

Line pinning effect reshapes nucleation at surface edges: A generalized theory for nanopore activation

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Heterogeneous nucleation at surface edges is pervasive across nature and industry, yet the role of line pinning effect, arising from asymmetric capillary interactions at geometric singularities, remains poorly understood. Herein, we develop a generalized nucleation theory that explicitly incorporates edge pinning energy, thereby extending classical frameworks to account for nanoscale confinement and interfacial asymmetry. Through analytical treatment of droplet formation within geometrically defined nanopores, we derive a closed-form expression for the line pinning energy as a function of Laplace pressure, pore geometry, and wettability. This formulation reveals that line pinning effect can significantly reshape the nucleation energy landscape, introducing nontrivial dependencies on contact angle and pore morphology. Our results uncover a tunable, geometry-mediated mechanism for controlling nucleation barriers, offering predictive insight into phase transitions in confined environments and suggesting strategies for design in applications ranging from nanofluidics to crystallization control.

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I. INTRODUCTION

Nucleation, the emergence of a new daughter phase from a metastable parent phase [1,2], is fundamental to countless natural and technological processes, including cloud and ice formation [3–5], amyloid fibril aggregation in Alzheimer's disease [6], pharmaceutical crystallization [7], and nanofabrication [8]. For over a century, classical nucleation theory and its heterogeneous extension have provided the foundational framework for describing nucleation in bulk and at idealized surfaces [9–14]. However, these models rely on oversimplified assumptions of smooth, regular geometries and neglect nanoscale features such as edges, crevices, and confinement, which are ubiquitous in real systems. In particular, the existence of line pinning effect, line tension, and curvature-dependent surface tension [15] further complicates the problem, and the role of line pinning effect and line tension in wetting and nucleation remains poorly understood [15–20].

Despite extensive efforts to infer line tension values from contact angle measurements [21], particle detachment [22],

and nucleation rate analyses [23,24], its magnitude and even sign remain controversial [25–28]. Line tension plays a significant role at the nanoscale, influencing wetting [29], nucleation [30,31], boiling [32], and drying [33] in confined geometries. Nanopores, in particular, exhibit a variety of confinement-induced phenomena. For instance, vapor nucleation within nanopores governs biological gating and ion transport [34–36]. Capillary condensation, freezing transition, and intrusion-extrusion processes in confined pore geometries are strongly influenced by molecular layering [37], electrostatic interactions [38], network connectivity [39], and contact angle hysteresis [39], all of which can modulate nucleation pathways beyond classical expectations. The long-term stability of surface nanobubbles has been linked to line tension and contact line pinning [40–43], which is tunable through surface structures [44–46]. However, despite progress in modeling nucleation on geometric defects [47–49] or chemical heterogeneities [50], a unified quantitative description of how sharp edges govern the nucleation energy landscape via pinning is absent. Current models typically incorporate line tension or line pinning energy as a phenomenological parameter [18,51,52], decoupled from the actual geometry constraints and thereby limiting predictive power.

In this work, we address this gap by developing a unified, quantitative framework for heterogeneous nucleation that explicitly couples line pinning energy to geometric confinement and contact line pinning. Our approach utilizes line pinning energy to capture the additional energetic penalty associated with edge-induced pinning. Derived from first principles, this

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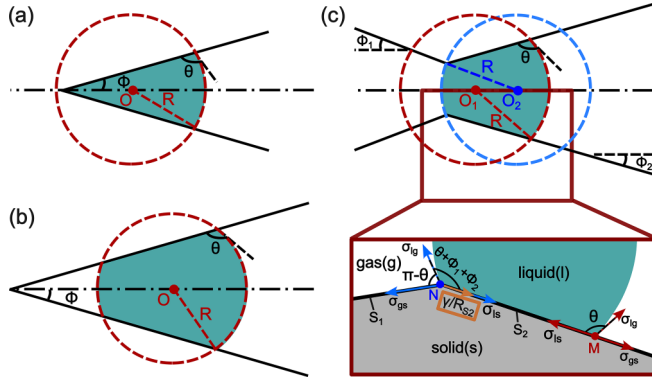


FIG. 1. Schematic cross-sectional view of critical nuclei (green, with radius R) forming within pore structures with given pore opening angles 2ϕ (or $2\phi_1$ and $2\phi_2$) and contact angles θ . Panels (a) and (b) illustrate classical scenarios in smooth conical pores. Panel (c) depicts a generalized asymmetric pore geometry, where a critical droplet bridges the neck between two sides with distinct opening angles (left: $2\phi_1$; right: $2\phi_2$). Red and blue dashed circles, centered at O_1 and O_2 , represent fitted curvature profiles on the right and left interfaces, respectively. The lower part of panel (c) is a close-up of on the three-phase contact region, showing a force balance sketch at the triple contact line. The points M and N denote the triple-phase contact locations, while S_1 and S_2 represent the inner pore surfaces. The surface edge at point N gives rise to a line pinning energy γ , and R_{S2} is the curvature radius of the contact line at N projected on surface S_2 .

effective parameter unifies disparate observations across geometries and quantitatively predicts nucleation barriers under a single thermodynamic framework.

II. THEORETICAL MODEL

Focusing on droplet formation in pore structures with defined geometries (see Appendix C for motivation on the geometry selection), we derive an analytical expression for the line pinning energy in terms of the Laplace pressure, geometric parameters, and wettability. To capture how line pinning energy emerges and reshapes the nucleation process in pore structures, we consider a quasiequilibrium liquid droplet nucleating inside a pore with geometrically defined edges, e.g., conical or asymmetric constrictions as seen in Fig. 1. The Gibbs free energy change related to the nucleation formation is

$$\Delta G = \Delta F_H - V \Delta p, \quad (1)$$

where ΔF_H is the variation in the Helmholtz free energy due to the formation of a cluster, which is formulated as

$$\Delta F_H = \sigma_{lg} A_{lg} + (\sigma_{ls} - \sigma_{gs}) A_{ls} + \gamma l, \quad (2)$$

where σ_{lg} , σ_{ls} , and σ_{gs} are interfacial tensions between liquid-gas, liquid-substrate, and gas-substrate, respectively. The parameters A_{lg} and A_{ls} denote liquid-gas and liquid-substrate interfacial areas, respectively. In the last term, γ is the line pinning energy and l stands for the length of the triple contact line along the surface edge. Here, “line pinning energy” is induced by an effective geometric energy correction ΔE_{geo} arising from the coupling between Laplace pressure and

edge-induced confinement. It is noteworthy that contributions from the contact line on smooth surfaces, where line tension can arise from intermolecular or long-range forces [53], have been neglected. We define $\gamma = \Delta E_{\text{geo}}/l$ to capture this scenario-dependent effect, offering insight into the potential ambiguity in experimental determination of line tension.

The second term on the right-hand side of Eq. (1) is the volumetric free energy, in which Δp is the pressure difference between the droplet and the surrounding supersaturated vapor. Its value is closely related to the supersaturation S by

$$\Delta p = \frac{k_B T \ln S}{v_m}, \quad (3)$$

with k_B , T , and v_m denoting the Boltzmann constant, temperature, and the molar volume, which are kept unchanged.

A nucleus will grow once the critical free energy barrier is overcome. The critical parameters for heterogeneous nucleation can be determined by minimizing the Gibbs free energy change. Thus, the critical nucleus corresponds to the condition $\partial \Delta G / \partial R = 0$, i.e.,

$$\left. \frac{\partial \Delta F_H}{\partial R} \right|_{R=R_c} - \Delta p \left. \frac{\partial V}{\partial R} \right|_{R=R_c} = 0, \quad (4)$$

where the critical nucleus radius R_c satisfies the Young-Laplace equation $\Delta p = 2\sigma_{lg}/R_c$. Throughout this work, we assume a constant liquid-gas surface tension σ_{lg} , so that the critical nucleus radius R_c depends solely on the pressure difference Δp or, equivalently, on the supersaturation S . Under the further assumption of constant supersaturation, R_c is treated as a fixed value. On the macroscopic scale, the line tension effect can often be neglected, and wetting is characterized by Young’s “macroscopic” contact angle θ , which is related to the interfacial tensions through Young’s equation $\cos \theta = (\sigma_{gs} - \sigma_{ls})/\sigma_{lg}$. At the nanoscale, however, line tension leads to a modified “microscopic” equilibrium contact angle, characterized by the Boruvka-Neumann equation [54]. It is also reported that, without contact line pinning, these two equilibrium contact angles are independent of the general external field exerted on the droplet [55].

