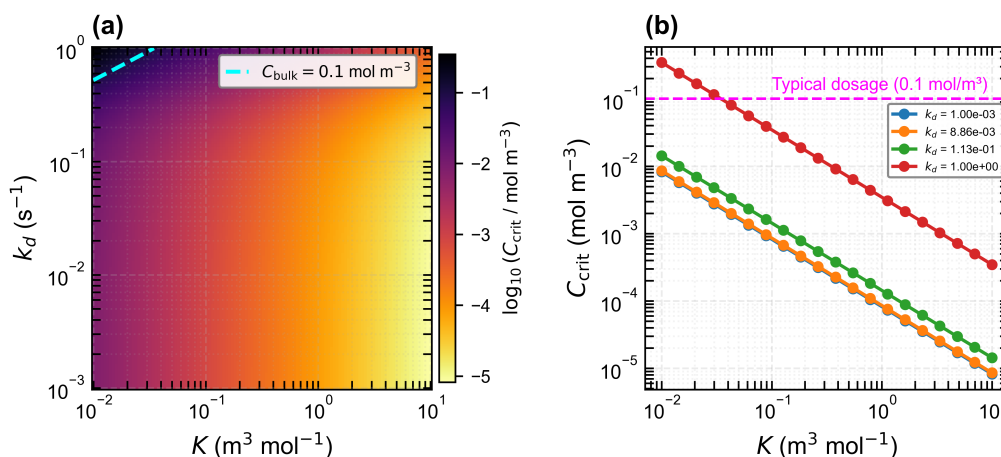


FIG. 5. (a) Critical bulk concentration C_{crit} required for jamming. Colour map: $\log_{10}(C_{\text{crit}}/\text{mol m}^{-3})$; cyan dashed contour marks the typical flotation dosage of 0.1 mol m^{-3} . The colour scale saturates at both ends of the true C_{crit} range. (b) Cross-sections at four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

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

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

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

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

3.5. Sensitivity to process parameters

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

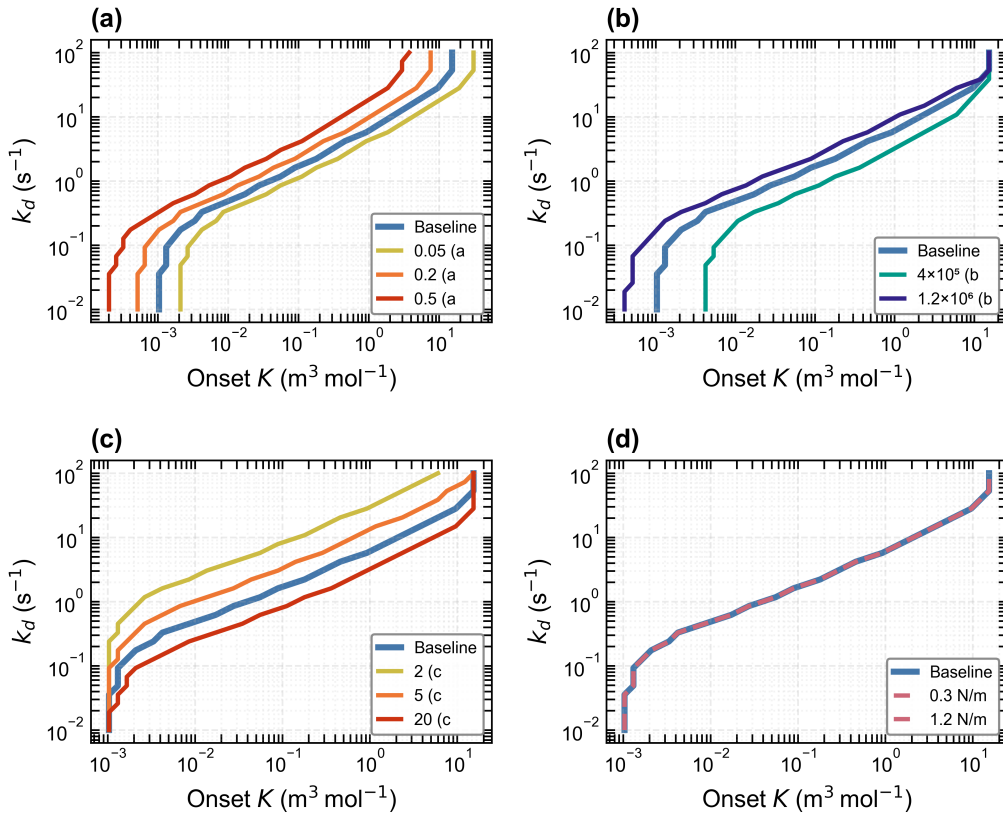


FIG. 6. Sensitivity of the jamming boundary to variations in (a) bulk concentration C_{bulk} , (b) maximum pressure P_{max} , (c) cycle time T_{cycle} , and (d) shell modulus E_s . In all panels, the blue solid line is the baseline boundary. Legend entries: (a) $C_{\text{bulk}} = 0.05, 0.2, 0.5 \text{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

