

Nanodroplet condensation on solid surfaces

Matteo Teodori , Dario Abbondanza , Mirko Gallo ,* and Carlo Massimo Casciola *Dipartimento di Ingegneria Meccanica e Aerospaziale, Sapienza Università di Roma, Via Eudossiana 18, 00184 Roma, Italy*

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This work addresses droplet condensation on surfaces spanning hydrophobic to hydrophilic wettabilities. A stochastic mesoscale model based on the theory of fluctuating hydrodynamics and the thermodynamics of a diffuse interface approach shows how direct simulation of the vapor-liquid transition from the nucleation process to droplet hydrodynamics can be achieved. Such simulations explain the role of wettability in filmwise and dropwise condensation regimes and the main limitations of classical nucleation theory.

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I. INTRODUCTION

Condensation is of central interest due to the innumerable conditions where vapor/liquid phase change takes place, from planetary—e.g., clouds [1]—to human—e.g., water harvesting and desalination [2,3]—and micro/nano scales—e.g., biotechnology applications, electronics cooling [4–6], and bionics/biomimetics [7,8]. Fluid mechanics has long been involved in deciphering condensation [9–13], an effort partially hindered by the poor understanding of the onset of the phenomenon, namely, the nucleation process [14].

The classical picture of condensation is known. Vapor transforms into liquid by decreasing the temperature below the saturation point or by increasing the pressure above the liquefaction threshold. However, this description is oversimplified because it does not take into account metastability. In reality, a vapor may remain in a metastable state (local free-energy minimum) for a long time well beyond its thermodynamic saturation limits. Here, the granular nature of matter plays a central role: molecules tend to aggregate with a certain probability, resulting in nanometric droplets. A rare event consisting of a large enough cluster—a critical droplet—requires a certain activation energy (nucleation barrier) to be exceeded, triggering the phase change. Associated with the atomistic features of the process, nucleation also involves the macroscopic hydrodynamics of the droplets, namely, the exchange of latent heat and coalescence.

Macroscopic approaches currently do not account for thermal fluctuations and cannot describe droplet nucleation. These simulations are always initialized with preexisting nuclei, which are only partially consistent with the thermodynamics of phase change. Consequently, it is impossible to predict whether the phase transformation begins within the vapor bulk (homogeneous nucleation) or in contact with a solid

surface (heterogeneous nucleation) and whether droplets form in a film/dropwise mode. At the fundamental level, these different nucleation mechanisms are inherently connected with thermodynamic conditions and surface chemistry, and proper modeling should take these aspects into account.

Currently, molecular dynamics (MD) is the universally trusted tool for such a task [15–17], but its computational cost limits its use to nanometric systems on the nanosecond timescales. The coupling with macroscopic hydrodynamics became feasible by exploiting a recent mesoscale model originally developed for the reverse liquid/vapor transformation [18–22].

The methodology is based on a diffuse interface description [23,24] combined with fluctuating hydrodynamics (FH) [25]. FH is a powerful tool for assessing the influence of thermal fluctuations on macroscopic fluid dynamics [26–31]. Properly accounting for thermal fluctuations (Einstein-Boltzmann distribution) allows for the spontaneous nucleation of liquid droplets, describing condensation from nucleation to hydrodynamics. Using a prototypal fluid, we analyze the dependency on the solid surface chemistry of the different (dropwise/filmwise) condensation modes, when the system temperature is initially uniform.

II. MATHEMATICAL MODEL

The proposed mesoscale model consists of the coupling between Landau-Lifshitz-Navier-Stokes equations and diffuse interface thermodynamics. Here, the conservation equations for mass, momentum, and energy are augmented with stochastic fluxes ($\delta\mathbf{\Sigma}$, $\delta\mathbf{q}$).

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (1)$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \nabla \cdot \mathbf{\Sigma} + \delta\mathbf{\Sigma}, \quad (2)$$

$$\frac{\partial E}{\partial t} + \nabla \cdot (\mathbf{v} E) = \nabla \cdot [(\mathbf{\Sigma} + \delta\mathbf{\Sigma}) \cdot \mathbf{v} - \mathbf{q}] + \delta\mathbf{q}, \quad (3)$$

where ρ is the mass density, $\mathbf{v}$ is the velocity, and E is the total energy density ($E = u_b(\rho, \theta) + 1/2\rho|\mathbf{v}|^2 + 1/2\lambda|\nabla\rho|^2$, with $u_b(\rho, \theta)$ the bulk internal energy density, θ the temperature, λ the capillary coefficient, and ∇ the gradient operator). $\mathbf{\Sigma}$ and $\mathbf{q}$