Figures 1(a) and 1(b) illustrate classical scenarios of critical nucleus formation in smooth conical pores, in the absence of surface-edge pinning effects. Specifically, panel (a) corresponds to the case where the pore is completely filled by the droplet, while panel (b) depicts a droplet forming as a spherical cap, intersecting only a portion of the pore interior. These classical configurations, partially explored in previous works [14,56], and detailed in the Appendix A, serve as baselines for comparison with our generalized model.

In contrast to classical approaches, we explicitly resolve the geometry and force balance at the three-phase junction on the surface edge for a more generalized pore geometry as shown in Fig. 1(c). In particular, we focus on pores with asymmetric opening angles, where sharp surface edges introduce geometric singularities that give rise to an additional capillary force that we interpret as line-pinning-related force, accounting for the deviation of the apparent contact angle from the Young’s contact angle on the droplet covered inner pore surface [denoted as S_2 in Fig. 1(c)] near the edge N . We assume that the droplet shows an apparent contact angle of $\theta + \phi_1 + \phi_2$ on surface S_2 , whereas it forms an apparent angle

of θ on surface S_1 . At position M , far from the edge, Young's equation applies and the local contact angle remains θ .

Through detailed geometrical analysis, we derive expressions for the droplet volume $V = V(\theta, \phi_1, \phi_2, R)$ and the interfacial areas A_{lg} and A_{ls} , as functions of the contact angle, geometric parameters, and droplet radius. By combining these expressions with Eqs. (2) and (4), we obtain a closed-form expression for a dimensionless line pinning energy, defined as $\gamma_* = \gamma/(\sigma_{lg}R_c)$, linking the critical radius of the nucleating droplet, the contact angle, and the local pore geometry,

$$\gamma_* = \frac{\gamma}{\sigma_{lg}R_c} = -\frac{\cos(\theta + \phi_1)}{\sin \phi_2} [\cos(\theta + \phi_1 + \phi_2) - \cos \theta]. \quad (5)$$

(See the Appendix B for a full derivation and experimental validation in the limit of the classical wetting model with pinning.) This equation shares the same form as the classical modified Young's equation considering the line tension effect. The physical interpretation is that the line-pinning-induced

capillary force accounts for the deviation of the apparent contact angle $\theta + \phi_1 + \phi_2$ on surface S_2 from the intrinsic Young's angle θ . The prefactor $-\frac{R_c \cos(\theta + \phi_1)}{\sin \phi_2}$ corresponds exactly to the radius of curvature of the contact line at N projected onto surface S_2 , denoted as R_{s2} in Fig. 1(c). The above geometric and force balance analysis reveals that the line pinning energy is not an intrinsic material constant, but a geometry-dependent quantity.

Building upon this theoretical framework of edge-pinned line energy, we introduce a geometric parameter $f(\theta, \phi_1, \phi_2)$ to characterize the ratio of the critical energy barrier in heterogeneous nucleation to that of the homogeneous nucleation, i.e.,

$$f(\theta, \phi_1, \phi_2) = \frac{\Delta G_c}{\Delta G_{\text{hom},c}} = \sum_{i=1}^3 f_i(\theta, \phi_1, \phi_2), \quad (6)$$

where $\Delta G_{\text{hom},c}$ and f_i are

$$\begin{aligned} \Delta G_{\text{hom},c} &= \frac{4}{3} \pi R_c^2 \sigma, \\ f_1 &= \frac{3 \cos^2 \theta_1}{2 \sin \phi_2} [\cos(\theta + \phi_1 + \phi_2) - \cos \theta], \\ f_2 &= \frac{3}{4} \left[4 - 2 \sin \theta_1 - 2 \sin \theta_2 - \frac{\cos \theta}{\sin \phi_2} (\cos^2 \theta_2 - \cos^2 \theta_1) \right], \\ f_3 &= -\frac{1}{2} \left[\sum_{i=1}^2 (2 + \sin \theta_i)(1 - \sin \theta_i)^2 + \frac{\cos^3 \theta_2 - \cos^3 \theta_1}{\tan \phi_2} \right], \end{aligned}$$

where $\theta_i := \pi - \theta - \phi_i$ ($i = 1, 2$). The geometric parameters f_1 , f_2 , and f_3 are contributions from the contact line, surface, and bulk energy terms, respectively. The factor f retains explicit dependence on contact angle θ and pore geometry (ϕ_1, ϕ_2) , allowing us to assess quantitative influence of these factors on the nucleation behavior.

III. RESULTS AND DISCUSSION

Remarkably, we find the line pinning effect significantly alters nucleation, with the energy barrier highly tunable via pore asymmetry and wettability. Figure 2(a) illustrates the geometric parameter f as a function of the contact angle for different opening angles of the pore. We first plot the predictions from the classical theory for critical droplets in conical pores with different opening angles, as indicated by dot-dashed lines. These results serve as a point of reference to highlight the significance of the energy barrier change we derive for the pores with edges. For comparison, we present predictions from our model incorporating line pinning effects at the surface edge (referred to as the LP model), shown as solid lines. In this case, we consider asymmetric pores with a fixed left opening angle $2\phi_1 = 0$ and varying right opening angles $2\phi_2$. Additional results for $\phi_1 = -20^\circ, 60^\circ$, and 90° are provided in the Appendix C. Our LP model predicts a pronounced suppression of the nucleation barrier compared to the

classical model, especially at moderate wettability, namely, from $\theta = 90^\circ$ to $\theta = \theta_i$, where θ_i denotes the intersection point between the solid and dot-dashed lines. The shaded region quantifies the suppression of nucleation attributable to line pinning effect, which classical theory neglects. In contrast, under strongly hydrophobic conditions with $\theta > \theta_i$, the nucleation barrier in asymmetric pores exceeds that of conical pores. The inset schematically illustrate a nucleated droplet within an asymmetric pore geometry characterized by $\phi_1 = 0$ and an adjustable ϕ_2 .

Figure 2(b) shows the geometric factor f_1 (solid lines) and the dimensionless line pinning energy factor γ_* (dot-dashed lines) as functions of the contact angle, both predicted by the LP model. It indicates that surface-edge pinning becomes profound at moderate contact angles within the range $\theta \in (90^\circ, \theta_c)$, where the threshold angle $\theta_c = 180^\circ - 0.5\phi_2$. Within this regime, the line pinning energy contributes a net negative energy. A striking finding is the nonmonotonic behavior of the line pinning energy factor and the associated geometric factor f_1 with contact angle. Local minima in f_1 are observed within $\theta \in (90^\circ, \theta_c)$ and these minima correspond to the largest deviations between LP models and the classical models.

Figure 2(c) shows that the sum of geometric parameters from the volume and surface energy contribution $f_2 + f_3$ monotonically increases with contact angle. Since the

