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Translational invariance in nucleation theories: Theoretical formulation

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The consequences of spontaneously broken translational invariance on the nucleation-rate statistical prefactor in theories of first-order phase transitions are analyzed. A hybrid, semiphenomenological approach based on field-theoretic analyses of condensation and modern density-functional theories of nucleation is adopted to provide a unified prescription for the incorporation of translational-invariance corrections to nucleation-rate predictions. A connection between these theories is obtained starting from a quantum-mechanical Hamiltonian and using methods developed in the context of studies on Bose-Einstein condensation. An extremum principle is used to derive an integro-differential equation for the spatially nonuniform mean-field order-parameter profile; the appropriate order parameter becomes the square root of the fluid density. The importance of the attractive intermolecular potential is emphasized, whereas the repulsive two-body potential is approximated by considering hard-sphere collisions. The functional form of the degenerate translational eigenmodes in three dimensions is related to the mean-field order parameter, and their contribution to the nucleation-rate prefactor is evaluated. The solution of the Euler-Lagrange variational equation is discussed in terms of either a proposed variational trial function or the complete numerical solution of the associated boundary-value integro-differential problem. Alternatively, if the attractive potential is not explicitly known, an approach that allows its formal determination from its moments is presented.

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I. INTRODUCTION

Nucleation theory has been a controversial topic for over 70 years now. It has attracted interest not only as a case study for the understanding of phase transitions within the framework of statistical mechanics, but also for such important applications as condensation of vapor droplets and cavitation/bubble formation in liquids. The original work of Becker and Döring [1] (based on the earlier work of Volmer and Farkas), and subsequently refined by Zeldovich [2], forms what is now referred to as classical nucleation theory. For the simplicity of such a theory, its predictions are in remarkably good agreement with experiments, especially regarding the supersaturation dependence of the classical rate of nucleation [3]. However, it is now accepted that classical nucleation theory does not predict correctly the temperature dependence of the nucleation rate: for the range of experimentally studied temperatures, the classical theory underpredicts the observed rates by several orders of magnitude (usually three to six orders) [4].

A proposal by Lothe and Pound [5] to resolve the discrepancy between classical and experimental predictions triggered a long-standing controversy in the field. They suggested that inclusion of the droplet's translational and rotational degrees of freedom in the calculation of the nucleation rate would modify classical predictions by a factor of $10^{14}-10^{19}$. Reiss, Katz, and Cohen [6] suggested a different calculation of the translational correction (in addition arguing that there is no rotational contribution) that was several orders of magnitude smaller. Subsequent counterarguments [7] left this an open problem, thereby questioning the validity of classical nucleation theory and, more generally, the formulation of a consistent theory of nucleation.

More recently, Oxtoby and co-workers [8–10], as well as Barrett [11], used density-functional theory to alleviate these discrepancies. In fact, Talanquer and Oxtoby [9] argued that corrections due to translational invariance are almost negligible. Moreover, detailed attempts of semiempirical fits [10] seem to overestimate the temperature dependence of the nucleation rate (except at very low temperatures). Ford [12] argued that nucleating clusters, as described by the classical theory, do not satisfy the two nucleation theorems that relate their properties to the supersaturation and temperature dependence of the rate. He suggested that the discrepancy emerges from the classical nucleation theory assumption that the free energy of the nucleating droplet refers to a fixed cluster rather than to one that may nucleate anywhere in the system volume.

In this work, rather than proposing an entirely new approach (since, for example, the correct prediction of the supersaturation dependence suggests that there are some sound arguments in the classical theory), we will attempt a hybrid approach to establish a connection between classical density-functional theories of nucleation and earlier work on field-theoretic descriptions of condensation. In doing so, we will obtain a consistent formalism that will incorporate in a unified way all the dependences of the nucleation rate including the translational correction.

Our starting point will be Langer's field-theoretic ap-

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proach [13–15], and in particular the phenomenological field-theoretic description of condensation and the theory of decay of metastable states. We will formulate the theory through a prism that can be characterized as quantum-mechanical: it has been inspired by quantum-mechanical phase transitions, specifically the condensation of a Bose gas to a macroscopically occupied ground state (Bose-Einstein condensation). In this framework, not only density-functional theory becomes manifest through the appropriate limit, but a unified theoretical framework can be established.

Whereas we will follow the approach of previous field-theoretic calculations and some results of a general theory of the decay of metastable states, we will concentrate on the contribution of the translational eigenmodes to the nucleation rate. According to Ref. [15], the nucleation rate may be expressed as a function of three factors: the dynamical prefactor, the statistical prefactor, and the excess droplet free energy. For the theory presented here, the determination of the statistical prefactor involves the calculation of the product of the eigenvalues of an integro-differential operator evaluated at the (metastable) uniform and (saddle) nonuniform mean-field configurations, a calculation considerably more complex than that for the square-gradient, local function of Refs. [13,15]. The calculation of the dynamical prefactor requires the determination of the dynamical equations of motion. The complete calculation of these two factors is left for future investigations: herein, we shall concentrate on the contribution of the translational eigenmodes. In deriving their contribution to the nucleation rate, we shall determine their functional form in three dimensions, a plausible result, but to our knowledge not proven before. Thus, we extend previous calculations of the translational eigenmodes to three dimensions without assuming the familiar one-dimensional hyperbolic-tangent density profile.

This work is structured as follows. In Sec. II, we present our formalism, and we establish a connection to density-functional theory by deriving the Euler-Lagrange equation for the order-parameter profile (be it uniform or nonuniform) starting from a quantum-mechanical Hamiltonian in second quantized notation. In Sec. III, we use symmetry arguments in three dimensions to relate the functional form of the translational eigenmodes to the mean-field droplet profile. In Sec. IV, we formally calculate the contribution of the translational eigenmodes to the nucleation rate. In Sec. V, as an alternative to the numerical solution of the boundary-value integro-differential problem associated to the Euler-Lagrange equation, we propose a variational solution, and we suggest a perturbative calculation involving moments of the proper (exact) attractive interaction potential. The final section discusses and summarizes our findings.

II. FORMALISM

A. Order parameter

Motivated by recent studies of Bose gases and their condensation transition and in an attempt to relate density-functional theories and field theoretic descriptions, we shall consider the physics of a classical first-order phase transition starting from a quantum-mechanical Hamiltonian. The rationale of our approach is based on recent experimental observations [16] that a gas of interacting bosons in an external potential (harmonic trap) condenses to a macroscopic ground state, i.e., a quantum-mechanical ground state that is macroscopically occupied. This quantum-mechanical phase transition, predicted by Einstein in the early days of quantum-statistical mechanics [17], is the well-known Bose-Einstein condensation. The behavior of the condensate below the condensation temperature has been found (cf. Ref. [18] and references therein) to be in very good agreement with predictions of classical mean-field theoretical analyses. The order parameter of the transition is the expectation value of the wave-function operator. Therein lies the proposed analog between condensed bosons forming a (quantum mechanical) ground state ‘‘droplet’’ and a cluster of condensed molecules forming a liquid droplet. This analog becomes more plausible by considering the classical droplet in terms of Langer’s [13] field-theoretic description of condensation.

To make these statements more precise, we consider the local particle density $\rho(\mathbf{r})$ and the total particle number of N interacting bosons to be

$$\rho(\mathbf{r})=\Psi^{\dagger}(\mathbf{r})\Psi(\mathbf{r}), \tag{1a}$$

$$N=\int_V d\mathbf{r}\,\rho(\mathbf{r}), \tag{1b}$$

where Ψ and $\Psi^{\dagger}$ are boson annihilation and creation field operators, and the integral is taken over the system volume V. The description of the system in terms of a local density is reminiscent of classical density-functional theories of fluids where the system free energy is expressed as a functional of the inhomogeneous fluid density $\rho(\mathbf{r})$.