*Contact author: mirko.gallo@uniroma1.it

are the deterministic stress tensor and energy flux as identified by nonequilibrium thermodynamics that include distributed capillary effects [32,33] (see also [34–36] for extensions to multicomponent systems),

$$\Sigma = \left[-p + \frac{\lambda}{2} |\nabla \rho|^2 + \rho \nabla \cdot (\lambda \nabla \rho) \right] \mathbf{I} - \lambda \nabla \rho \otimes \nabla \rho + \eta_1 (\nabla \mathbf{u} + \nabla \mathbf{u}^T) + \eta_2 \nabla \cdot \mathbf{u} \mathbf{I}, \quad (4)$$

$$\mathbf{q} = \lambda \rho \nabla \rho \nabla \cdot \mathbf{u} - k \nabla \theta, \quad (5)$$

where $p(\rho, \theta)$ is the thermodynamic pressure, $\mathbf{I}$ is the identity matrix, $\eta_1(\rho, \theta)$ and $\eta_2(\rho, \theta)$ are the viscosity coefficients of the fluid, and $k(\rho, \theta)$ is the thermal conductivity.

The fluctuation-dissipation balance provides the statistical properties of the Gaussian stochastic fluxes [20]:

$$\begin{aligned} \langle \delta \mathbf{q}(\hat{\mathbf{x}}, \hat{t}) \rangle &= 0, \quad \langle \delta \Sigma(\hat{\mathbf{x}}, \hat{t}) \rangle = 0, \\ \langle \delta \Sigma(\hat{\mathbf{x}}, \hat{t}) \otimes \delta \Sigma^\dagger(\tilde{\mathbf{x}}, \tilde{t}) \rangle &= \mathbf{Q}^\Sigma \delta(\hat{\mathbf{x}} - \tilde{\mathbf{x}}) \delta(\hat{t} - \tilde{t}), \\ \langle \delta \mathbf{q}(\hat{\mathbf{x}}, \hat{t}) \otimes \delta \mathbf{q}^\dagger(\tilde{\mathbf{x}}, \tilde{t}) \rangle &= \mathbf{Q}^q \delta(\hat{\mathbf{x}} - \tilde{\mathbf{x}}) \delta(\hat{t} - \tilde{t}), \end{aligned} \quad (6)$$

where $\delta(\mathbf{x})$ and $\delta(t)$ are the spatial and temporal Dirac delta functions, respectively, and

$$\begin{aligned} \mathbf{Q}^\Sigma_{\alpha\beta\gamma\eta} &= 2k_B\theta[\eta_1(\delta_{\alpha\gamma}\delta_{\beta\eta} + \delta_{\alpha\eta}\delta_{\beta\gamma}) + \eta_2\delta_{\alpha\beta}\delta_{\gamma\eta}], \\ \mathbf{Q}^q_{\alpha\beta} &= 2k_B\theta^2 k \delta_{\alpha\beta}, \end{aligned} \quad (7)$$

with the subscript Greek indices denoting the Cartesian components of tensors, k_B the Boltzmann constant, and $\delta_{\alpha\beta}$ the Kronecker delta symbols. Different components of the stochastic heat flux are not correlated, while the components of the stochastic stress tensor have a nontrivial correlation induced by compressibility. To account for the fluid-solid interaction (i.e., the solid wettability), we have recently proposed a free-energy contribution [20], which enforces the following boundary condition for the mass density:

$$\lambda \nabla \rho \cdot \hat{\mathbf{n}} = -\frac{df_w}{d\rho} = \cos \phi \sqrt{2\lambda(\omega_b(\rho, \theta) - \omega_b(\rho_V))}, \quad (8)$$

with ϕ the Young contact angle, $\omega_b(\rho, \theta) = f_b - \rho \partial f_b / \partial \rho$ and $f_b(\rho, \theta)$ the Landau and Helmholtz bulk free-energy densities, respectively, and $\hat{\mathbf{n}}$ the unit normal vector. It is worth stressing that the bulk energies u_b , f_b , ω_b , and the pressure p are identified by a proper equation of state (EoS). The EoS also defines the surface tension [37,38]. The capillary coefficient λ is selected to reproduce the planar interfacial tension σ_∞ measured experimentally. Specifically, defining z as the coordinate orthogonal to the planar interface, one has $\sigma_\infty = \lambda \int_{-\infty}^{\infty} (d\rho/dz)^2 dz$. For curved interfaces, the same variational structure naturally captures the curvature dependence of the surface tension, including the Tolman length and higher-order (elastic) corrections [38,39], a feature that is particularly important for nanodroplets [40]. In addition, consistent with the thermodynamic of van der Waals squared gradient theory, which has the following Helmholtz free-energy functional

$$F[\rho, \theta] = \int_V \left(f_b(\rho, \theta) + \frac{\lambda}{2} |\nabla \rho|^2 \right) dV, \quad (9)$$

the equilibrium condition for the (two-phase) fluids requires $\mu = \delta F / \delta \rho = \partial f_b / \partial \rho - \lambda \nabla^2 \rho = \mu_{\text{eq}}$, meaning that the generalized chemical potential is constant. As shown in Ref. [41],

this condition recovers the Young-Laplace-Kelvin in the sharp interface limit.