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

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

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

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

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

3.6. Numerical convergence

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

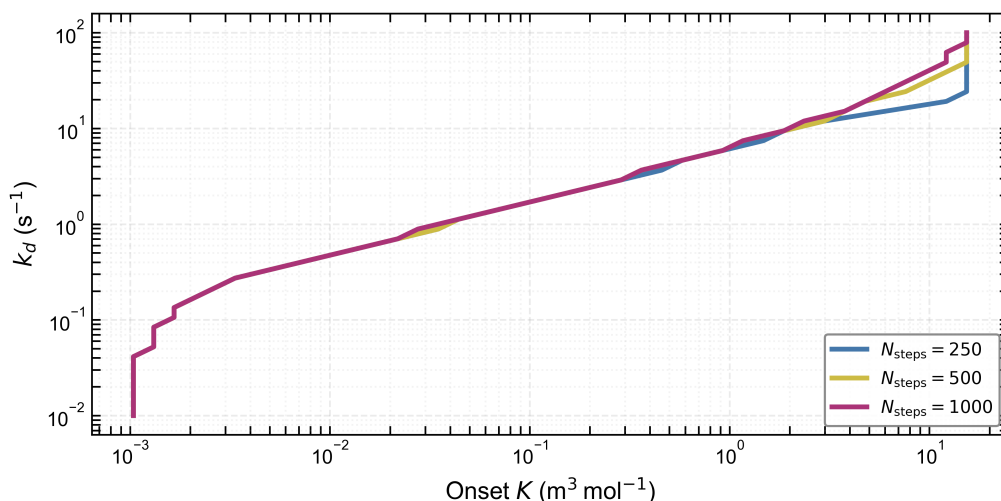


FIG. 7. Convergence of the jamming boundary with time-step refinement. Boundaries computed with $N_{\text{steps}} = 250$ (soft blue), 500 (ochre), and 1000 (magenta) are virtually indistinguishable across the entire parameter range, confirming grid-independence

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

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

3.7. Dynamical sensitivity along the jamming boundary

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

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

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

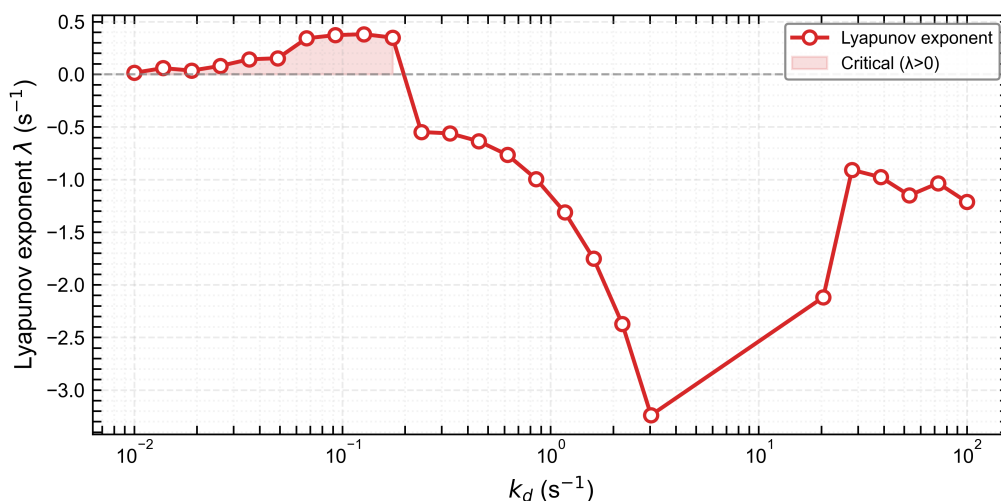


FIG. 8. One-cycle divergence analysis along the jamming boundary. Crimson line with white circles: one-cycle divergence exponent Λ . Light crimson shading: region of positive Λ (critical sensitivity). Grey dashed line: $\Lambda = 0$. The exponent peaks at $+0.42 \text{ s}^{-1}$ near $k_d \approx 0.17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