The dynamics of the system are determined by the many-body Hamiltonian that in second quantization is written as [18]

$$\hat{H}=\int d\mathbf{r}\,\hat{\Psi}^{\dagger}(\mathbf{r})\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\right]\hat{\Psi}(\mathbf{r})+\tfrac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,\hat{\Psi}^{\dagger}(\mathbf{r})\hat{\Psi}^{\dagger}(\mathbf{r}')\times V_{\mathrm{int}}(\mathbf{r}-\mathbf{r}')\hat{\Psi}(\mathbf{r}')\hat{\Psi}(\mathbf{r}), \tag{2}$$

where V_{int} is the two-particle interaction potential.

Following ideas introduced by Bogoliubov [19], and later elaborated by Gross [20] and Pitaevskii [21], the wave function may be separated as

$$\hat{\Psi}(\mathbf{r},t)=\Phi(\mathbf{r},t)+\hat{\Psi}'(\mathbf{r},t), \tag{3}$$

where the function Φ is the expectation value of the field operator and it becomes the Bose macroscopic wave function. It is no longer an operator, but a regular wave function, and it plays the role of the order parameter for the phase transition, the local condensate density being its magnitude squared. Even though more complicated theories exist (such as the Hartree-Fock-Bogoliubov approximation [22]) where corrections to the expectation value are taken into account, many theoretical studies [18] have shown that the mean-field approximation of neglecting (quantum) fluctuations $\hat{\Psi}'$

gives good agreement with experimental findings. For Bose gases, the validity of the mean-field approximation improves with decreasing temperature.

The interaction potential is decomposed into two parts: a nonlocal part and a local part. In this work, the nonlocal part will be considered to be solely attractive, whereas the local part will be repulsive. Thus, the interaction potential is decomposed as follows:

$$V_{\mathrm{int}}(\mathbf{r}-\mathbf{r}')=V_{\mathrm{att}}(|\mathbf{r}-\mathbf{r}'|)+g\,\delta(\mathbf{r}-\mathbf{r}'). \qquad (4)$$

Inclusion of an explicit attractive term in the two-particle interaction term signifies a departure from usual analyses of Bose-Einstein condensation. However, it is important in this work because the attractive interaction is essential in descriptions of gas-to-liquid transitions. We will also show that it has the significant consequence of breaking the symmetry between the two uniform stable states. A similar decomposition is performed in classical density-functional theories where the interaction potential is divided into a repulsive, hard-core part and an attractive part, which for simplicity is usually taken to be a Yukawa or Lennard-Jones (6-12) potential. It should be noted, however, that the nucleation rate will be sensitive to the (choice of the) pair potential. This very sensitive dependence, that arises from the dependence of the surface tension on the inverse range of the attractive potential and is explicit in classical nucleation theory, indicates that it would be very useful, if possible, to determine a method to provide information on the pair potential based on experimentally measured quantities. We will return to this point later in the text.

The local part is characterized by a single parameter g. In the quantum-mechanical literature, this approximation, known as the Hartree-Fock approximation, corresponds to considering only binary, hard-sphere collisions, characterized by the parameter g. The representation of short-range (local) interactions via a single parameter is approximate and it implies the existence of a length scale. In the case of Bose-Einstein condensation, g is proportional to the s-wave scattering length, which is a measure of the strength and range of the pair potential: in particular, for a hard-sphere fluid the scattering length is the hard-sphere diameter. In the case of a classical theory, the presence of the δ function ensures a hard-sphere excluded volume. Its origin becomes apparent by starting from a lattice (discrete) formulation where the δ function avoids double occupancy of a given lattice site.

The nonlocal part of the interaction will be left unspecified for the moment: we shall only require that it be spherically symmetric and of finite range. We will see in Sec. V how a physically motivated, approximate ansatz for the droplet profile can be used to determine self-consistently the moments of the attractive interaction weighted by the assumed droplet profile squared. Considering the plausibility (and the connection to the experimental observations) of this ansatz, we expect that this methodology will reflect quite accurately the properties of the nonlocal term.

For a time-independent, real order parameter $\phi(\mathbf{r})$, the free-energy functional that arises from the many-body Hamiltonian becomes

$$E[\phi]=\int d\mathbf{r}\left[\frac{\hbar^2}{2m}(\boldsymbol{\nabla}\phi)^2+\tfrac{1}{2}f(\mathbf{r})\phi^2+\frac{g}{2}\phi^4\right], \qquad (5)$$

where the attractive term $f(\mathbf{r})$ has been defined to be

$$f(\mathbf{r})=\int d\mathbf{r}'\,V_{\mathrm{att}}(|\mathbf{r}-\mathbf{r}'|)\phi^2(\mathbf{r}')<0. \qquad (6)$$

The functional corresponding to the grand-canonical partition function, the appropriate ensemble for analyzing first-order phase transitions, is obtained by performing a Legendre transformation to $S=E-\mu N$, where μ is the thermodynamic chemical potential and $N=\int_V d\mathbf{r}\,\phi^2(\mathbf{r})$. Accordingly,

$$S[\phi]=\int d\mathbf{r}\left\{\frac{\hbar^2}{2m}(\boldsymbol{\nabla}\phi)^2-[\mu-\tfrac{1}{2}f(\mathbf{r})]\phi^2+\frac{g}{2}\phi^4\right\}. \qquad (7)$$

The grand-canonical partition function is obtained by evaluating a functional integral over all possible field configurations, weighted by the Boltzmann probability distribution [with $\beta=(k_BT)^{-1}$, where T is the absolute temperature and k_B the Boltzmann constant],

$$\Xi\equiv\int D[\phi]e^{-\beta S[\phi]}, \qquad (8)$$

and the appropriate thermodynamic potential is

$$\beta\Omega\equiv-\ln(\Xi). \qquad (9)$$

The functional integral may be evaluated by the saddle-point method. The stationary extremum equation is obtained by extremizing the exponent $\beta S[\phi]$ with respect to variations of the field $\phi(\mathbf{r})$. The appropriate functional derivatives are discussed in Appendix A. Consequently, for a spherically symmetric attractive potential, the Euler-Lagrange equation for the mean-field order parameter becomes

$$\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\phi+[\mu-f(\mathbf{r})]\phi-g\phi^3=0. \qquad (10)$$

In Appendix A, we also derive Eq. (10) by considering a time-dependent variational principle: the presentation follows closely the derivation of the static Gross-Pitaevskii equation in theories of Bose-Einstein condensation. The final Euler-Lagrange equation is obtained by rescaling the chemical potential and the attractive and local interactions by $2m/\hbar^2$ to obtain

$$\boldsymbol{\nabla}^2\phi+[\mu-f(\mathbf{r})]\phi-g\phi^3=0. \qquad (11)$$

B. Comparison with previous theories

Equation (11), derived from a quantum-mechanical Hamiltonian and valid in d dimensions, is the integro-differential equation whose study is the main aim of our work. We will be interested in spatially nonuniform solutions, and in particular in the heteroclinic solitary wave solution that corresponds to the saddle-point configuration of