Finally, the extension to nonequilibrium process, with the dynamics governed by the deterministic Navier-Stokes with a diffuse-interface (DI) formulation, are able to reproduce the Rayleigh-Plesset and cavitation dynamics for bubbles [42–45] and the Hertz-Knudsen scaling [46] for the condensation of a planar interface, where the interfacial mass flux is linear in the departure from equilibrium, i.e., $\propto (\rho_V - \rho_V^{\text{sat}})$, where ρ_V is the actual vapor density and ρ_V^{sat} is its saturation value. These aspects will also be discussed in Sec. IV.

In the present case, we adopt the modified Benedict-Webb-Rubin equation for mimicking a Lennard-Jones (LJ) fluid [47]. However, one of the key advantages of this approach is that it can be applied to any real fluid, provided an appropriate EoS, surface tension, and transport coefficients are supplied. These macroscopic inputs are widely available, with high accuracy, from standard correlations and databases (e.g., the IAPWS formulations for water [48]).

III. NUMERICAL SETUP

Condensation simulations are based on the system of Eqs. (1)–(3). They are made dimensionless using the LJ reference quantities: $\sigma = 3.4 \times 10^{-10}$ m as length, $\epsilon = 1.65 \times 10^{-21}$ J as energy, $m = 6.63 \times 10^{-26}$ kg as mass, $\theta_r = k_B/\epsilon = 119.56$ K as temperature, $v_r = (\epsilon/m)^{1/2} = 155.83$ m s⁻¹ as velocity, and $t_r = \sigma/v_r = 2.15 \times 10^{-12}$ s as time. To reproduce the surface tension of an LJ fluid and its temperature dependence, we set $\lambda = 5.224$, with $\lambda_r = (\sigma^5 \epsilon)/m^2 = 1.52 \times 10^{-18}$ kg m⁷ s⁻² [49]. Simulations consist of homogeneous metastable vapor enclosed in a box with two flat solid surfaces parallel to the $y-z$ -plane. The boundary conditions on these surfaces are $\rho \mathbf{v} = 0$, $\theta = \theta_w$, with the contact angle ϕ prescribed through Eq. (8), and periodicity in z and y directions.

The equations to be solved in a box of volume $V = 400 \times 1000 \times 1000$ are discretized on a uniform $40 \times 100 \times 100$ grid with the scheme proposed in Ref. [50] using a second-order Runge-Kutta scheme for time evolution ($\Delta t = 0.1$). This scheme was shown to preserve the fluctuation-dissipation balance at the discrete level [50–53] and to guarantee converged statistics of thermal fluctuations [18,20,42].

IV. RESULTS AND DISCUSSION

The present simulation campaign investigates the dependence of condensation on the wettability of solid surfaces. The system is initialized with a uniform temperature $\theta = 1.25$ and an initial vapor density $\rho_V = 0.16$, changing the contact angle in the range 15° – 95° . In these conditions, the vapor is metastable; hence, condensation is expected to occur. Snapshots of the density field along the simulation for $\phi = 30^\circ$ are reported in Fig. 1.

Starting from a homogeneous metastable vapor, after a certain incubation time where subcritical embryos are randomly formed and reabsorbed, droplet nucleation begins to take place [Fig. 1(a)]. In a successive phase, the number and size of droplets are sufficiently large to give rise to a number of coalescence events [Figs. 1(b) and 1(c)]. Eventually, a liquid film is formed as the precursor of the well-known film