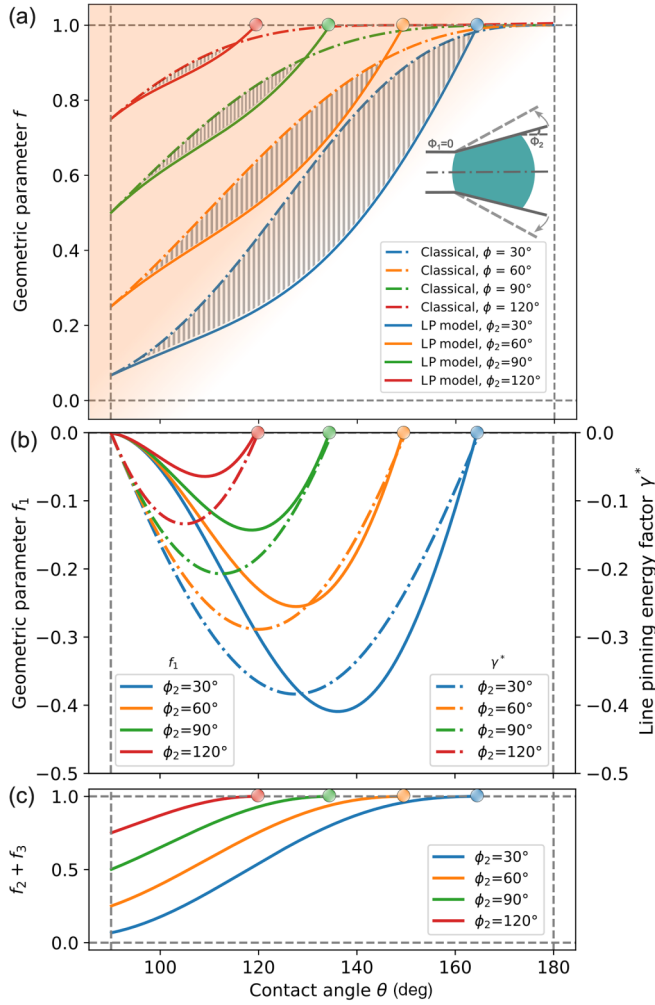


FIG. 2. Geometrical parameters of critical nuclei as a function of contact angles θ for a fixed left opening angle $2\phi_1 = 0$ and varying right opening angles $2\phi_2$. (a) Comparison between predictions from the LP model and classical models for droplets in conical pores without pinning. Shaded regions indicate deviations arising from the inclusion of line pinning energy. The inset illustrates the pore geometry and the nucleated droplet configuration. Panels (b) and (c) show the variations of geometrical parameters from line energy and surface energy contributions, respectively, with respect to θ . Panel (b) also includes the corresponding dimensionless line pinning energy γ_* as a reference. Colored dots in panels (a)–(c) highlight the conditions where homogeneous nucleation occurs, representing the upper limit of θ for which the LP model remains valid.

contribution from line pinning energy is relatively smaller, f still monotonically increases with contact angle, but the increase rate is different from that of $f_2 + f_3$. It should be noted that the contact angle range $\theta \in (90^\circ, \theta_c)$ is divided into two intervals, i.e., (1) $\theta \in (90^\circ, \theta_i)$ and (2) $\theta \in (\theta_i, \theta_c)$. In the first interval [shaded areas in Fig. 2(a)], the negative line energy leads to the lower nucleation barrier for asymmetric pores, while in the second interval, the pinning effect changes the droplet profile, leading to the increase of the sum $f_2 + f_3$, which dominates over the line pinning effect, so that the nucleation barrier for asymmetric pores becomes higher than that of the conical pores.

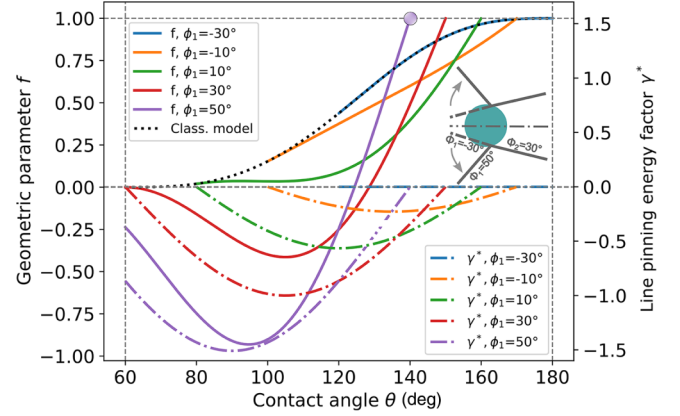


FIG. 3. Geometrical parameter and line pinning energy factor of critical nuclei as functions of the contact angle θ for fixed $\phi_2 = 30^\circ$ and varying ϕ_1 . The inset depicts the critical nucleus configuration within the pore structure, matching the violet dot. Prediction from classical model for droplets in smooth conical pores with $\phi = 30^\circ$ is indicated as black dotted line for comparison.

When $\theta = \theta_c$, the droplet becomes suspended, symmetrically positioned between S_1 and S_2 , and the pinning effect vanishes. In this configuration, the spherical droplet exhibits identical contact angles with both the left and right pore walls (or S_1 and S_2). This geometrically induced upper limit for the contact angle ($\theta_c = 180^\circ - 0.5\phi_2$) represents a critical threshold for heterogeneous nucleation, as indicated by the colored circles in Figs. 2(a)–2(c). This limit is absent in classical frameworks for conical pores and establishes a fundamental constraint on nucleation or phase transition in nanoconfinement. This critical state corresponds to a spherical droplet undergoing homogeneous nucleation ($f = 1$), with the upper limit angle $\theta_c = 180^\circ - 0.5\phi_2$ matching our prior theoretical predictions for capillary adsorption in funnel-like structures [57]. For $\theta > \theta_c$, the droplet detaches from the right wall and remains spherical, yielding constantly a homogeneous nucleation barrier with $f = 1$.

As ϕ_2 decreases, the line pinning energy contribution becomes more profound, facilitating nucleation over a broader range of contact angles. This trend is evident from the enlarged shaded regions in Fig. 2(a) as ϕ_2 decreases from 120° to 30° . Specifically, when $\phi_2 > 120^\circ$ (i.e., the pore takes on a thornlike geometry), the shaded area is expected to largely decrease due to the reduced contribution of line energy and the lowering of θ_c . In this case, the critical nucleus droplet shows a spherical shape over a wider range of contact angles ($\theta > \theta_c = 180^\circ - 0.5\phi_2$), consistent with the classical Cassie-Baxter model. This model predicts that nano/microstructures can induce superhydrophobicity by minimizing droplet-substrate contact, even at low intrinsic contact angles [58].

To further explore the effect of pore asymmetry, we fix ϕ_2 and vary ϕ_1 to examine a broader range of pore geometries. Figure 3 illustrates how the geometric parameter f and the line pinning energy factor γ_* evolve with θ for increasing ϕ_1 under fixed values of $\phi_2 = 30^\circ$. Further results corresponding to $\phi_2 = 60^\circ$ and 90° can be found in the Appendix C. The valid contact angle range for the LP model is defined as $(\theta_0, \theta_c]$,

where $\theta_0 = \max\{90^\circ - \phi_1, 90^\circ - \phi_2\}$ (see Appendix B for an explanation). As presented in Fig. 3, when $\phi_1 = -30^\circ$, the pore shows a conical geometry; thus, the LP model prediction aligns with that of the classical model with $\phi = 30^\circ$, particularly in the highly hydrophobic regime. This agreement arises because the LP model assumes equal curvature radii on both sides of the droplet. In this special case, the LP model recovers the classical solution corresponding to the case shown in Fig. 1(b), rather than Fig. 1(a). As ϕ_1 increases to $\phi_1 = -10^\circ$ and 10° , the geometric factor f continues to increase with θ , though at different rates depending on the specific left-side angle $2\phi_1$. A further increase to $\phi_1 = 30^\circ$ and 50° introduces a nonmonotonic trend in the f - θ relationship, attributed to the enhanced influence of line pinning. The occurrence of negative values of f in certain θ ranges reflects the dominance of line pinning in driving nucleation under those geometric configurations.

Similar to Fig. 2, there is an upper limit contact angle $\theta_c = 180^\circ - 0.5(\phi_1 + \phi_2)$ for the LP model, marking the transition to homogeneous nucleation ($f = 1$ and $f_1 = 0$). This critical state is indicated by the violet circle in Fig. 3 for $\phi_1 = 50^\circ$. It is also found that both θ_i and θ_c decrease with increasing ϕ_1 . The contact angle range is divided into (1) $\theta \in (\theta_0, \theta_i)$, where line pinning reduces the nucleation barrier, and (2) $\theta \in (\theta_i, \theta_c)$, where the nucleation barrier increases relative to classical predictions. Both asymmetric and conical pores enhance nucleation compared to the homogeneous case, reaffirming that homogeneous nucleation represents the upper limit of the nucleation barrier [59]. Overall, the LP model enables the construction of a comprehensive energy landscape for nucleation in diverse pore geometries by freely adjusting ϕ_1 and ϕ_2 , highlighting the model's broad applicability to realistic nano/microstructured systems.

The above detailed investigation reveals one nontrivial feature. For a given pore geometry, the line pinning energy term becomes especially significant when a particular contact angle is achieved. For example, with $\phi_1 = 0^\circ$ and $\phi_2 = 30^\circ$ (see Fig. 2), the line pinning energy factor reaches a minimum $\gamma_{\min}^* \approx -0.4$ at $\theta = 125^\circ$. Assuming a critical radius of water nucleus $R_c = 50$ nm [60] and a surface tension $\sigma_{lg} = 0.07$ N/m, Eq. (5) yields a line pinning energy of approximately -1.4×10^{-9} N, an order of magnitude larger than previously reported line tension values of 10^{-11} to 10^{-10} N for water droplets on the flat quartz considering intermolecular forces [61]. By tuning R_c , pore geometry, and wettability, the line pinning energy can even vary by orders of magnitude, helping to explain the wide variability in the literature [62] and deviations from classical predictions in nanoscale systems, including nanobubble stability [33,63], pore size and shape dependence of nucleation rate [60,64–66], ice nucleation shifts [67], and wettability-dependent evaporation in nanopores [68].