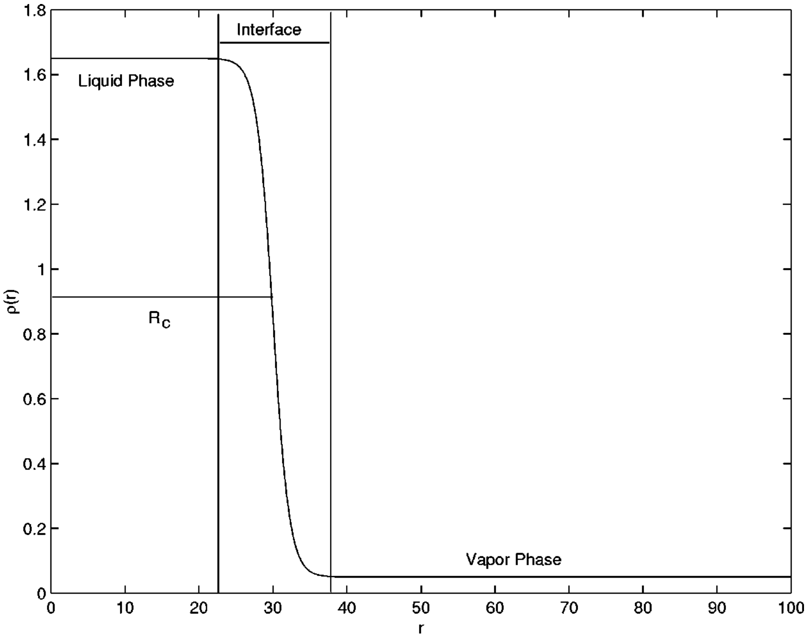

FIG. 1. A schematic diagram of the density profile for a spherically symmetric droplet as a function of the distance from the droplet center. Three different fluid-density regions are clearly indicated: liquid phase, interface, and vapor phase. The droplet radius is R_c, while the interfacial region, the region between the two vertical lines, is approximately 2ξ, where ξ is interfacial correlation length.

the functional integral. The applicability of this equation, and of the associated formalism, is quite general since it has been derived from first-principles quantum mechanics. Of course, the validity of the theory depends on our assumptions about the nature of interparticle interactions (two-body), the pair-potential decomposition, and the continuum approximation (an approximation valid for an order parameter that varies slowly over distances of the order of the interaction range, which, in a lattice formulation, should be much larger than the lattice spacing). The theory can be used equally well in studies of liquids (such as helium) where quantum effects may be significant, and of classical gases. In the latter case the square gradient term can be safely neglected (the formal limiting procedure is $\hbar \rightarrow 0$) to obtain a classical field-theoretic description of inhomogeneous systems. Such a description has many features, and significant differences, with density-functional theory, as discussed in Ref. [24] and Appendix B. The approximation of neglecting the kinetic energy of the condensate is known in the Bose gas literature as the Thomas-Fermi approximation [23]. Thus, in the classical limit the Thomas-Fermi approximation becomes, for all measurement purposes, exact.

Equation (11) [and the initial functional Eq. (7)] provides the desired connection between density-functional theories of nucleation and field-theoretic descriptions of condensation. Similarities to density-functional theories of nucleation become apparent by noting that the attractive term $f(\mathbf{r})$ is the term referred to as $\phi_{\text{eff}}(\mathbf{r})$ in density-functional theories; see, for example, Ref. [8]. A more detailed comparison of our work (and in particular the limit $\hbar \rightarrow 0$) with classical density-functional theory is presented in Appendix B.

For concreteness, we consider the gas-to-liquid transition, even though the arguments used to study supercooling and condensation apply equally well to superheating and cavitation. We are looking for solutions of Eq. (11) that describe a liquid dropletlike configuration in contact with a metastable vapor at a fixed chemical potential. Since the vapor is metastable, its chemical potential is greater than the chemical potential of either phase at coexistence, and hence it is supersaturated with respect to its vapor pressure at coexistence. Consequently, the density of the liquid inside the dropletlike solution is not expected to be the liquid density at coexistence, as shown numerically in Ref. [8]; its value is to be determined from the solution of the integro-differential equation.

We will use the boundary conditions to specify the local-interaction parameter. For a uniform fluid the derivatives vanish, and the attractive term $f(\mathbf{r})$ becomes position-independent: its value is determined by the spherically symmetric interaction at an arbitrary position $\mathbf{r}$ in the system volume with a background of the uniform fluid of density ρ. Thus, it becomes $f(\mathbf{r}) = f = -\alpha\rho$, where α is the (positive) integrated strength of the attractive potential,

$$\alpha = -4\pi \int dr\, r^2 V_{\text{att}}(r). \tag{12}$$

As in density-functional theories where a reference state, usually taken to be a uniform hard-sphere fluid of density ρ, is defined, Eq. (12) may be used to determine an appropriate ''reference'' state with a density-dependent chemical potential as follows:

$$\mu_{\text{ref}}(\rho) \equiv \mu + \alpha\rho. \tag{13}$$

Since the density of a uniform fluid satisfies Eq. (11), the local-interaction parameter is $g = \mu_{\text{ref}}/\rho$. Note that this procedure ensures that the uniform fluid density is an extremum (minimum) of the mean-field thermodynamic potential.

We now consider the case of the droplet being at the origin of the (spherical) coordinate system. Looking at the density from the origin outwards, we observe a profile similar to the one sketched in Fig. 1, or, equivalently, to the profile shown in density-functional-theory works, cf., for example, Refs. [8–10]. Given the generic form of the nonuniform density profile, the local-interaction parameter can be specified by considering the $r\to\infty$ limit, namely at $r\gg R_c$, where R_c is the droplet radius. The approach to the uniform steady state (the metastable vapor with density ρ_v) will yield outside the dropletlike solution $\phi\to\sqrt{\rho_v}$. As before, the derivatives vanish in that limit, the attractive term becomes position-independent, and its value is $\lim_{|\mathbf{r}|\to\infty} f(\mathbf{r}) = -\alpha\rho_v$. Since far away from the center of mass of the dropletlike solution the uniform state ρ_v is an asymptotically exact solution,

$$g=\frac{\mu+\alpha\rho_v}{\rho_v}=\frac{\mu_{\mathrm{ref}}(\rho_v)}{\rho_v}. \tag{14}$$

These similarities with density-functional theory should not obscure some important differences. The nonuniform solution of the Euler-Lagrange equation is a mean-field solution, thus fluctuations about it are only accounted for perturbatively in the evaluation of the functional integral. In density-functional theories, the nonuniform density profile is taken by construction to be the profile that minimizes the free energy; the corresponding free energy evaluated at the extremum becomes the intrinsic equilibrium free energy. Therefore, the resulting profile contains fluctuation corrections to infinite order, as discussed in Ref. [11] and the Appendix of Ref. [24]. Of course, applications of density-functional theories to real fluids necessitate approximate expressions for the reference (hard-sphere) state. The perturbative nature of our work and the associated approximations with respect to density-functional theory become more precise in Appendix B, where we also argue that in the classical limit the natural choice for the order parameter is the fluid density (and not its square root).

The droplet-profile equation and the corresponding functional Eq. (7) are very similar to the Euler-Lagrange equation and the corresponding ϕ^4 functional proposed in the original field-theoretic treatment of condensation [13]. Langer's arguments were based on the expectation of universality of the phenomenology of condensation, hence the justification for the simplest possible ϕ^4 model that could describe the nucleation process. The original analysis was later applied [15] to the condensation of a supersaturated vapor close to the critical point by deriving the appropriate free energy by a coarse-graining procedure. Our attempt to relate density-functional theory to macroscopic theories of Bose-Einstein condensation is similar in spirit. A significant difference with Langer's analysis is the treatment of the symmetry-breaking term, i.e., the external field that breaks the symmetry between the two uniform stable states.

In the usual ϕ^4 Landau-Ginzburg free-energy functional (without a cubic nonlinearity), the Euler-Lagrange equation has three uniform solutions. Two of them are stable with the same free energy while the third is unstable with higher free energy: it corresponds to a saddle point of the functional integral. The ad hoc introduction of an external field breaks the symmetry of the two stable states. Thus, the presence of the external field becomes essential in analyses of first-order transitions (and consequently of nucleation) since nucleation is associated to the occurrence of an unusually large fluctuation of the metastable state order parameter that is large enough to overcome the saddle-point free-energy barrier. As a result, the system ends up at the stable uniform state, which is the free-energy global minimum. It is this configuration that spatially mediates the transition from the metastable to the globally stable state through the saddle point that has the primary weight and significance in assessing the rate at which nucleation occurs.