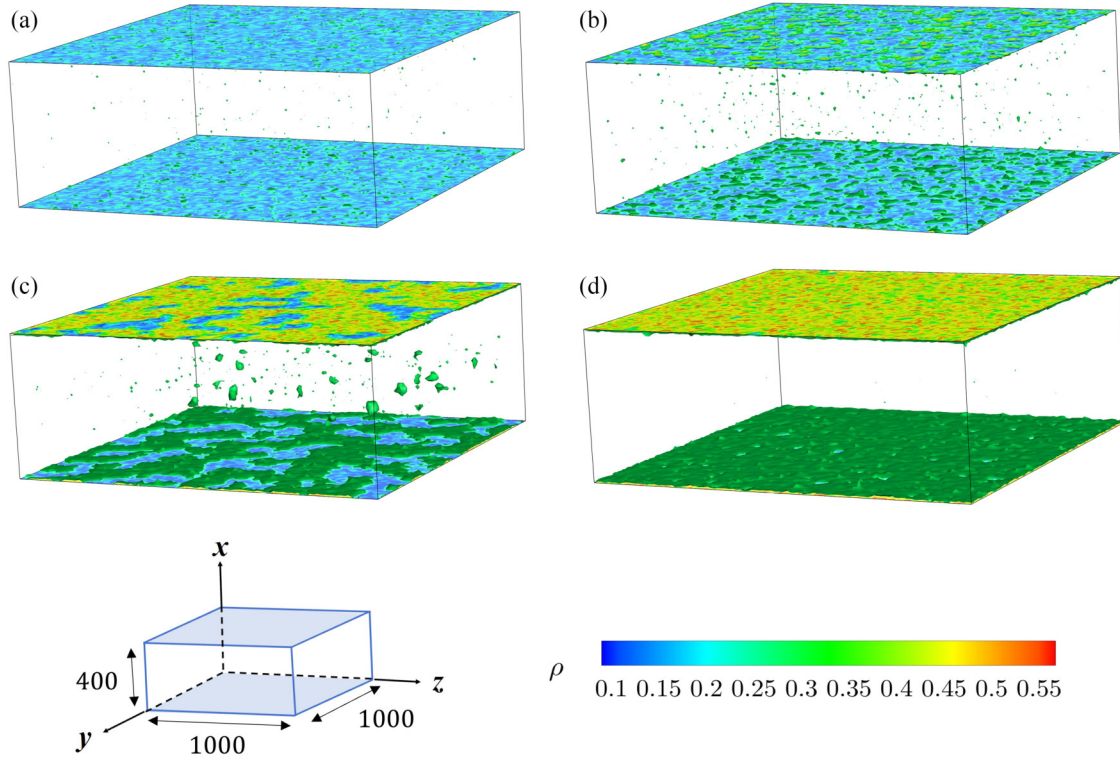


FIG. 1. Filmwise condensation: snapshots of the density field at the solid walls, $\rho_V = 0.16$, $\phi = 30^\circ$. (a) $t = 600$, (b) $t = 2000$, (c) $t = 20000$, and (d) $t = 150000$. The isosurfaces at the critical density $\rho = 0.33$, taken to discern liquid from vapor, are shown in green. A sketch of the simulation box setup is also illustrated.

condensation mode in macroscopic experiments [Fig. 1(d)]. For $\rho_V = 0.16$, filmwise condensation is observed for contact angles below 60° , where walls are rapidly covered by many nanodroplets that coalesce to form a continuous film.

At larger contact angles, the phenomenology is different. Only a few droplets nucleate (see Fig. 2), where $\phi = 90^\circ$. After the condensation nuclei appear, Fig. 2(a), individual droplets form, Fig. 2(b), that have enough time to grow as distinct entities, Fig. 2(c), to occasionally coalesce, Fig. 2(d). Here, we witness a sort of dropwise condensation mode at the nanoscale.

The evolution of the number of droplets over time, $N_d(t)$, at various wall wettabilities, is illustrated in Fig. 3. As described in our previous work for bubble nucleation [18], we identify a liquid embryo as the connected cluster of cells whose local density exceeds a threshold set by the critical droplet. The critical droplet is evaluated with the string method [54], here, adopted in the context of nucleation [18,55]. After identify, the critical droplet as the saddle point of the minimum-energy profile, we take $\rho_{th} \equiv \bar{\rho}(\mathbf{x})^\dagger$, with $\bar{\rho}(\mathbf{x})^\dagger$ mean density inside the critical droplet. We then label as liquid all cells with $\rho(\mathbf{x}) \geq \rho_{th}$. The droplet volume is $V_d = N_c \Delta V$, where N_c is the number of cells in the connected liquid cluster and ΔV is the computational cell volume. A droplet is deemed supercritical if $V_d > V_{crit}$, with V_{crit} taken from the critical droplet. After the incubation time, the number of droplets initially increases linearly in time during a first phase. Successively, the growth saturates, and eventually, the number of detected drops steadily decreases. In part, some droplets are reabsorbed. This is due to the combined volume and total mass constraint,

which, after a certain amount of fluid liquefies, forces part of it to re-evaporate to occupy all the available space. This phenomenon is partly attributable to coalescence events, which, while maintaining the overall volume of the liquid phase, lead to a decreased number of larger droplets. This picture is also observed in MD simulations [56]. Figure 3 illustrates that the maximum number of formed droplets significantly decreases with increasing contact angle. Furthermore, following the peak, the subsequent decline in droplet count becomes more gradual.