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

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

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

4. Conclusion

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

References

- [1] Lohse D., Zhang X. Surface nanobubbles and nanodroplets. *Reviews of Modern Physics*, 2015, **87**, P. 981–1035.
- [2] Qian J., Craig V.S.J., Jeon S. Long-term stability of surface nanobubbles in undersaturated aqueous solution. *Langmuir*, 2019, **35**, P. 718–728.
- [3] Cotrina-Teatino M.A., Jairo J.C., et al. Nanobubbles and the flotation process in mineral recovery: a bibliometric and systematic literature analysis covering the period 2005–2024. *Minerals Engineering*, 2025, **227**, P. 109310.
- [4] Chen Q., Liu Y., Edwards M.A., White H.S. Single-entity electrochemistry of nano- and microbubbles in electrolytic gas evolution. *Journal of Physical Chemistry Letters*, 2022, **13**, P. 6153–6163.
- [5] Harinder, Singh G., Kaur H., et al. A critical review on the properties and applications of bulk micro and nanobubbles for the degradation of organic pollutants in wastewater treatment. *Science of the Total Environment*, 2025, **976**, P. 179310.
- [6] Seza A., Mozahheb Yousefi K., Minaeian S. Engineering ultrasound contrast agents for targeted therapeutics: a theranostic approach to drug delivery, gene therapy, and immunomodulation. *Advanced NanoBiomed Research*, 2026, **6**, P. 2500176.
- [7] Lohse D., Zhang X. Pinning and gas oversaturation imply stable single surface nanobubbles. *Physical Review E*, 2015, **91**, P. 031003.

- [8] Sullivan P., Mifsud J., Borg M.K., Gibelli L., Dockar D. Ionic adsorption on bulk nanobubble interfaces and its uncertain role in diffusive stability. *Journal of Colloid and Interface Science*, 2025, **695**, P. 137747.
- [9] Eklund F., Swenson J. Stable air nanobubbles in water: the importance of organic contaminants. *Langmuir*, 2018, **34**, P. 11003–11009.
- [10] Zhang H., Chen S., Guo Z., Zhang X. The fate of bulk nanobubbles under gas dissolution. *Physical Chemistry Chemical Physics*, 2022, **24**, P. 9608–9617.
- [11] O'Hern C.S., Silbert L.E., Liu A.J., Nagel S.R. Jamming at zero temperature and zero applied stress. *Physical Review E*, 2003, **68**, P. 011306.
- [12] Lee S., Kim S., Char K. Controlling the roughness of Langmuir–Blodgett monolayers. *Journal of Physical Chemistry B*, 2017, **121**, P. 5078–5085.
- [13] Abkarian M., Subramaniam A.B., Kim S.H., Larsen R.J., Yang S.M., Stone H.A. Dissolution arrest and stability of particle-covered bubbles. *Physical Review Letters*, 2007, **99**, P. 188301.
- [14] Han G., et al. An insight into flotation chemistry of pyrite with isomeric xanthates: A combined experimental and computational study. *Minerals*, 2018, **8**(4), P. 166.
- [15] Amankeldi F.B., Ospanova Z.B., Musabekov K.B., Miller R. History of thermodynamic models for the adsorption of surfactants at liquid interfaces. *Eurasian Chemico-Technological Journal*, 2024, **26**, P. 89–96.
- [16] Butt H.J., Graf K., Kappl M. *Physics and Chemistry of Interfaces*, 4th edn. Wiley-VCH, Weinheim, 2023.
- [17] Wentworth-Nice P., Ridout S.A., Jenike B., Liloia A., Graves A.L. Structured randomness: jamming of soft discs and pins. *Soft Matter*, 2020, **16**, P. 5305–5313.
- [18] Barter J.D. Surface strain modulation of insoluble surface-film properties. *Physics of Fluids*, 1994, **6**, P. 2606–2616.
- [19] Goldman S. Generalizations of the Young–Laplace equation for the pressure of a mechanically stable gas bubble in a soft elastic material. *Journal of Chemical Physics*, 2009, **131**, P. 184502.
- [20] Press W.H., Teukolsky S.A., Vetterling W.T., Flannery B.P. *Numerical Recipes: the Art of Scientific Computing*, 3rd edn. Cambridge University Press, Cambridge, 2007.
- [21] Ghadiali S.N., Halpern D., Gaver D.P. A dual-reciprocity boundary element method for evaluating bulk convective transport of surfactant in free-surface flows. *Journal of Computational Physics*, 2001, **171**, P. 534–559.
- [22] Dormand J.R., Prince P.J. High order embedded Runge–Kutta formulae. *Journal of Computational and Applied Mathematics*, 1981, **7**, P. 67–75.
- [23] Atkins P., de Paula J. *Atkins' Physical Chemistry*, 10th edn. Oxford University Press, Oxford, 2014.
- [24] Beland L.K., Richard P. Yielding and plasticity in amorphous solids. *Nature Reviews Physics*, 2025, **7**, P. 313–330.

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

Information about the authors:

Liyu Hou – Department of Mineral Processing Engineering, College of Mining Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China; ORCID 0009-0000-3735-0440; 3314869283@qq.com

Hongliang Li – Department of Mineral Processing Engineering, College of Mining Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China; ORCID 0000-0002-4496-5846; lihongliang222@126.com

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