IV. CONCLUSIONS

To conclude, we extend classical nucleation theory to explicitly incorporate line pinning energy arising from surface-edge pinning, uncovering a confinement-dominated regime of nucleation. It not only provides a quantitative, unified, and extendable expression for the edge-pinned line energy, but

also exposes how geometry and wetting jointly govern nucleation thresholds. These insights offer a physically grounded tool for understanding and controlling nucleation in confined systems with broad applications in areas such as targeted drug delivery, pharmaceutical crystallization, and nanofabrication. The proposed model is testable via restrained molecular dynamics simulations [47–49] and high-precision nucleation experiments. The present framework is a continuum, free-energy-based model intended to capture the leading geometric and interfacial contributions to nucleation barrier reshaping, rather than a full molecular description of all nanoscale fluctuation physics. Looking forward, this framework can be generalized to incorporate fluctuations [69,70], instabilities [71], active wetting [72], and even two-step nucleation [73], laying the foundation for a unified theory of phase transitions [74] and nanobubbles [41] under nanoscale confinement, where geometrical edge effects are essential.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [75].

APPENDIX A: CLASSICAL MODELS FOR CRITICAL NUCLEI IN SMOOTH CONICAL PORES

We begin by outlining classical nucleation theory applied to conical confinement without considering contact line pinning effects. In this framework, the critical nucleus is constrained by the conical geometry and governed solely by macroscopic parameters such as the contact angle θ and the cone opening angle 2ϕ . Figure 4(a) illustrates the dependence of the dimensionless free energy barrier, normalized by the barrier for homogeneous nucleation (or the geometric parameter $f(\theta, \phi) = \Delta G_c / \Delta G_{\text{hom},c}$), on the contact angle for various conical opening angles 2ϕ . As the contact angle increases, the shape and position of the critical nucleus transition between two regimes, depicted in Figs. 4(b) and 4(c). In regime 1, shown by solid lines in panel (a), the nucleus spans the full width and depth of the pore, effectively wetting both walls. In regime 2, shown as dotted lines in panel (a), the nucleus adopts a partial-sphere shape, intersecting only part of the pore interior.

In the full-filling regime [panel (b), solid lines in panel (a), labeled with model 1], the nucleus wets both conical walls, and its shape is determined by geometrical constraints and wettability. The geometric parameter can be expressed

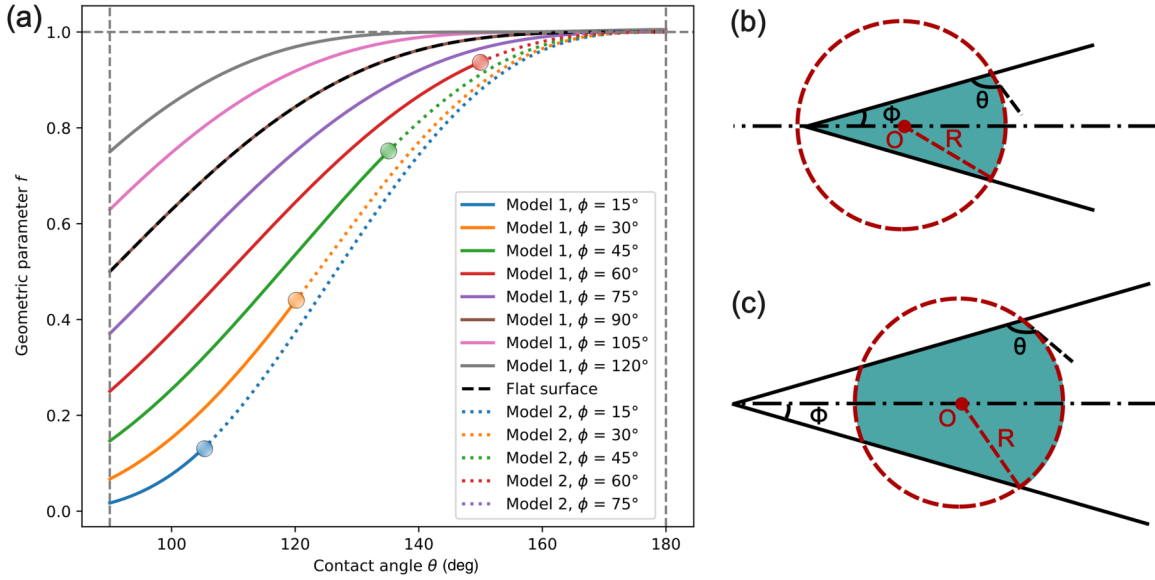


FIG. 4. (a) Geometrical parameters of critical nuclei via classical models as a function of contact angles θ for varying half opening angles ϕ . (b) and (c) Schematic cross-sectional view of critical nuclei (green, with critical radius R) forming within symmetric conical pores with given pore opening angles 2ϕ and contact angles θ . Solid lines show the cases for panel (b) where the whole pore is fully filled, while dotted lines represent the cases for panel (c) where the droplet is part of a sphere. The colored circles show the boundary between the two scenarios [panels (b) and (c)]. The special case for droplets on a flat surface with $\phi = 90^\circ$ is indicated as black dashed line for comparison.

analytically as

$$f = \frac{1}{4}[2 - 3 \sin(\theta + \phi) + \sin^3(\theta + \phi) - \cos^3(\theta + \phi) \cot \phi], \quad \theta < 90^\circ + \phi. \quad (\text{A1})$$

This expression captures the combined influence of intrinsic wettability and pore geometry. As a reference, the classical case of nucleation on a flat surface ($\phi = 90^\circ$) is shown as a dashed line in panel (a), corresponding to the well-known expression [60] for the geometric factor $f = \frac{1}{4}(2 - 3 \cos \theta + \cos^3 \theta)$, which is consistent with the general form above.

In the partial-filling regime [panel (c), dotted lines in panel (a), labeled with model 2], the nucleus adopts a partial-sphere shape and the geometric parameter takes the form

$$f = 1 - \sin^3 \theta \cos \phi, \quad \text{for } \theta > 90^\circ + \phi \text{ and } \phi < 90^\circ. \quad (\text{A2})$$

These expressions, partially derived in prior works [14,56] and adapted here, enable quantitative predictions of nucleation thresholds in smooth conical geometries. The colored circles ($\theta = 90^\circ + \phi$) in panel (a) mark the boundary between these two regimes. This classical treatment serves as a baseline for comparison with our generalized model, i.e., LP model, where edge pinning effects are explicitly incorporated.

APPENDIX B: DERIVATION OF THE LP MODEL

This Appendix presents a detailed formulation of the LP model that accounts for the geometric asymmetry and contact line pinning in confined nucleation. In contrast to classical models assuming smooth and conical geometries, we consider pores with left and right opening angles forming a neck, a configuration frequently observed in natural and synthetic sys-

tems, as illustrated in Figs. 5(a)–5(d). Examples include the shell structures of Foraminifera and transmembrane protein pores MspA and ClyA, where pore geometry plays a critical role in mediating mass transport and phase behavior, partially motivating our specific geometry choices (see more detailed discussion of pore geometry in the following).

The protein nanopore examples shown in Fig. 5 are intended only to illustrate the broader class of confined geometries with nanoscale constrictions. We do not suggest that the droplet-in-constriction scenario considered here directly applies to all biological nanopore systems, which typically operate in aqueous environments. Rather, the intended connection is that geometric constrictions and associated interfacial energetic penalties may also affect activation processes in such confined settings, including bubble nucleation or liquid-vapor fluctuations in hydrophobic nanopores [34]. The present framework should therefore be viewed as a continuum, geometry-based description whose direct applicability to specific biological nanopores requires further system-specific validation.