The incorporation of a small external field may be physically motivated (for example, the stabilizing gravitational field in studies of gas/liquid interfaces), however it cannot significantly contribute to breaking the symmetry of the steady states. Langer's methodology [13] and ansatz are valid only in the limit of a small external field. In particular, the density (the square of the order parameter) of the two uniform states cannot be altered significantly by the small asymmetric term. In this spirit, the order-of-magnitude difference between a classical liquid and gas density cannot be accounted for by such a small perturbation. Our theory, being an integro-differential ϕ^4-type theory, breaks the symmetry of the steady states by the long-range nature of the attractive potential (as happens in density-functional theory, Refs. [8–11]). The attractive term $f(\mathbf{r})$ *distinguishes* between the uniform density states (gas and liquid), and it gives rise to a nonuniform profile that asymptotes to the liquid density close to the origin and to the gas density at $r\to\infty$. In this sense, even though the rest of the terms are similar to the ones appearing in a typical ϕ^4 theory, the symmetry-breaking long-range interaction term has replaced the qualitatively admissible, but quantitatively insufficient, small external field perturbation.

Even without solving Eq. (11), a qualitative argument shows how the attractive term breaks the symmetry in nonuniform fluids. Far away from the center of mass of a spherically symmetric dropletlike solution, the background fluid is a metastable vapor of constant density. Thus, the attractive term becomes $-\alpha\rho_v$. As the center of mass of the droplet is approached, the value of the attractive term becomes dependent on position, thereby differentiating between the two phases. The requirement that the liquid density be a solution of the Euler-Lagrange equation at the center of the droplet implies

$$\lim_{|r|\to 0} f(\mathbf{r})=\frac{1}{\rho_v}[\mu(\rho_v-\rho_l)-\alpha\rho_v\rho_l]. \tag{15}$$

Interestingly, at the critical point, $\rho_l=\rho_v$, the theory becomes symmetric. Furthermore, the $r\to 0$ limit of the attractive term implies that the density profile has a nonzero (possibly very small) gradient within the range of the attractive potential.

In closing this subsection, we would like to summarize the aim of this work in presenting such an approach for the theory of nucleation. Our purpose is to unify under a first-principles setting (based on firm quantum-mechanical grounds) two different theories that have been used to study nucleation problems: the simplest phenomenological theory that captures the essential characteristics but has many approximations and is not necessarily physically realistic (Langer's field theoretic description of condensation), and the more physically realistic but not motivated by first principles, nor clearly related to translational invariance, density-functional theory. We believe that the theory discussed in this work puts under firm ground the connection between the two showing how the features of the phenomenological theory are manifested, incorporating in a unified way translational-invariance effects, and finally having the appropriate limit for a classical gas.

III. BROKEN SYMMETRY AND TRANSLATIONAL INVARIANCE

The importance of translational invariance in calculations of the nucleation rate stems from the observation that the contribution of the translational eigenmodes renders it extensive. Formally this arises from the integration over the zero-eigenvalue modes of the linearization around the spatially nonuniform mean-field solution. These Goldstone eigenmodes, corresponding to a spontaneously broken continuous symmetry (translational invariance), are infinitesimal translations of the droplet interface that leave the functional integrand invariant. Their degeneracy equals the number of spatial dimensions. For a finite but large system, the eigenvalues are not exactly zero, but tend to zero as the system size goes to infinity.

As in the case of the ϕ^4 functional, the translational eigenmodes of the functional Eq. (7) may be related to the spatial derivatives of the mean-field order-parameter profile, even in the presence of the nonlocal attractive term. The derivation follows Ref. [13], without the additional approximation to neglect the first-order derivative term in the equation that determines the mean-field profile: this approximation is valid close to the coexistence curve, as may be easily seen by scaling lengths by the critical radius and taking the large R_c limit.

To leading order in fluctuations, these eigenvectors are obtained by linearizing Eq. (11). We exploit spherical symmetry to decompose the order-parameter field into

$$\phi(\mathbf{r}) = \phi_0(r) + \epsilon \Phi_1(r,\theta,\phi). \tag{16}$$

The zeroth-order equation becomes

$$\nabla^2 \phi_0(r) + [\mu - f_0(r)]\phi_0(r) - \frac{\mu_{\text{ref}}(\rho_v)}{\rho_v}\phi_0^3(r) = 0, \tag{17a}$$

with

$$f_0(r) = \int_V d\mathbf{r}'\, V_{\text{att}}(|\mathbf{r}-\mathbf{r}'|)\phi_0^2(r'). \tag{17b}$$

Equation (17a) is just the Euler-Lagrange equation that determines the droplet profile; in addition, the cubic coupling constant has been specified as discussed in Sec. II. The order-parameter decomposition ensures that f_0, for a central attractive potential, is spherically symmetric. Consequently, by choosing appropriately the coordinate system, Eq. (17b) takes the form

$$f_0(r) = \frac{2\pi}{r}\int_0^\infty dr'\, r'\, \phi_0^2(r') \int_{|r-r'|}^{r+r'} dz\, z V_{\text{att}}(z). \tag{18}$$

In the case of the Yukawa potential, Eq. (C1), integration over the variable z gives the first equation in the Appendix of Ref. [8].

The order ϵ equation is

$$\nabla^2 \Phi_1(\mathbf{r}) + [\mu - f_0(r)]\Phi_1(\mathbf{r}) - 3\frac{\mu_{\text{ref}}(\rho_v)}{\rho_v}\phi_0^2(r)\Phi_1(\mathbf{r}) - 2\phi_0(r) f_1(\mathbf{r}) = 0, \tag{19a}$$

where

$$f_1(\mathbf{r}) = \int_V d\mathbf{r}'\, V_{\text{att}}(|\mathbf{r}-\mathbf{r}'|)\phi_0(r')\Phi_1(\mathbf{r}'). \tag{19b}$$

We express $\mathbf{r}$ in spherical coordinates and separate variables as follows:

$$\Phi_1(r,\theta,\phi) = \phi_1(r) Y_{lm}(\theta,\phi), \tag{20}$$

where $Y_{lm}(\theta,\phi)$ are the (l,m) spherical harmonics. Equation (19a) reexpressed in spherical coordinates and using properties of the spherical harmonics becomes

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} + \mu - f_0(r) - 3\frac{\mu_{\text{ref}}(\rho_v)}{\rho_v}\phi_0^2(r)\right] \times \phi_1(r) Y_{lm}(\theta,\phi) - 2\phi_0(r) f_1(r,\theta,\phi) = 0. \tag{21}$$

The functional form of $\phi_1(r)$ is obtained by considering the explicit differentiation of Eq. (17a) with respect to one Cartesian coordinate, say x. Differentiation yields

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{2}{r^2} + \mu - f_0(r) - 3\phi_0^2(r)\frac{\mu_{\text{ref}}(\rho_v)}{\rho_v}\right]\frac{\partial \phi_0(r)}{\partial x} - \phi_0(r)\frac{\partial f_0(r)}{\partial x} = 0. \tag{22a}$$

The derivative of the attractive term may also be expressed as

$$\frac{\partial f_0(r)}{\partial x} = \sin\theta\cos\phi\frac{d f_0(r)}{dr} \tag{22b}$$

$$= 2\int_V d\mathbf{r}'\, V_{\text{att}}(|\mathbf{r}-\mathbf{r}'|)\phi_0(r') \times \frac{d\phi_0(r')}{dr'}\sin\theta'\cos\phi'. \tag{22c}$$

The first equality is a consequence of f_0 being a function of magnitude r due to spherical symmetry; the same change of variables, of course, applies to $\partial\phi_0(r)/\partial x$. The second was obtained by changing the differentiation variable from x to x', integrating by parts, and finally dropping the boundary terms since the interaction potential has a finite range.

Equations (21) and (22) may be compared by considering real combinations of the $l=1$ spherical harmonics: the l-dependent angular part of Eq. (21) remains unchanged since the eigenvalue is independent of m and any linear combination of eigenfunctions of a degenerate energy level remains an eigenfunction with the same eigenvalue. Since Eq. (21) is linear in Y_{11}, and $Y_{11}+Y^{\star}_{11}\sim\sin\theta\cos\phi$, the appropriate combination is obtained by adding it to its complex conjugate. Comparison of the resulting equation with Eq. (22a) shows that $\phi_1(r)$ may be identified with $d\phi_0(r)/dr$.