In nucleation phenomena, the crucial observable is the nucleation rate J , related to the time history of the number of droplets, $N_d(t)$. In heterogeneous nucleation, it is defined as the number of droplets formed per unit time and unit wall area. In most MD simulations, where single droplet nucleation occurs due to the small spatial extent of the domain, the average time needed to observe a droplet is directly estimated from repeated simulations in identical thermodynamic conditions. For systems as large as the one currently addressed (fraction of micrometers), multiple nucleation events are observed in a single simulation. In this case, J can be accurately determined from a single simulation [57]. As done in the context of cavitation [20], we adopt the same threshold method and measure J from the slope of the linear fit to the $N_d(t)$ curve in the (stationary) nucleation phase, where $N_d \propto t$, i.e., $J = 1/A_w dN_d(t)/dt$, with A_w the area of the condensing solid wall. Classical nucleation theory (CNT) is the cornerstone of any discussion of (first-order) phase transition; therefore, it is natural to compare our estimates for the nucleation rates at different contact angles with those provided

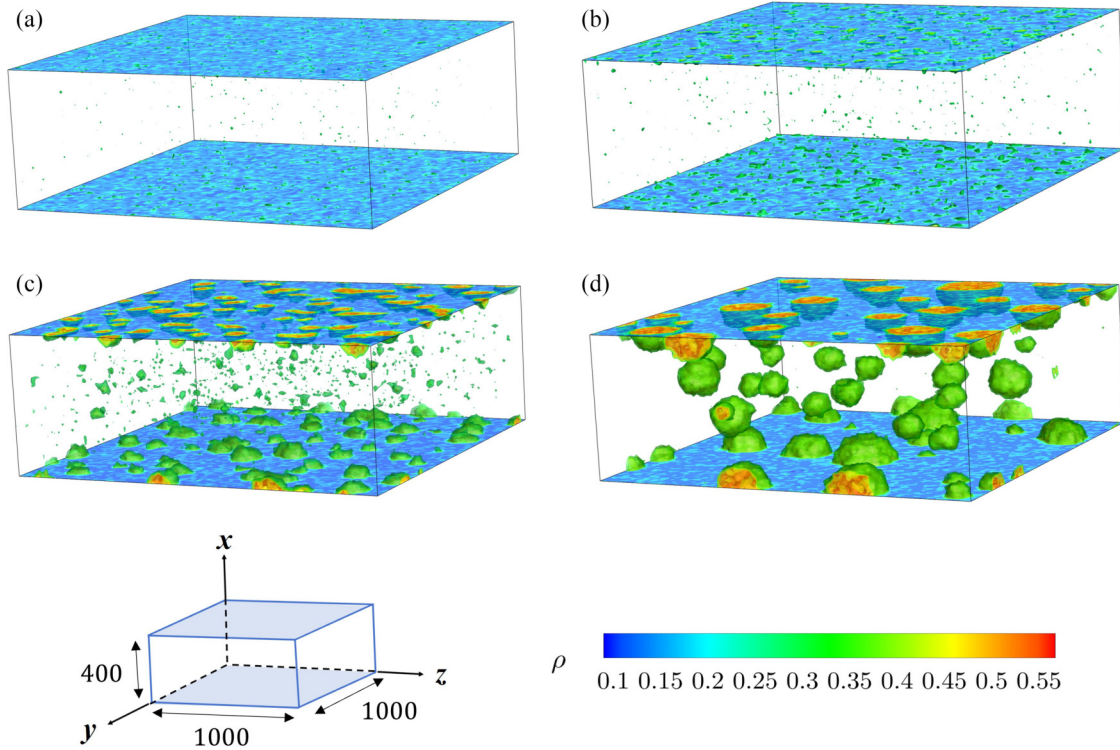


FIG. 2. Dropwise condensation: snapshots of numerical simulations for the case $\rho_V = 0.16$ and $\phi = 90^\circ$. (a) $t = 600$, (b) $t = 2000$, (c) $t = 20000$, and (d) $t = 150000$. The isosurfaces at $\rho = \rho_{\text{cut}} = 0.33$ that delimit the liquid phase are shown in green, and the density field at the wall is reported. A sketch of the simulation box setup is also illustrated.

by CNT in the heterogeneous case $J_{\text{CNT}} = n_V^{2/3} (n_V/n_L) (1 - \cos(\phi)) / 2\sqrt{2\sigma/(\pi m \psi)} \exp(-\Delta\Omega^\ddagger/(k_B\theta))$, where $n_{V/L}$ is the number density of molecules in the vapor and liquid state, respectively, and $\psi = (2 - 3\cos(\phi) + \cos^3(\phi))/4$ is a geometric factor that takes into account the contact angle [58]. The comparison reported in the bottom panel of Fig. 4 shows that CNT gives an acceptable prediction for $\rho_V = 0.16$ only for contact angles near neutral wettability $\phi \simeq 90^\circ$. By decreasing the contact angle, CNT remains qualitatively accurate, i.e., higher nucleation rates at smaller contact angles, but the difference between prediction and numerical results is not negligible (orders of magnitude). This is not