Figure 5(e) illustrates the geometric setup of a droplet nucleated within an asymmetric pore, which is a cross-sectional view. The pore comprises two conical sections with different opening angles: $2\phi_1$ on the left and $2\phi_2$ on the right. The droplet spans across the conical surfaces, forming two spherical caps of radius R centered at O_1 and O_2 . The three-phase contact lines occur at points M_1, M_2 (right) and N_1, N_2 (left), with θ denoting the intrinsic Young's contact angle.

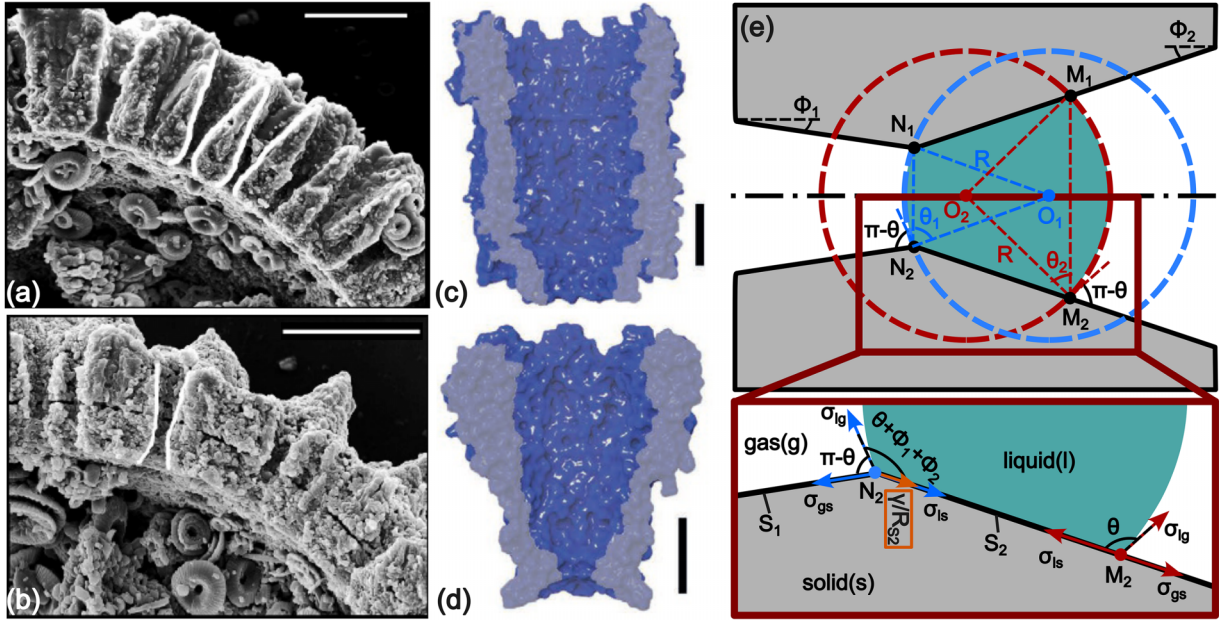


FIG. 5. Pore structures and force balance analysis for a droplet within an asymmetric pore. (a) and (b) The pores in cross section of the external shell of “Foraminifera.” [76]. Scale bar: 20 μm . (c) and (d) X-ray structures of protein pores MspA and ClyA, which span the lipid bilayer to achieve certain functions [77]. Scale bar: 3 nm. (e) Geometry of a generalized pore structure (opening angles on right: $2\varphi_1$; on left: $2\varphi_2$) with an equilibrated droplet (green color) sitting within. The blue and red dashed circles with radii R centered on O_1 and O_2 fit the left and right interfaces, respectively. The M_1, M_2, N_1 , and N_2 are contact points of the three phases, and θ represents the Young’s contact angle. The bottom panel, highlighted by the red frame, shows a close-up of the image and sketch of force balance at the contact line. S_1 and S_2 are inner surfaces of the pore. R_{S2} denotes curvature radius of the contact line at N_2 on the surface S_2 . The angles $\theta_1 := \pi - \theta - \varphi_1$ and $\theta_2 := \pi - \theta - \varphi_2$.

We assume that the droplet shows an apparent contact angle of $\theta + \varphi_1 + \varphi_2$ with surface S_2 , whereas the droplet contacts the surface S_1 with an apparent angle of θ . The contact line at the position M_1M_2 is far away from the surface edge; thus, the Young’s equation is valid, showing an apparent contact angle of θ .

The volume conservation of the droplet leads to

$$V = V_1 + V_2 + V_3, \quad (\text{B1})$$

where V_1, V_2 , and V_3 are the volumes of the geometries formed by rotating the segment M_1M_2 confined by the arch and chord M_1M_2 corresponding to $\angle M_1O_2M_2$, the segment N_1N_2 confined by the arch and chord N_1N_2 corresponding to $\angle N_1O_1N_2$, and the trapezoid $M_1M_2N_1N_2$ along the dot dashed center line, respectively. Defining the angles $\theta_1 := \pi - \theta - \varphi_1$ and $\theta_2 := \pi - \theta - \varphi_2$, V_1, V_2 , and V_3 can be expressed as

$$\begin{aligned} V_1 &= (\pi R^3/3)(2 + \sin \theta_1)(1 - \sin \theta_1)^2, \\ V_2 &= (\pi R^3/3)(2 + \sin \theta_2)(1 - \sin \theta_2)^2, \\ V_3 &= (\pi R^3/3)(\cos^3 \theta_2 - \cos^3 \theta_1)/\tan \varphi_2. \end{aligned} \quad (\text{B2})$$

The above volumes correspond to the surface areas of liquid-gas interface on the right and left sides A_1 and A_2 , and the liquid-solid contact area A_3 , which are formulated as

$$\begin{aligned} A_1 &= 2\pi R^2(1 - \sin \theta_1), \\ A_2 &= 2\pi R^2(1 - \sin \theta_2), \\ A_3 &= \pi R^2(\cos^2 \theta_2 - \cos^2 \theta_1)/\sin \varphi_2. \end{aligned} \quad (\text{B3})$$

Substituting the expressions for V_1, V_2 , and V_3 into Eq. (B1) gives the volume of a nucleus $V = V(R, \varphi_1, \varphi_2, \theta)$ as a function of the droplet size, pore geometry, and wettability. The Gibbs free energy change related to the nucleation formation is

$$\Delta G = \Delta F_H - V \Delta p, \quad (\text{B4})$$

where ΔF_H is the variation in the Helmholtz free energy due to the formation of a cluster, which is formulated as

$$\Delta F_H = \sigma_{lg}A_{lg} + (\sigma_{ls} - \sigma_{gs})A_{ls} + \gamma l, \quad (\text{B5})$$

where σ_{lg} , σ_{ls} , and σ_{gs} are interfacial tensions between liquid-gas, liquid-substrate, and gas-substrate, respectively. The parameters $A_{lg} = A_1 + A_2$ and $A_{ls} = A_3$ denote liquid-gas and liquid-substrate interfacial areas, respectively. In the last term of Eq. (B5), γ is the line pinning energy induced by pinning effect and $l = 2\pi R \cos \theta_1$ stands for the length of the triple contact line along the neck of the pore.

The second term on the right-hand side of Eq. (B4) is the volumetric free energy, in which Δp is the pressure difference between the droplet and the surrounding supersaturated vapor. Its value is a function of the supersaturation S ,

$$\Delta p = \frac{k_B T \ln S}{v_m}, \quad (\text{B6})$$

with the constants k_B , T , and v_m denoting the Boltzmann constant, temperature, and the molar volume. The critical parameter of heterogeneous nucleation can be obtained by extremizing the Gibbs free energy change. The critical nuclei

therefore correspond to $\partial \Delta G / \partial R = 0$, i.e.,

$$\left. \frac{\partial \Delta F_H}{\partial R} \right|_{R=R_c} - \Delta p \left. \frac{\partial V}{\partial R} \right|_{R=R_c} = 0, \quad (\text{B7})$$

where the critical nuclei radius R_c meets with the Young-Laplace equation $\Delta p = 2\sigma/R_c$. Substituting Eqs. (B1) and (B5) into the above equation gives

$$\frac{\gamma}{\sigma R_c} = -\frac{\cos(\theta + \phi_1)}{\sin \phi_2} [\cos(\theta + \phi_1 + \phi_2) - \cos \theta]. \quad (\text{B8})$$

This equation shares the same form as the modified Young's equation considering the line tension effect.