A similar procedure for the other Cartesian coordinates leads to the conclusion that the three complex translational eigenmodes of the three-dimensional Euler-Lagrange equation, in the presence of the nonlocal attractive term, are

$$\Phi_{1,m}(r,\theta,\phi)=\frac{d\phi_0(r)}{dr}Y_{1m}(\theta,\phi)\quad\text{with}\quad m=0,\pm1. \tag{23}$$

IV. TRANSLATIONAL EIGENMODES AND NUCLEATION RATE

The determination of the nucleation rate from the functional integral Eq. (8) has been discussed extensively in the past, starting from Langer's initial calculation [13] (see, also, Ref. [27]) and summarized in Ref. [28]. Under some general assumptions, for example the existence of a coarse-grained free energy, small supersaturation, and a Gaussian approximation of the functional integral, the nucleation rate may be expressed as

$$I=\frac{\kappa}{2\pi}\Omega_0\exp(-\beta\Delta S), \tag{24}$$

where κ is referred to as the dynamical prefactor, Ω_0 as the statistical prefactor, and ΔS is the excess droplet free energy (activation energy of the nucleating droplet),

$$\beta\Delta S=\beta S_{\text{saddle}}-\beta S_{\text{metastable}}. \tag{25}$$

The dynamical prefactor, which depends on dynamical properties of the system, is the initial growth rate of a droplet that is slightly larger than the critical size. The statistical prefactor Ω_0, a generalization of the Zeldovich factor, is a measure of the phase-space volume of the saddle point. It contains contributions of Gaussian fluctuations about the (uniform) metastable and the (spatially nonuniform) saddle-point configurations. It consists of two parts: $\mathcal{V}$, the phase-space volume spanned by the translational eigenmodes (in general, by all the eigenmodes that correspond to spontaneously broken symmetries), and another term that incorporates the effect of all other fluctuations about the metastable and saddle configurations. The latter part may be viewed as a leading-order correction to the droplet excess free energy, arising from the configurational entropy of the droplet. The complete expression for Ω_0 is shown in, for example, Ref. [15], whereas an alternative formal expression that relates the nucleation rate to the imaginary part of the (true) system free energy is presented in Ref. [28].

As mentioned in the Introduction, herein we shall concentrate on the factor that arises from the translational eigenmodes. The phase-space volume $\mathcal{V}$ may be reexpressed as (see, for example, Refs. [26,27])

$$\mathcal{V}=VJ_{\text{tran}}, \tag{26}$$

where V is the system volume and J_{tran} is the Jacobian for a change of variables to the collective coordinates associated to the translational eigenmodes. The Jacobian J_{tran} may be evaluated by integrating over the translational eigenmodes. The volume that these modes span is calculated by noting that the free-energy functional is invariant under translations of the droplet center of mass, i.e., it is invariant under transformations of the form

$$\delta\phi_i(\mathbf{r})=\Phi_{1,i}(\mathbf{r})dx_i\quad\text{for}\quad i=x,y,z. \tag{27}$$

The vectors $\Phi_{1,i}(\mathbf{r})$ are orthogonal, real combinations of the complex translational eigenvector. Since their length is related to a volume integral of $\Phi_1(\mathbf{r})$, their contribution to the nucleation-rate prefactor becomes

$$VJ_{\text{tran}}=\int|\delta\phi_x\delta\phi_y\delta\phi_z|=\int_V d\mathbf{r}\left[\tfrac{1}{3}\int_V d\mathbf{r}'|\Phi_1(\mathbf{r}')|^2\right]^{3/2} \tag{28a}$$

$$=V\left[\frac{4\pi}{3}\int_0^\infty dr\,r^2\left(\frac{d\phi_0}{dr}\right)^2\right]^{3/2}. \tag{28b}$$

V. DROPLET PROFILE

Our calculations up to this point have been fairly general: under the previously mentioned assumptions, and specifically the interaction-potential decomposition and the requirement that the attractive potential be central, the functional form of the attractive pair potential was left unspecified. If an attractive potential is specified explicitly, then Eq. (17a) can be solved numerically as an integro-differential boundary value problem to identify the density profile of the droplet.

However, in the literature on the subject [8–11], a number of potentials—with different decay properties—have been used to model the attractive interaction [such as the Yukawa potential, or the Lennard-Jones (6-12) potential usually decomposed according to the Weeks-Chandler-Anderson [25] perturbative scheme]; the reason for such choices (in the density-functional theory approaches) has been mostly simplicity in the ensuing numerical computations rather than detailed modeling of the intermolecular interaction. For this reason, we follow a different approach: since detailed information on the interaction potential may not be available for an arbitrary system, we will use physical intuition to develop an approximate but self-consistent strategy. In particular, we know that close to the center of the droplet, the density is almost constant and equal to a liquid density ρ_l. On the other hand, away from the droplet surface the density quickly becomes the metastable vapor density ρ_v. Hence, the main density variation occurs over a short interfacial length scale and is quite rapid there, while away from the interfacial region the asymptotic properties (of the liquid inside and the vapor outside) are rapidly reached. Furthermore, as pointed out by Langer, a simpler (symmetric) theory with the expected phenomenological behavior is a Landau-Ginzburg ϕ^4 free energy in which the density follows a hyperbolic tangent profile. Hence, based on this argument and the universality suggested by Langer [14], in addition to the physical intuition mentioned above, we postulate a droplet profile of the form

$$\phi_0(r) = c_1 \tanh\left(\frac{r-R_c}{\xi}\right) + c_2, \tag{29}$$

where the constants c_1 and c_2 are chosen such that the profile satisfies the boundary conditions at the origin and at infinity,

$$c_1 = \tfrac{1}{2}(\sqrt{\rho_v} - \sqrt{\rho_l}), \quad c_2 = \tfrac{1}{2}(\sqrt{\rho_v} + \sqrt{\rho_l}). \tag{30}$$

The variable R_c is the radius of the critical droplet and ξ is the interfacial correlation length. Equation (29) defines a family of curves parametrized by the critical radius, a quantity that remains unspecified by the differential equation (and the boundary conditions): it may, however, be calculated from the classical theory of nucleation. The density at the center of mass of the droplet will be specified from the normalization condition on the average number of particles in the system volume (neglecting fluctuation corrections). A plot of the proposed droplet-profile trial function is shown in Fig. 1.

The proposed profile is a reasonable approximation only for $R_c \gg \xi$, i.e., close to the coexistence curve and far away from the spinodal or the critical point. It should be remarked that in modeling the density profile, it is desirable to have a smooth functional dependence. Lack of smoothness (as, e.g., would be the case for a piecewise constant profile near the origin) would result in highly unphysical discontinuities and blowups in the derivatives of the profile. Furthermore, previous modeling attempts (see, for example, Langer's work in Ref. [13]) have used a similar tanh-like approximation that we believe is the most intuitively appropriate since the profile approaches the steady-state value *exponentially fast* away from the surface of the droplet. Nevertheless, for cases where $R_c \approx \xi$, other profiles have been proposed [26], but additional parameters are introduced that have to be determined variationally.