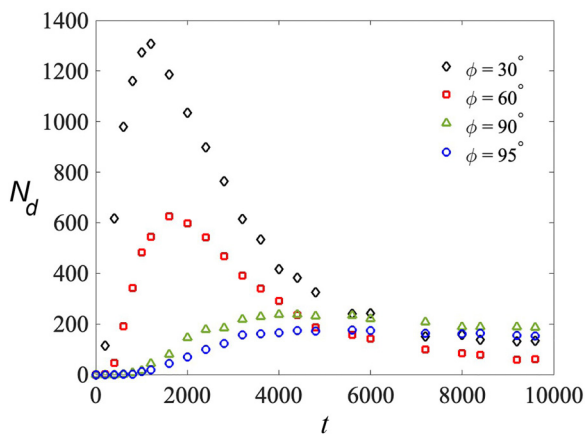


FIG. 3. Evolution of the number of supercritical droplets (N_d) over time. Different contact angles (ϕ) are shown.

dissimilar to what is observed in homogeneous and heterogeneous condensation when comparing molecular dynamics results with CNT (Refs. [59,60], respectively). However, it is worth stressing that a direct MD-continuum benchmark is delicate, as it requires matching the metastable state and interfacial thermodynamics: In MD, these depend sensitively on the intermolecular potential, cutoff/long-range corrections, and wall models (wettability), whereas in our approach they are encoded in the free-energy functional; small mismatches generate changes in J . On the other hand, microscopic experimental rates at the relevant scales are likewise scarce [see Ref. [61] and the references therein].

This being said, as is common in nucleation studies, an order-of-magnitude comparison with some MD data can be established. For example, the typical rate in Refs. [17,58,62–65] is $J \sim 10^{24} - 10^{28} \text{ s}^{-1} \text{ m}^{-2}$, while our results are $J \sim 10^{23} - 10^{25} \text{ s}^{-1} \text{ m}^{-2}$, consistent within orders of magnitude; our slightly lower values likely reflect access to larger domains and longer times.

Now, we focus on identifying the primary source of error in the estimation of the nucleation rate, $J = J_0 \exp(-\Delta\Omega^\ddagger/(k_B\theta))$, whether it originates from the pre-exponential factor J_0 or from the energy barrier $\Delta\Omega^\ddagger$ associated with the nucleation process. When dealing with nanodrops/bubbles, the typical dimension of the liquid/vapor interface is comparable with that of the droplet/bubbles; hence, sharp-interface predictions—as CNT—may fail [38,66]. Therefore, to precisely identify $\Delta\Omega^\ddagger$, the string method [54] is employed on top of diffuse interface thermodynamics ($\Delta\Omega_{\text{DI}}^\ddagger$). This is expected to be the barrier that the vapor phase

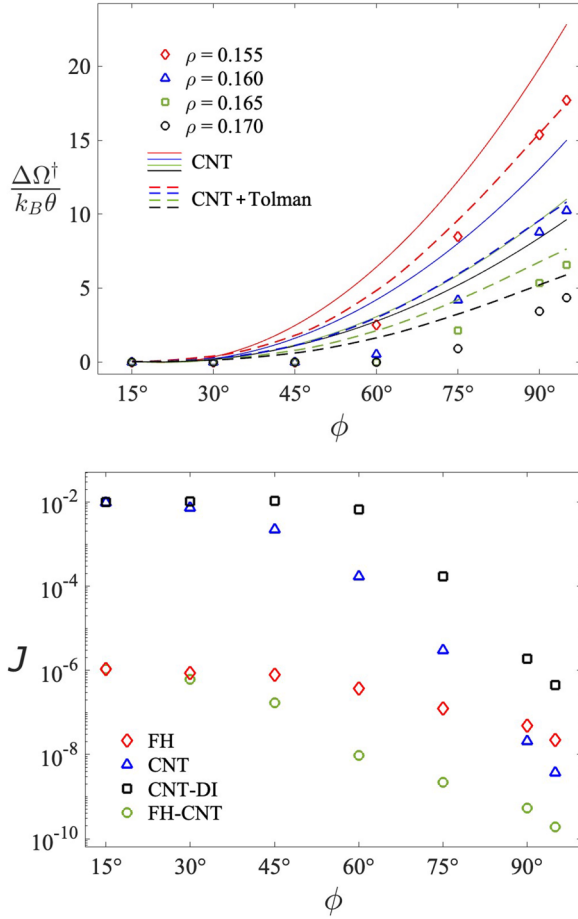


FIG. 4. Top panel: Normalized free energy barrier ($\Delta\Omega^\ddagger/k_B\theta$) vs contact angle (ϕ). Continuous lines depict CNT, dashed lines Tolman correction to CNT and symbols correspond to diffuse interface predictions. Bottom panel: Nucleation rates (J) vs contact angle (ϕ). Numerical simulations (red diamonds), CNT coupled with diffuse interface (CNT-DI black squares), CNT (blue triangles), and FH coupled with CNT (green circles).

experiences in our simulations. Figure 4 compares our numerical results with CNT and CNT-DI, where the actual energy barrier is $\Delta\Omega^\ddagger_{\text{DI}}$ and $J_{\text{CNT-DI}} = J_0 \exp(-\Delta\Omega^\ddagger_{\text{DI}}/(k_B\theta))$, with $J_0 = n_V^{2/3}(n_V/n_L)(1 - \cos(\phi))/2\sqrt{2\sigma/(\pi m\psi)}$ the usual CNT pre-exponential factor.