Specifically, when $\phi_1 = -\phi_2$, the surface edge vanishes, transforming the asymmetric pore into a conical one. In this configuration, the line pinning disappears, recovering the classical models illustrated in Fig. 4. Moreover, when $\theta = \pi/2 - \phi_1$, the prefactor on the right-hand side of Eq. (B8) becomes zero, which correspond to the situation where the critical nucleus becomes infinitely large (i.e., $R_c = \infty$, liquid-gas interface is flat). In this limit, the effect of line pinning is negligible. This analysis reveals that when $\theta < \pi/2 - \phi_1$ or $\theta < \pi/2 - \phi_2$, there is no stable equilibrium state with the droplet pinned at the pore neck. In such hydrophilic cases, the droplet forms a liquid bridge that spans the pore, with the neck positioned between two distinct contact lines on the left and right surfaces. This special scenario involves droplets with negative curvature, which is beyond the scope of the current study. In this work, we focus on the regime where $\theta > \theta_0$ with $\theta_0 = \max\{90^\circ - \phi_1, 90^\circ - \phi_2\}$. In this range, the nucleus is pinned at the neck of the pore and maintains a constant curvature radius R_c .

When the two chords M_1M_2 and N_1N_2 coincide (see Fig. 5) and we set $\phi_2 = \pi/2$ and $\phi_1 = -\pi/2 + \epsilon$, where ϵ follows a certain random distribution (e.g., a Gaussian distribution for a statistically homogeneous rough surface), the original double-conical pore degenerates into a flat surface whose local orientation varies irregularly along the droplet's contact line. In this limit, Eq. (B8) reduces to

$$\gamma_* = \frac{\gamma}{\sigma R_c} = -\sin(\theta + \epsilon) [\cos(\theta + \epsilon) - \cos \theta], \quad (\text{B9})$$

which recovers the classical modified Young's equation incorporating the line tension effect on a flat surface. Here, $\theta + \epsilon$ denotes the apparent contact angle, i.e., $\theta_{\text{app}} = \theta + \epsilon$. If the contact-angle hysteresis is taken into account, the apparent angle has two limiting values, namely, the receding and advancing contact angles θ_R and θ_A . Substituting these limits into Eq. (B9) gives

$$\begin{aligned} \gamma_R^* &= \frac{\gamma_R}{\sigma R_c} = -\sin \theta_R [\cos \theta_R - \cos \theta], \\ \gamma_A^* &= \frac{\gamma_A}{\sigma R_c} = -\sin \theta_A [\cos \theta_A - \cos \theta]. \end{aligned} \quad (\text{B10})$$

The parameters γ_R and γ_A are line pinning energy values corresponding to the receding and advancing contact angles, respectively. According to Tadmor [78], for a given droplet on

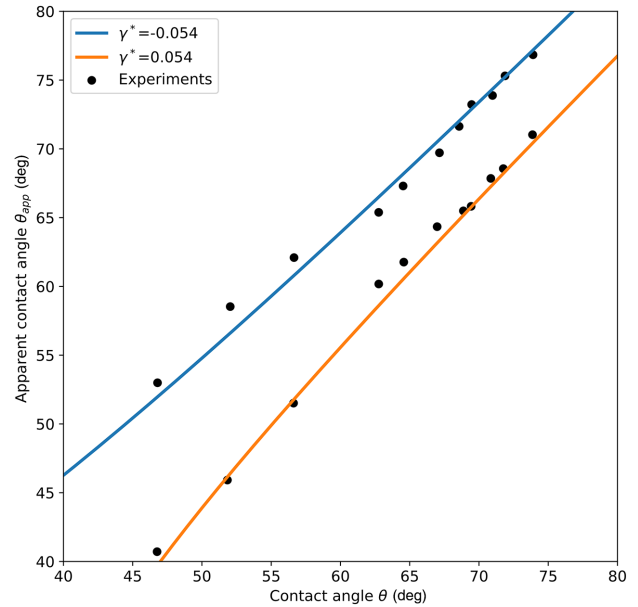


FIG. 6. Two limits of the apparent contact angles (advancing and receding contact angles) as a function of the intrinsic contact angles θ . The points indicate experimental data directly taken from Ref. [78]. Theoretical predictions from the current model are represented by the solid lines using $\gamma_* = \pm 0.054$.

a given surface, the line pinning energy coefficient γ_* depends solely on the surface irregularities. If these irregularities are isotropic, we expect $\gamma_R = -\gamma_A$, since both resistances arise from the pinning of the contact line to similar surface features, albeit in opposite directions for receding and advancing motion.

From the two equations above, a functional relation between the intrinsic contact angle and the receding/advancing angles can be obtained. Figure 6 compares this relation and experimental data from the literature [78], showing excellent agreement. The analysis in Fig. 6 is presented as a consistency check. Its purpose is to show that the generalized framework proposed here can be extended to describe edge-induced pinning effects on rough surfaces, thereby illustrating the broader applicability of the theory.

APPENDIX C: DISCUSSION OF GEOMETRIC PARAMETERS

The geometric parameter $f(\theta, \phi_1, \phi_2)$ can be divided into three contributions from the contact line, surface, and bulk energy terms, respectively, as given in

$$f(\theta, \phi_1, \phi_2) = \frac{\Delta G_c}{\Delta G_{\text{hom},c}} = f_1 + f_2 + f_3, \quad (\text{C1})$$

with $\Delta G_{\text{hom},c} = \frac{4}{3}\pi R_c^2 \sigma_{lg}$. Applying the above geometric analysis and calculating the Gibbs free energy change for critical nuclei in the asymmetric pore gives each individual