For the postulated form of the droplet profile, the Jacobian may be evaluated, up to exponentially small corrections to extensivity, in terms of the polylogarithm function $F(n,z)$,

$$J_{\mathrm{tran}} = \left(\frac{4\pi}{3} c_1^2 \xi\right)^{3/2} \left\{\frac{-2[z + (1+z)F(2,-z)]}{3(1+z)}\right\}^{3/2}, \tag{31a}$$

where

$$z \equiv \exp(2R_c/\xi), \tag{31b}$$

and the polylogarithm function, also called Jonqière's function, is

$$F(n,z) \equiv \sum_{k=1}^{\infty} \frac{z^k}{k^n}. \tag{31c}$$

Having analyzed the properties of (and some of the results that can be obtained using) the postulated droplet wave function, let us analyze now our methodology. Since this profile is physically plausible, it is natural to expect that the properties of the attractive interaction that are consistent with such an ansatz [for the solution of Eq. (17a)] should be a very good approximation to the unknown (exact) attractive potential. Hence, we will use the droplet profile to determine the intermolecular interaction potential perturbatively. In essence, this becomes an inverse problem, i.e., how to reconstruct the attractive potential from the requirement that the proposed function satisfy the integro-differential equation perturbatively (to every order, even though for numerical computations the series has to be truncated at a finite order). The reason we consider such an approach is the previously mentioned sensitive dependence of the nucleation rate on the interaction range.

This is done by dividing the system volume into three regions and matching the solution order-by-order in perturbation. The system volume is divided into a region close to the center of the droplet where $\phi_0 = \sqrt{\rho_l}$ (region A), a region far away from the origin where $\phi_0 = \sqrt{\rho_v}$ (region B), and the transition region where the interface lies (region C). This division is valid as long as the system is not close to the critical region nor to the mean-field spinodal ($\xi \ll R_c$), namely the interface is well-defined. The consistency requirement that $\phi_0(r)$ be a solution in regions A and B is easily obtained by noting that gradients vanish and the order parameter attains its limiting value. In the transition region, the solution is expanded about $r = R_c$. Schematically, the profile and the attractive term should satisfy the following.

Region A,

$$r \ll R_c \quad (r \to 0), \quad \phi_0 = \sqrt{\rho_l}$$

with

$$f_0(r) = \frac{1}{\rho_v}[\mu(\rho_v - \rho_l) - \alpha \rho_v \rho_l]; \tag{32a}$$

region B,

$$r \gg R_c \quad (r \to \infty), \quad \phi_0 = \sqrt{\rho_v}$$

with

$$f_0(r) = -\alpha \rho_v; \tag{32b}$$

transition region,

$$r = R_c + y \quad (y \ll R_c),$$

$$\phi_0(R_c+y)=c_2+c_1\left(\frac{y}{\xi}-\frac{y^3}{3\xi^3}+\frac{2y^5}{15\xi^5}\right)+O[(y/\xi)^7]. \tag{32c}$$

The consistency conditions are obtained by requiring that the perturbative expansion in the transition region satisfy the integro-differential equation order-by-order. The ensuing first four self-consistency equations are (it is easy to extend the series to higher orders)

$$c_2[\mu-f_0^{(0)}]-c_2^3\frac{\mu_{\mathrm{ref}}(\rho_v)}{\rho_v}+\frac{2c_1}{\xi R_c}=0, \quad O(0), \tag{33a}$$

$$-\frac{2c_1}{\xi^3}+\frac{c_1}{\xi}[\mu-f_0^{(0)}]-3\frac{c_1c_2^2}{\xi}\frac{\mu_{\mathrm{ref}}(\rho_v)}{\rho_v}-c_2f_0^{(1)}-\frac{2c_1}{\xi R_c^2}=0, \quad O(1), \tag{33b}$$

$$-\frac{c_2}{2}f_0^{(2)}+\frac{2c_1}{\xi R_c}\left(\frac{1}{R_c^2}-\frac{1}{\xi^2}\right)-3\frac{c_2c_1^2}{\xi^2}\frac{\mu_{\mathrm{ref}}(\rho_v)}{\rho_v}-\frac{c_1}{\xi}f_0^{(1)}=0, \quad O(2), \tag{33c}$$

$$\frac{8c_1}{3\xi^5}-\frac{2c_1}{\xi R_c^2}\left(\frac{1}{R_c^2}-\frac{1}{\xi^2}\right)-\frac{c_2}{6}f_0^{(3)}-\frac{c_1}{2\xi}f_0^{(2)}+\frac{c_1}{\xi^3}\frac{\mu_{\mathrm{ref}}(\rho_v)}{\rho_v}(c_2^2-c_1^2)-\frac{c_1}{3\xi^3}[\mu-f_0^{(0)}]=0, \quad O(3). \tag{33d}$$

The parameters $f_0^{(n)}$ are the coefficients of the Taylor-series expansion of the attractive term about the critical radius,

$$f_0^{(n)}(R_c)\equiv\left.\frac{d^nf_0(r)}{dr^n}\right|_{r=R_c}, \tag{34}$$

and they provide information on the interaction potential: they may be considered ''moments,'' each one involving an nth-order derivative of the potential weighted by the mean-field droplet profile squared. If we assume that $f_0^{(0)}$ is a known property of the potential, in the spirit of knowing the integrated strength of the attractive potential α, a set of closed equations is obtained. The lowest-order equation (33a) specifies the correlation length (via a complicated nonlinear equation), and as before the liquid density is determined from the normalization condition, and R_c from the classical theory. Higher-order consistency equations are used to specify higher-order terms. Having determined the Taylor expansion coefficients of the attractive term, the attractive potential may be obtained by inverting the equations. A method to perform this inversion and obtain the interaction potential is detailed in Appendix C. It is clear that even though this procedure is formally well-defined, its numerical implementation is nontrivial.

A remark about the implementation and potential usefulness of this method, we believe, is in order here. We argued earlier that the tanh-like profile may be a physically motivated choice for the form of the density profile. It is true that this is only an ansatz and hence the technique presented above is only approximate. However, the purpose of this exposition was more general. It was to highlight a theoretical methodology to extract information on fundamental relations and interactions (here, about the attractive potential) from density profiles: these profiles may be estimated from experimental measurements or theoretically suggested. In this spirit, we suggest that the ansatz be considered only as a case example of the method via the following procedure: (i) to form the density profile (estimated either from the experimental data or theoretical arguments), (ii) to fit it to a smooth function, (iii) to Taylor-expand it near the droplet surface, and (iv) subsequently to follow the same steps as for the case-study ansatz used above. It should be noted that currently such measurements of density profiles are not available, but partly our scope is to potentially trigger the interest of experimentalists in attempting to obtain such information. We believe that such measurements, in conjunction with theoretical methods such as the one presented above, could possibly provide important insights into the nature of fundamental interactions of the systems under study.

So far we have described two approaches. First, if the attractive interaction potential is known explicitly, the resulting boundary-value integro-differential problem (BVIDP) can be solved numerically. Second, if the potential is not known, properties of the droplet profile and of the potential may be determined (approximately) self-consistently, as described above. However, an alternative and simpler approach to the solution of the BVIDP may be chosen if the full potential is known analytically. Specifically, the solution ansatz, Eq. (29), may be used as a variational trial function in Eq. (7). The extremum of the functional will yield a nonlinear equation connecting ρ_l and ξ. The second required equation will be the normalization condition: thus the solution of this constrained extremization problem will then give the physical quantities of interest. In the case of a known potential, the third approach is less cumbersome than the first since it involves a solution of only two nonlinear (algebraic) equations rather the solution of the BVIDP on (all of) the positive semiaxis (in addition to the algebraic normalization condition); however, it is consequently more approximate.

VI. CONCLUSIONS

In this work, a connection between density-functional theories of nucleation and macroscopic theories of Bose-Einstein condensation was established; it was achieved by adopting a field-theoretic approach along the lines of Langer's [13] semiphenomenological theory of condensation. The motivation for our work was the statistical mechanics of Bose-Einstein condensation where the wave function of the macroscopically occupied ground state of a Bose gas becomes the superfluid order parameter. The explicit, suggested analog (appropriate order parameter) is between condensed bosons in the (quantum-mechanical) ground state and, given Langer's field-theoretic description of condensation, a cluster of molecules in the condensed phase that forms a liquid droplet.