As shown on the top panel of Fig. 4, CNT overestimates the energy barrier over the entire range of observed contact angles at various degrees of metastability, in agreement with molecular dynamics simulations of heterogeneous condensation [60]. The discrepancy can be mitigated by correcting the surface tension using Tolman's length. We have estimated the Tolman length δ to correct the CNT barrier and benchmark it against the DI prediction (which already embeds Tolman and higher-order curvature effects). Specifically, we use the curvature-corrected surface tension $\sigma(R) = \sigma_\infty(1 - 2\delta/R)$ in the free energy $\Delta\Omega_{\text{CNT}}(R, \rho_L) = (-4/3\pi R^3(p_L - p_V) + 4\pi R^2\sigma(R))\psi(\phi)$, where σ_∞ is the planar surface tension, R is the droplet radius, p_L and p_V are the liquid and vapor pressures, respectively. We set $p_V = p(\rho_V, \theta)$ since ρ_V and θ are known in the metastable state. The barrier $\Delta\Omega^\ddagger_{\text{CNT}} =$

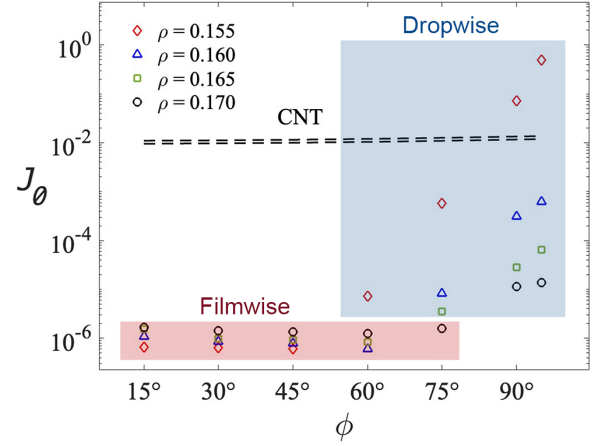


FIG. 5. Numerical values of $J_0(\rho, \phi)$ vs ϕ for different densities. The two dashed lines represent the minimum and maximum CNT prediction J_0 for each ϕ in the 0.155–0.170 density range.

$\Delta\Omega_{\text{CNT}}(R^\ddagger, \rho_L)$ is obtained by imposing $\partial\Delta\Omega_{\text{CNT}}/\partial R = 0$ and $\mu(\rho_V) = \mu(\rho_L)$, which identify $R^\ddagger$ and ρ_L . In the present case, δ is estimated at the weakest metastability for neutral wettability ($\rho_V = 0.155$, $\phi = 90^\circ$), where the curvature expansion is most reliable; we got $\delta = 0.55$ fixed for all other conditions at the same temperature. It is worth stressing that this value (fraction of nanometers) is in line with MD results [67,68]. With this Tolman-corrected CNT, the barrier height shows a marked improvement and approaches the DI prediction. The nucleation rate J for the CNT and CNT-DI approaches overlaps only for low contact angles, where the barrier goes to zero and the nucleation rate is dominated by J_0 , which is the same in both models. As the contact angle grows, the contribution of J_0 becomes less and less important, and the nucleation rate heavily depends on the free-energy barrier. It is also apparent that our numerical results, FH on the bottom panel of Fig. 4, and the CNT-DI model are comparable only for more hydrophobic chemistry, where the role of J_0 is not negligible. Hence, when the nucleation barriers are not so high, a significant part of the misalignment between CNT predictions and numerical data stems from a poor estimation of the factor J_0 . From a physical perspective, the prefactor J_0 reflects both droplet diffusion in the vapor medium and the density of potential nucleation sites. In the homogeneous case, theoretical predictions [69] and numerical simulations [18] suggest that FH offers a comprehensive description of both the energetic barrier ($\Delta\Omega^\ddagger$) and the kinetic aspects (J_0) of nucleation. Therefore, given a numerically obtained nucleation rate J_{FH} , we extract the corresponding FH pre-exponential factor as $J_{0\text{FH}} = J_{\text{FH}} \exp(\Delta\Omega^\ddagger_{\text{DI}}/(k_B\theta))$. For full context, we also report in the bottom panel of Fig. 4 the nucleation rate resulting from the FH factor and CNT barrier (green circles). In this case, J is underestimated due to the higher barriers predicted by CNT. Figure 5 shows $J_{0\text{FH}}$ evaluated at various ϕ for different initial vapor densities. For comparison, the range of CNT prefactors is also plotted (region between the two dashed lines). Two distinct trends, associated with different condensation regimes, are evident. In the filmwise condensation regime, J_{FH} remains nearly constant and is largely independent of the degree of metastability. In contrast, during