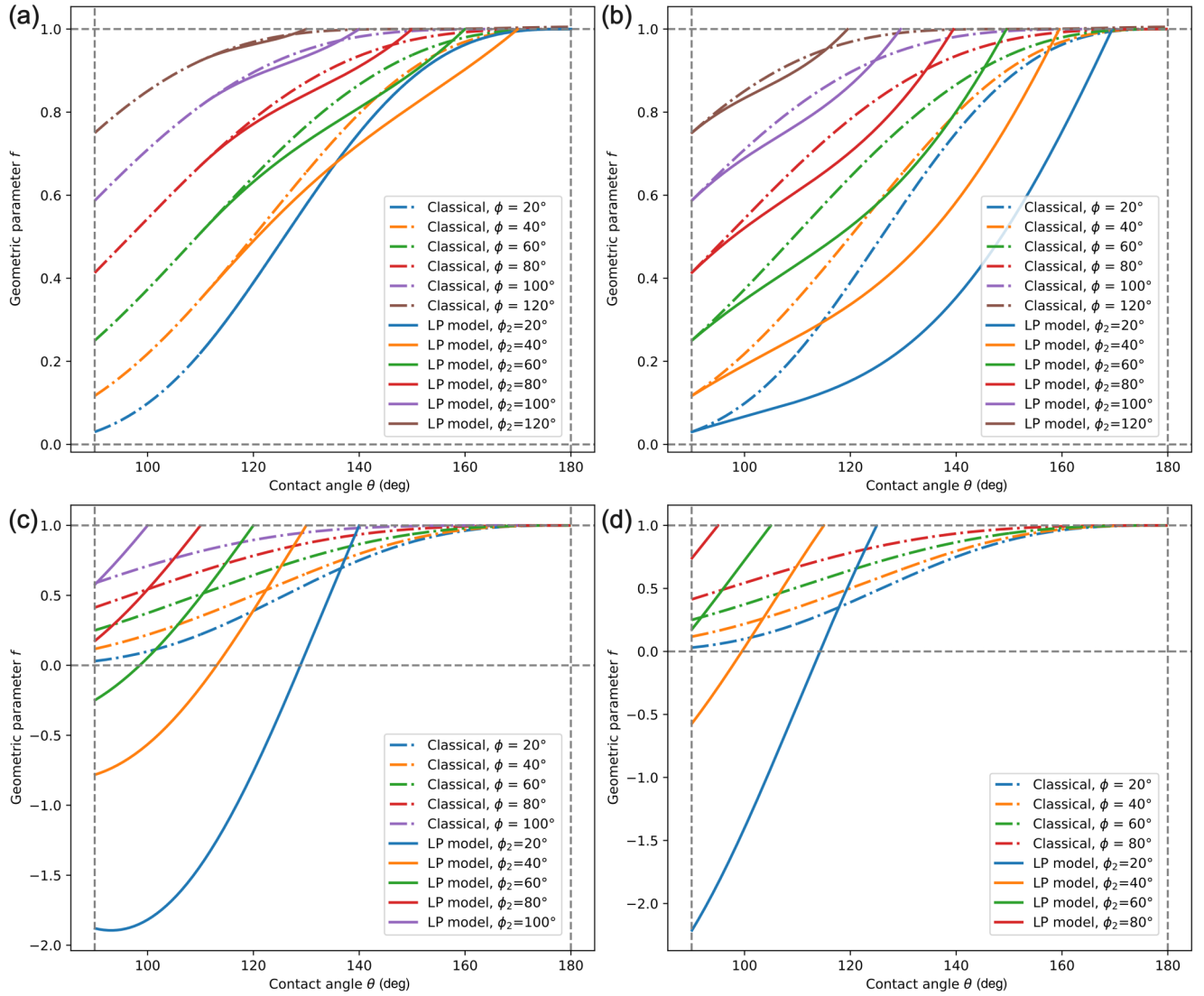


FIG. 7. Geometrical parameters of critical nuclei via the LP model (solid lines) as a function of the contact angles θ for a fixed left opening angle $2\phi_1$ and varying right opening angles $2\phi_2$. Panels (a)–(d) correspond to $\phi_1 = -20^\circ, 0^\circ, 60^\circ, 90^\circ$, respectively. Predictions from classical models for droplets in symmetric conical pores with half opening angle ϕ are indicated as dot-dashed lines for comparison.

geometric parameter as

$$\begin{aligned}
 f_1 &= \frac{3 \cos^2 \theta_1}{2 \sin \phi_2} [\cos(\theta + \phi_1 + \phi_2) - \cos \theta], \\
 f_2 &= \frac{3}{4} \left[4 - 2 \sin \theta_1 - 2 \sin \theta_2 - \frac{\cos \theta}{\sin \phi_2} (\cos^2 \theta_2 - \cos^2 \theta_1) \right], \\
 f_3 &= -\frac{1}{2} \left[(2 + \sin \theta_1)(1 - \sin \theta_1)^2 + (2 + \sin \theta_2)(1 - \sin \theta_2)^2 + \frac{\cos^3 \theta_2 - \cos^3 \theta_1}{\tan \phi_2} \right].
 \end{aligned} \tag{C2}$$

Specifically, when $\phi_1 = -\phi_2$, the line pinning energy term disappears, with $f_1 = 0$, and Eq. (C1) is reduced to $f(\theta, \phi_1, \phi_2) = 1 - \sin^3 \theta \cos \phi$, corresponding to the case of the droplet in the partial-filling regime, as shown in Fig. 4(c).

Figure 7 illustrates the geometric characteristics of critical nuclei predicted by the LP model in asymmetric conical pores. The plots show how the geometric parameter of the critical

droplet depends on the intrinsic contact angle θ for a fixed left opening angle $2\phi_1$ and various right opening angles $2\phi_2$. Panels (a)–(d) correspond to $\phi_1 = -20^\circ, 0^\circ, 60^\circ$, and 90° , respectively.

In each panel, solid lines denote the predictions from the LP model, which incorporates contact line pinning effect. Dot-dashed lines indicate the classical model results for

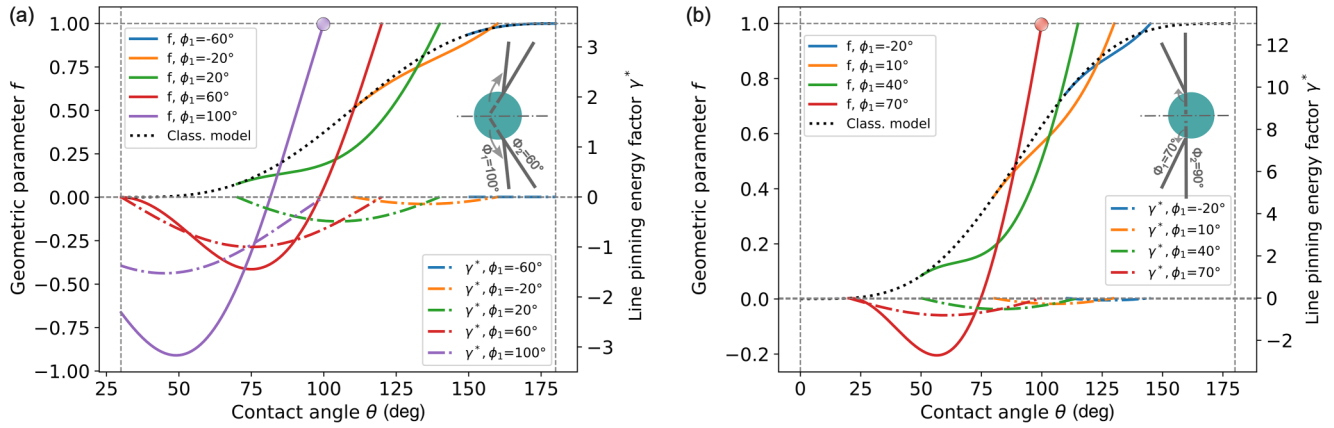


FIG. 8. Geometrical parameters and line pinning energy factors of critical nuclei as functions of the contact angle θ for fixed ϕ_2 and varying ϕ_1 . The insets depict the critical nucleus configurations within the pore structures, matching the colored dots. Panels (a) and (b) represent cases with $\phi_2 = 60^\circ$ and 90° , respectively. Predictions from classical models for droplets in smooth conical pores with $\phi = \phi_2$ are indicated as black dotted lines for comparison.

smooth conical pores with opening angle 2ϕ , included for direct comparison. As ϕ_2 increases (wider right opening), deviations from classical predictions become more pronounced, demonstrating the critical role of asymmetry and edge effects in confined nucleation. Overall, from panel (a) to panel (d), increasing ϕ_1 leads to progressively larger deviations from classical predictions. Both the intersection angle θ_i and the critical angle θ_c vary significantly with ϕ_1 , revealing a broad design space for tuning nucleation behavior.

Figures 8(a) and 8(b) illustrate how the geometric parameter f and the line pinning energy factor γ_* evolve with θ for increasing ϕ_1 under fixed values of $\phi_2 = 60^\circ$ and 90° , respectively. The valid contact angle range for the LP model is defined as $(\theta_0, \theta_c]$, where $\theta_0 = \max\{90^\circ - \phi_1, 90^\circ - \phi_2\}$ (see Appendix B for an explanation). There is an upper limit contact angle $\theta_c = 180^\circ - 0.5(\phi_1 + \phi_2)$ for the LP model, which corresponds to the critical case where the droplet tran-

sitions into a homogeneous nucleation state. This critical state is indicated by the violet and red circles in Figs. 8(a) and 8(b) for $\phi_1 = 100^\circ$ and 70° , respectively, with corresponding schematic insets. Figures 8(a) and 8(b) show trends similar to those in Fig. 3. However, the tunable contact angle range shifts with varying ϕ_2 , and the influence of line pinning energy differs significantly from the case with a smaller half-opening angle ($\phi_2 = 30^\circ$) in Fig. 3.

The LP model enables construction of a comprehensive energy landscape for nucleation across diverse pore geometries by tuning ϕ_1 and ϕ_2 , capturing steps, double-conical pores, inverted conical pores, cones, and crevices, which are widely utilized in industrial applications (see Fig. 9). By explicitly incorporating line pinning energy, it reveals barrier shifts and nucleation pathways beyond the reach of classical symmetric models, demonstrating broad applicability to realistic nano/microstructured systems.