By expressing the grand-canonical partition function as a functional integral, and performing a steepest-descent evaluation, an integro-differential Euler-Lagrange equation for the spatially nonuniform, mean-field droplet profile was derived. The resulting equation is reminiscent of the extremum equation in density-functional theories of nucleation in that it contains a nonlocal attractive term, but it differs in the evaluation of reference-state properties. A suggested redefinition of the chemical potential in terms of a reference chemical potential was similar to the approach taken in density-functional theories, where the reference potential is usually identified with that of a hard-sphere fluid. For a classical fluid, where the Thomas-Fermi approximation of neglecting the kinetic energy term is applicable, a classical field-theoretic description of inhomogeneous fluids is obtained, a description that was compared and contrasted to classical density-functional theory.

Apart from the derivation of the profile equation, the emphasis of our work was on the evaluation of the contribution of the droplet translational eigenmodes to the nucleation rate. As shown in the past [13], the contribution of the translational eigenmodes to the rate was expressed as the product of the system volume times the Jacobian for the change of integration variables to collective coordinates. We extracted the part corresponding to the translational modes, leaving the complete evaluation of the statistical and dynamical prefactors to future investigations. The functional form of these eigenvectors for the three-dimensional Euler-Lagrange equation was determined under the assumption that the mean-field density profile be spherically symmetric, i.e., without assuming its explicit functional form, and its relation to the gradient of the mean-field order parameter was demonstrated.

The solution of the Euler-Lagrange equation that determines the (mean-field) droplet profile was viewed as a boundary value integro-differential problem (BVIDP): the solution is necessary for the evaluation of the translational contribution to the nucleation-rate statistical prefactor. We discussed three ways to obtain the solution: (i) If the attractive potential is known, a complete numerical solution of the BVIDP on the positive real semiaxis would give an accurate, numerical profile of the fluid density; (ii) a simpler approach to obtain the profile numerically, if the attractive potential is known, is to use a variational trial function and extremize the functional integral as a function of a single parameter (the second parameter is enslaved to it by the normalization condition); and (iii) for the most relevant case in which the intermolecular interaction is not known explicitly, a physically motivated ansatz profile was proposed. This ansatz in conjunction with the Euler-Lagrange equation provides sufficient information to obtain formally the parameters of the ansatz as well as the (approximate evaluation of) properties of the attractive potential in an inverse-problem sense, as highlighted in Sec. V and in Appendix C.

It should be remarked that in this first part of our work on the role of translational invariance in theories of nucleation, we were primarily concerned with the formulation of a general theory to tackle such problems. The formulation is quite general, subject, of course, to the assumptions discussed in the text (for example, the continuum approximation and the assumptions about the interaction potential) and can be applied to various systems of experimental interest. It has the major advantage that it puts in contact and in perspective the connection between the simplest phenomenological theory that captures the essential physics of a first-order phase transition and more rigorous and modern methodologies of density-functional theory, thereby providing a unified viewpoint to such methodologies. The second part of this study, currently in progress, will instead focus on special case studies of systems for which other theoretical approaches as well as experimental results have appeared in the literature.

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APPENDIX A: TIME-DEPENDENT VARIATIONAL PRINCIPLE

We rederive the droplet-profile equation by following the arguments used to obtain the Gross-Pitaevskii equation in theories of Bose-Einstein condensation. In doing so, we will also show how the functional derivatives of Eq. (7) are evaluated to obtain Eq. (10). As argued in Ref. [18], the Euler-Lagrange equation for the steady-state, nonuniform droplet configuration may be derived from the variational principle

$$i\hbar\frac{\partial}{\partial t}\Phi(\mathbf{r},t)=\frac{\delta E[\Phi,\Phi^\star]}{\delta\Phi^\star(\mathbf{r},t)},\tag{A1}$$

where the energy functional E is

$$E[\Phi,\Phi^\star]=\int d\mathbf{r}'\left[\frac{\hbar^2}{2m}|\boldsymbol{\nabla}\Phi(\mathbf{r}',t)|^2+\tfrac{1}{2}F(\mathbf{r}',t)|\Phi(\mathbf{r}',t)|^2+\frac{g}{2}|\Phi(\mathbf{r}',t)|^4\right].\tag{A2}$$

The contribution of the attractive potential has been incorporated in the function

$$F(\mathbf{r}',t)=\int d\mathbf{r}''V_{\mathrm{att}}(|\mathbf{r}'-\mathbf{r}''|)|\Phi(\mathbf{r}'',t)|^2.\tag{A3}$$

The Euler-Lagrange equation for the order parameter $\Phi(\mathbf{r},t)$ is obtained by extremizing the energy functional $E[\Phi,\Phi^\star]$. The functional derivatives of the kinetic energy and the local repulsive interaction term are easily obtained, keeping in mind that the fields Φ and $\Phi^\star$ are independent. The extremum of the nonlocal attractive interaction term

$$\mathbf{U}_{\rm attr}[\Phi,\Phi^\star]\equiv\tfrac{1}{2}\int d\mathbf{r}'\,F(\mathbf{r}',t)\Phi(\mathbf{r}',t)\Phi^\star(\mathbf{r}',t) \tag{A4}$$

becomes

$$\frac{\delta\mathbf{U}_{\rm att}[\Phi,\Phi^\star]}{\delta\Phi^\star(\mathbf{r},t)}=\tfrac{1}{2}F(\mathbf{r},t)\Phi(\mathbf{r},t)+\tfrac{1}{2}\int d\mathbf{r}'\,\frac{\delta F(\mathbf{r}',t)}{\delta\Phi^\star(\mathbf{r},t)}\Phi(\mathbf{r}',t)\times\Phi^\star(\mathbf{r}',t). \tag{A5}$$

The functional derivative in the integrand evaluates to

$$\frac{\delta F(\mathbf{r}',t)}{\delta\Phi^\star(\mathbf{r},t)}=V_{\rm att}(|\mathbf{r}'-\mathbf{r}|)\Phi(\mathbf{r},t). \tag{A6}$$

Note that in the above two equations, we have used the lemma

$$\frac{\delta\Phi^\star(\mathbf{r},t)}{\delta\Phi^\star(\mathbf{r}',t)}=\delta(\mathbf{r}-\mathbf{r}'). \tag{A7}$$

Upon substitution to the initial equation (A5), the functional derivative becomes

$$\frac{\delta\mathbf{U}_{\rm att}[\Phi,\Phi^\star]}{\delta\Phi^\star(\mathbf{r},t)}=\tfrac{1}{2}F(\mathbf{r},t)\Phi(\mathbf{r},t)+\tfrac{1}{2}\Phi(\mathbf{r},t)\times\int d\mathbf{r}'\,V_{\rm att}(|\mathbf{r}'-\mathbf{r}|)|\Phi(\mathbf{r}',t)|^2. \tag{A8}$$

As argued in the main text, and in agreement with density-functional studies of nucleation [8–11], the main assumption about the attractive potential is that it be central [thus, $V_{\rm att}(\mathbf{r}'-\mathbf{r})=V_{\rm att}(\mathbf{r}-\mathbf{r}')$]. Therefore,

$$\frac{\delta\mathbf{U}_{\rm att}[\Phi,\Phi^\star]}{\delta\Phi^\star(\mathbf{r},t)}=F(\mathbf{r},t)\Phi(\mathbf{r},t). \tag{A9}$$

Consequently, the time-dependent variational equation becomes

$$i\hbar\frac{\partial}{\partial t}\Phi(\mathbf{r},t)=-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\Phi(\mathbf{r},t)+F(\mathbf{r},t)\Phi(\mathbf{r},t)+g|\Phi(\mathbf{r},t)|^2\Phi(\mathbf{r},t). \tag{A10}$$

The Euler-Lagrange equation for the time-independent (nonuniform) spatial profile of the droplet wave function $\phi(\mathbf{r})$ that will mediate the transition between the liquid and vapor phase is obtained by considering a time-dependent solution of the form

$$\Phi(\mathbf{r},t)=\phi(\mathbf{r})\exp(-i\mu t/\hbar), \tag{A11}$$

where μ is, as defined in the main text, the thermodynamic chemical potential associated to the N particles in the system volume, and as before ϕ is real and normalized to the total number of particles, $N=\int_V d\mathbf{r}\,\phi^2(\mathbf{r})$. Then the Euler-Lagrange equation (a modified static Gross-Pitaevskii equation) becomes

$$\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\phi+[\mu-f(\mathbf{r})]\phi-g\phi^3=0, \tag{A12}$$

where the function $f(\mathbf{r})$ has been defined in the main text, Eq. (6): Equation (A12) is identical to Eq. (10) in the main text.