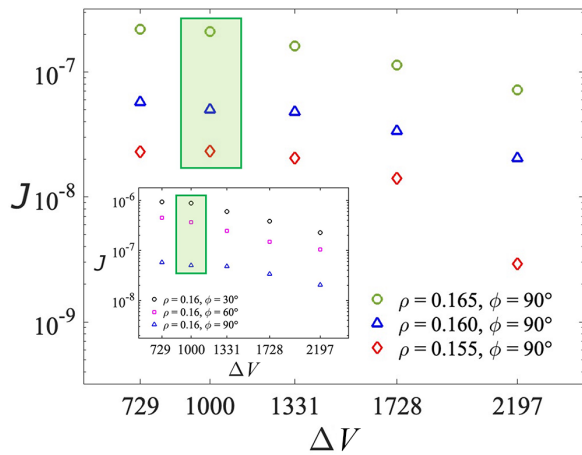


FIG. 6. Nucleation rate (J) vs computational grid volume (ΔV) at different initial densities. In the inset, the effect of various contact angles is also shown. In the green boxes, the current simulation campaign.

dropwise condensation, the prefactor J_0 exhibits dependence on both ϕ and ρ . This behavior can be qualitatively interpreted using Langer’s theory [69], originally formulated for homogeneous nucleation. According to this framework, the prefactor scales with the system volume divided by the cube of the correlation length. In DI thermodynamics, the correlation length increases with metastability and diverges near the spinodal limit [49]. Consequently, the prefactor is expected to decrease as metastability increases—an effect not captured by CNT. Although Langer’s theory has not been formally extended to heterogeneous nucleation, its core concepts plausibly apply to dropwise condensation, which closely mirrors the dynamics of the homogeneous case.

As a final analysis, we discuss how the nucleation rate J depends on the computational grid volume ΔV . Before addressing this point, a clarification is in order regarding the nature of the fluctuating-hydrodynamics equations employed here. From a mathematical standpoint, FH lacks a traditional continuum limit and exhibits ultraviolet divergences; physically, a microscopic cutoff is implied, so FH is best viewed as a low-wave-number effective field theory with modes $k \gtrsim 1/\sigma_M$ (molecular radius σ_M) removed, which regularizes the stochastic-PDE pathologies. As described in Ref. [70], the discretized FH equations are a coarse-grained representation of atomistic dynamics: mass, momentum, and energy are cell averaged over ΔV , field variances scale as $1/\Delta V$, and coherently with the Einstein-Boltzmann equilibrium distribution. For nucleation, the coarse-graining cell must contain many

molecules yet not average out embryos; here, the interfacial thickness is $\sim 4\text{--}5\text{ nm}$, we set $\Delta x = (\Delta V)^{1/3} = 3.3\text{ nm}$ (≈ 10 LJ units), and the critical nucleus radius is $\approx 13\text{ nm}$. We performed several numerical experiments by varying ΔV (Fig. 6). We found the nucleation rate J is essentially insensitive to ΔV over the relevant range (LJ units, $\Delta V \lesssim 1331$) across different metastable vapor densities and contact angles; for very small ΔV numerical instabilities arise (strong noise), whereas for larger ΔV the noise amplitude decreases and J correspondingly drops. Consequently, there exists a window of coarse-graining lengths around the interfacial thickness within which FH provides a robust description of nucleation, and the predicted rates J are essentially insensitive to ΔV .

V. CONCLUSIONS

Condensation is a complex phenomenon rooted in atomistic processes but also involving macroscopic hydrodynamic scales. For this reason, it has traditionally been studied at separate levels: nucleation through molecular dynamics simulations and bulk fluid behavior through Navier-Stokes-based solvers. In this work, we adopt a holistic approach, describing the entire process using a mesoscale model that combines hydrodynamic equations with the inherent granularity of matter treated as stochastic processes. This approach offers insights into the various observed condensation regimes. Moreover, the relatively low computational cost ($\sim 10^3$ core hours per simulation) together with the straightforward extension to real fluids paves the way for physically grounded, large-scale simulations of condensation in systems of significant technological relevance.

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The authors report no conflict of interest.

DATA AVAILABILITY

The data that support the findings of this article are openly available [71].

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