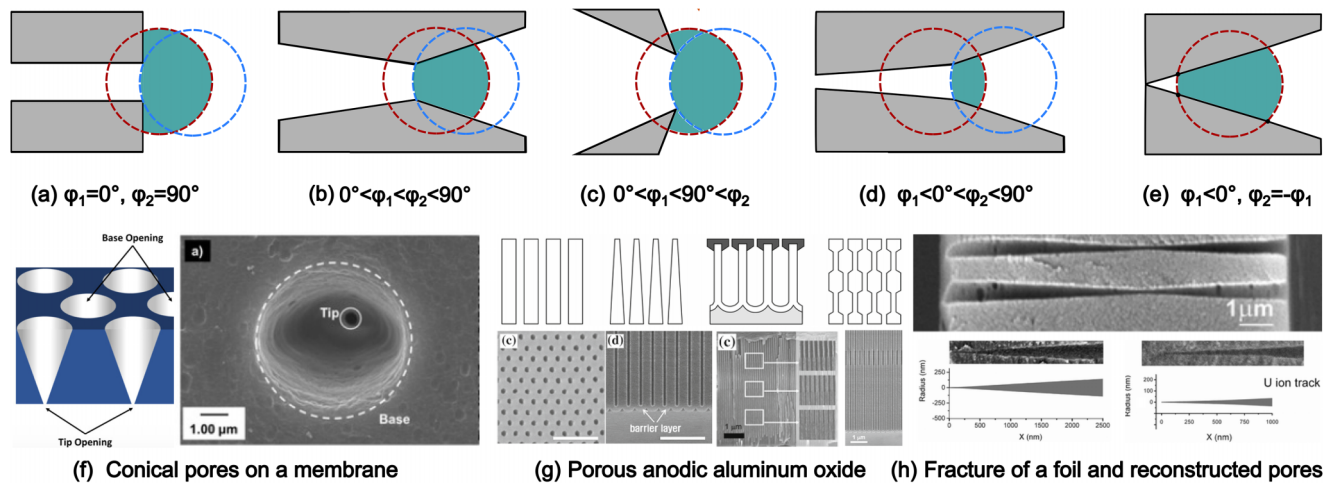


FIG. 9. (a)–(e) Schematics of critical nuclei formation in different pore geometries for varying opening angles ϕ_1 and ϕ_2 . (f)–(h) Different pore geometries used in engineering applications. (f) Schematic illustration of conical pores and a scanning electron microscopy (SEM) image of the base opening in a track-etched conical pore in a polycarbonate membrane used in an electroosmotic flow pump cell [79]. (g) Schematic structures and cross-sectional SEM micrographs of porous anodic aluminum oxide fabricated by anodization techniques, which can serve as templates for functional materials [80]. (h) SEM characterization of pore profiles in polymer foils used for biosensors [81]. Reproduced with permission from Ref. [81]. Copyright 2014, The Royal Society of Chemistry.

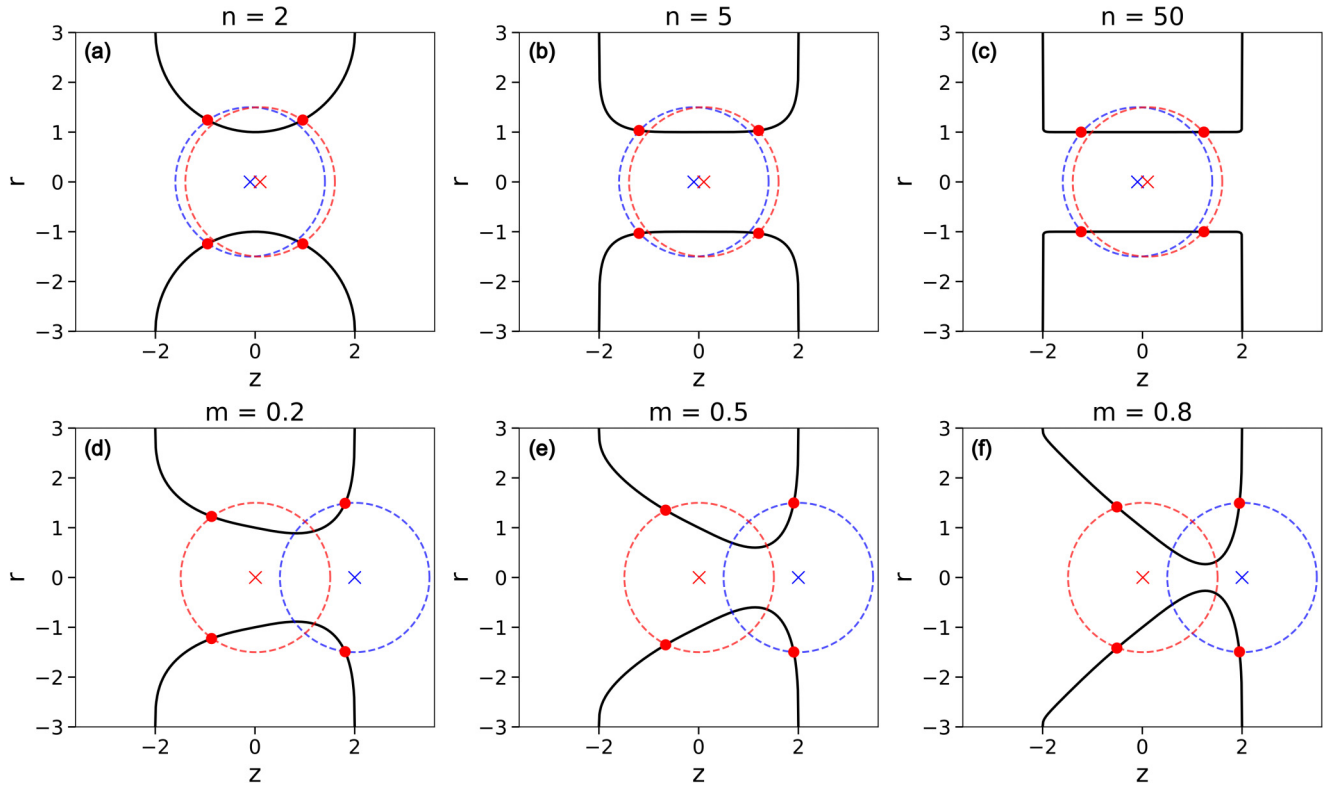


FIG. 10. Schematics of critical nucleus formation in different pore geometries with rounded corners (except for large n values). The blue and red circles are the fitting circles corresponding to the left and right sides of the nucleus interface profile, where the nucleus is in contact with the pore surface marked by red dots. The pore profile is described by the equation $r(z) = a \times (1 + \frac{mz}{b}) \times (1 - |\frac{z}{b}|^n)^{1/n} - r_L$, where $2r_L$ denotes the external diameter of the pore. Parameters a and b are the lengths of the semimajor and semiminor axes of the pore profile, respectively; n and m control the pore curvature and asymmetry, respectively. We set $a = 2$, $b = 2$, $r_L = 3$. Specifically, $m = 0$ was used for panels (a)–(e), while $n = 3$ was adopted for panels (d)–(f).

In addition, our nucleation model can be readily extended to more generalized rounded-corner pore geometries (see Fig. 10). Because the pore profile is fully differentiable, the contact line pinning behavior differs fundamentally from that of sharp-edged pores, allowing us to neglect the line pinning effect induced by surface discontinuities. In this limit, the nucleation barrier depends solely on pore geometry and wettability, which will be explored in detail in a forthcoming study.

In this framework, both wettability and geometric confinement (including pore shape and the associated critical nucleus size) play essential roles in determining nucleation behavior. For a given geometry, the position and energy state of the critical nucleus can be identified by searching for the locations where the two equal-curvature circles are simultaneously satisfied, as illustrated by the blue and red circles in Fig. 10. This provides a straightforward computational route to determine the nucleation site and the corresponding activation state in generic confined geometries.

It can also help identify metastable states. In particular, as shown in Fig. 11, different combinations of wettability and pore shape can give rise to different candidate nucleation locations and distinct interfacial configurations. These corre-

spond to local energetic extrema in the free-energy landscape. Therefore, the method is not limited to predicting the critical nucleus alone, but can also be used to reveal metastable nucleation states and pathway competition in general pore geometries.

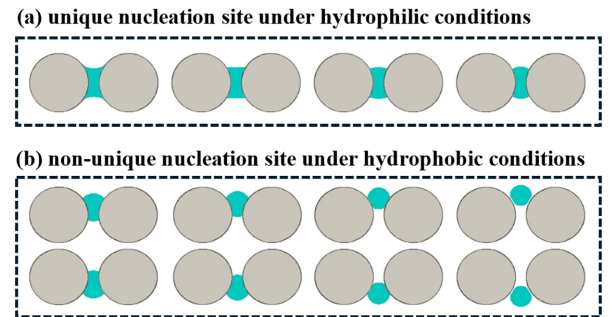


FIG. 11. Critical nucleus formation in pores at different contact angles. From left to right, in panel (a), $\theta = 30^\circ, 60^\circ, 75^\circ, 90^\circ$, respectively; in panel (b), $\theta = 100^\circ, 110^\circ, 130^\circ, 150^\circ$, respectively.

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