APPENDIX B: CLASSICAL LIMIT

As argued in the main text, the Thomas-Fermi approximation is applicable to classical fluids. This approximation, which consists of dropping the kinetic-energy term, is obtained by taking the $\hbar\to0$ limit of Eq. (7) to yield

$$S[\phi]=\int d\mathbf{r}\left\{-[\mu-\tfrac{1}{2}f(\mathbf{r})]\phi^2+\frac{g}{2}\phi^4\right\}. \tag{B1}$$

The leading-order term in the saddle-point evaluation of the functional integral Eq. (8) gives the following mean-field expression for the grand-canonical thermodynamic potential [via Eq. (9)]:

$$\Omega[\phi_0]=\int d\mathbf{r}\left\{-[\mu-\tfrac{1}{2}f_0(r)]\phi_0^2(r)+\frac{g}{2}\phi_0^4(r)\right\}, \tag{B2}$$

where $\phi_0(r)$ is the solution of the Euler-Lagrange equation [Eq. (17a)] and f_0 was defined in Eq. (17b). Equation (B2) may be reexpressed in terms of the local density $\rho(r)$ as follows:

$$\Omega[\rho(r)]=\frac{g}{2}\int d\mathbf{r}\,\rho^2(r)-\mu\int d\mathbf{r}\,\rho(r)+\tfrac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,V_{\rm att}(|\mathbf{r}-\mathbf{r}'|)\rho(r)\rho(r'). \tag{B3}$$

This equation is to be compared to the density-functional expression for the grand-canonical potential [for example, Eq. (2.8) in Ref. [8]], namely

$$\Omega_{\rm DFT}[\rho(\mathbf{r})]=\int d\mathbf{r}\,f_h[\rho(\mathbf{r})]-\mu\int d\mathbf{r}\,\rho(\mathbf{r})+\tfrac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,w_2(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r})\rho(\mathbf{r}'), \tag{B4}$$

where we have followed their notation for the pair attractive potential $w_2(\mathbf{r})$, and $f_h[\rho]$ is the Helmholtz free energy per unit volume of a uniform hard-sphere fluid of density ρ. In the spirit of density-functional theory, the density of the fluid (be it uniform or nonuniform) is obtained by setting the functional derivative of Ω with respect to $\rho(\mathbf{r})$ equal to zero.

Comparison of Eqs. (B3) and (B4) shows the similarities and differences between the two approaches. Equation (B3) is a mean-field expression: higher-order terms may be added perturbatively by considering fluctuation corrections. The density-functional expression contains fluctuations of all orders, but it necessitates the introduction of a reference state [in the case of Eq. (B4) taken to be the uniform hard-sphere fluid].

For a concrete comparison of the two approaches, we consider the limit of a uniform fluid. As argued in the main text, g is related to properties of the reference state, and it is specified by the requirement that the solution of the Euler-Lagrange equation have the appropriate asymptotic (physical) limits [see the discussion above Eq. (14)]. Hence, its value ensures that the uniform-state Ω is evaluated at its minimum. The uniform fluid density, however, is not determined self-consistently, but it is specified as a boundary condition. On the other hand, in classical density-functional theory, the uniform fluid density is determined from the extremum (minimum) equation, at the expense of introducing a physically reasonable and numerically accurate reference state. Finally, Eq. (B3) suggests that in the classical limit the natural choice for the order parameter is the local fluid density $\rho(\mathbf{r})$.

APPENDIX C: DETERMINATION OF THE ATTRACTIVE POTENTIAL AS AN INVERSE PROBLEM

We argued in the main text that the consistency conditions specify $f_0^{(n)}(R_c)$, the Taylor expansion coefficients of the attractive term $f(\mathbf{r})$ about the critical radius. The inversion to determine the potential may be done perturbatively, based on the spherically symmetric form Eq. (18). For simplicity we require that, as the second integrand in this integral suggests, $zV_{\text{att}}(z)$ be differentiable at the origin: this is the case for the most frequently used potentials, such as, the Yukawa potential,

$$V_{\text{Yukawa}}(r) = -\alpha\lambda^3 \frac{\exp(-\lambda r)}{4\pi\lambda r}, \tag{C1}$$

where α is the integrated strength and λ the range of the attractive potential, or a model potential with an r^{-6} attractive tail [29],

$$V_6(r) = -\epsilon\sigma^6(r^2+\sigma^2)^{-3}, \tag{C2}$$

with σ a measure of the molecular diameter and ϵ a (positive) constant that characterizes the strength of the potential. Furthermore, to simplify the formal calculations, we shall require that the potential $V_{\text{att}}(r)$ be an even function. Thus the expansion gives

$$zV_{\text{att}}(z) \equiv \tilde{V}_{\text{att}}(z) = \sum_{n=0}^{\infty} \frac{z^{2n+1}}{(2n+1)!}\tilde{V}_{\text{att}}^{(2n+1)}(0). \tag{C3}$$

The general expansion of Eq. (18) about the critical radius is

$$\begin{aligned} f_0(R_c+y) = {} & \frac{2\pi}{R_c}\int_0^\infty dr'\, r'\, \phi_0^2(r') \sum_{l=1}^{\infty} \left(-\frac{1}{R_c}\right)^{l-1} \\ & \times \sum_{n=0}^{\infty} \frac{\tilde{V}_{\text{att}}^{(2n+1)}(0)}{[2(n+1)]!} \sum_{k=0}^{2(n+1)} \binom{2(n+1)}{k} \\ & \times [(R_c+r')^{2(n+1)-k} \\ & - |R_c-r'|^{2(n+1)-k}] y^{l+k-1}. \end{aligned} \tag{C4}$$

This expansion is to be compared and equated order-by-order in perturbation with the Taylor-series expansion of the attractive term. Such a comparison gives

$$f_0^{(m)}(R_c) = \frac{2\pi}{R_c}\sum_{n=0}^{\infty} \frac{\tilde{V}_{\text{att}}^{(2n+1)}(0)}{[2(n+1)]!} c_n(R_c, m), \tag{C5}$$

where $m = l+k-1$ and the coefficients are

$$\begin{aligned} c_n(R_c, m) = {} & \int_0^\infty dr'\, r'\, \phi_0^2(r') \sum_{l=1, 0\leq k\leq 2(n+1)}^{l+k-1=m} \left(-\frac{1}{R_c}\right)^{l-1} \\ & \times \binom{2(n+1)}{k} [(R_c+r')^{2(n+1)-k} \\ & - |R_c-r'|^{2(n+1)-k}]. \end{aligned} \tag{C6}$$

Hence, an explicit expression for the nth-order derivative $f_0^{(n)}(R_c)$ was obtained in terms of properties of the attractive interaction potential, Eqs. (C5) and (C6). If the expansion of the attractive potential, Eq. (C3), is truncated to the first n terms, and the $(n-1)$th-order derivatives are obtained from the self-consistency conditions, Eqs. (33), a linear system of n equations for n unknowns, the $\tilde{V}_{\text{att}}^{(2k+1)}(0)$ with $k = 0, \ldots, n-1$, is obtained. Thus the $n\times n$ system of equations may be inverted to obtain the unknown attractive-interaction parameters. It is apparent that whereas the scheme is formally well-defined, it is difficult to implement it numerically.

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