Classical nucleation theory revisited

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A field-theoretic derivation of the correction to classical nucleation theory due to translational invariance of a nucleating droplet is proposed. The correction is derived from a functional integral representation of the classical partition function, where the two-body interaction potential is decomposed into a short-range repulsive part and a long-range attractive part. The functional integral is evaluated in the mean-field approximation, and the spatially nonuniform density solution of the Euler-Lagrange equation is approximated by a physically motivated hyperbolic tangent profile. Leading-order effects of the nonlocal attractive interaction are highlighted through a density-gradient expansion. The capillarity approximation to the droplet free energy of formation is obtained by performing a density resummation of the uniform state, low-density expansion of the Helmholtz free energy density, and by retaining the leading-order density-gradient term. The resulting translational-invariance correction modifies the droplet free energy by an additive mixing-entropy term. The additional contribution, which contains a logarithmic correction to the surface-energy term, defines a scaling volume that depends on the range of the coarse-grained attractive potential.

I. INTRODUCTION

The proposal by Lothe and Pound [1] that translational and rotational degrees of freedom of a nucleating embryo (droplet) are not properly accounted for in classical nucleation theory has resulted in extensive investigations of classical nucleation theory. The so-called translation-rotation paradox, a paradox closely linked to subtle issues in equilibrium statistical mechanics, has triggered detailed studies of the statistical mechanics of molecular clusters. Simultaneously, nucleation-rate measurement techniques have considerably improved, see, for example, Ref. [2], and references therein, as have careful analyses of the associated heat and mass transfer processes in these devices (laminar flow diffusion chamber, thermal diffusion chamber, and expansion chamber). The considerable improvements in experimental techniques and theoretical developments have only partially improved agreement between theory and experiment. The additional term originally proposed by Lothe and Pound increased theoretical predictions by approximately 10^{18}, but subsequent refinements and modifications resulted in lower factors of the order of 10^4–10^6 (see, e.g., Ref. [3]), factors that are still relatively high. Theoretical developments have, on the other hand, removed inherent inconsistencies in classical nucleation theory and they have provided corrections that are theoretically well founded. The work presented herein provides an alternative approach to the theoretical basis of classical nucleation theory and the necessary modifications due to translational invariance.

Reiss and co-workers [3–5] have emphasized the important relation between a proper counting of translational degrees of freedom and the mixing entropy in mesoscopic, con-

tinuum descriptions of nucleation phenomena (and other systems such as microemulsions). They argued that in phase-space representations of a physical system the natural scale to distinguish different states, and hence to calculate the total entropy via an enumeration of distinct states, is Planck's constant h (the scale of action). In the semiclassical limit position and momenta become continuum variables and, thus, there is no natural length scale to distinguish distinct physical states. The translation-rotation paradox may be resolved by a proper determination of a length scale capable to distinguish different states. Such a length scale, a scale that necessarily becomes dependent on the model adopted, leads to a proper incorporation of the mixing entropy in the droplet free energy of formation: this additional term has been called "replacement free energy." Recently, Reiss, Kegel, and Katz [5] suggested that the volume scale for the mixing entropy (in particular, the positional entropy) becomes the variance of volume fluctuations: a nucleating droplet may be identified as a distinct physical object up to its volume fluctuations. This scale ensures that physical states are not overcounted. A similar problem arises in cell theories of liquids where a "communal entropy" is introduced [6].

The effect of center-of-mass fluctuations of a nucleating cluster on the nucleation rate has been calculated either via detailed analyses of the statistical mechanics of molecular clusters or via density-functional studies. For example, Reiss and co-workers and Ford [7] attempted to resolve the paradox via detailed analyses of the statistical mechanics of molecular clusters. On the other hand, Barrett [8], following the pioneering work of Langer [9] on a field-theoretic description of condensation, adopted such an approach. In the context of a mixing entropy associated to the droplet's translational degrees of freedom, his suggestion reduces to the choice of the molecular volume in the liquid state as the required volume scale. Classical nucleation theory, on the other hand, implicitly assumes that the volume scale is the

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molecular volume in the vapor phase [5]. Talanquer and Oxtoby [10] also adopted a density-functional approach to calculate the correction due to cluster translations to conclude that the correction is relatively small. The paradox has also been addressed in terms of nonequilibrium kinetics of the nucleation process [11].

In this work, we pursue further the approach developed in Ref. [12], henceforth referred to as Paper I, to calculate modifications of classical nucleation rate due to the translational eigenmodes of a nucleating droplet. There we considered the physics of a classical first-order phase transition starting from a quantum-mechanical many-body Hamiltonian. The approach was based on a proposed analog between a (classical) cluster of condensed molecules forming a liquid droplet and a (quantum-mechanical) ground state "droplet" of condensed bosons. Such a description of a cluster of condensed molecules is implicit in field-theoretic descriptions of condensation.

The quantum partition function for a system of pairwise interacting Bose particles is presented in Sec. II. The interaction potential is decomposed into a short-range (which will be taken to be local) repulsive term and a long-range (nonlocal) attractive term. We explicitly introduce the symmetry property of the many-body Bose wave function and the h normalization of the partition function in the functional-integral measure to obtain the classical partition function as a functional integral. The extremal Euler-Lagrange equation is shown to contain leading-order terms in the low-density expansion of the chemical potential. We argue that this is a consequence of keeping only two-body interactions in the original microscopic Hamiltonian. The strength of the repulsive interactions is specified in terms of an effective hard-sphere diameter by comparing the second virial coefficient to that of a van der Waals fluid. Similarities and differences with density-functional theory conclude the analysis of Sec. II.

In Sec. III, we show how the droplet free energy of formation is obtained from the saddle point evaluation of the partition function. The droplet free energy is expressed in the form expected from classical nucleation theory in the capillarity approximation, namely in terms of a volume and a surface term. Thus, a heuristic justification of classical nucleation theory starting from molecular considerations is provided. The derivation is based on a physically motivated ansatz for the nonuniform density profile that allows us to express the saddle point free energy in terms of a local term and a nonlocal term. A judicious resummation of the local part of the free energy density gives the Helmholtz free energy for the uniform states, whereas the gradient expansion of the nonlocal attractive parts leads to the surface-energy term.

As shown in Paper I, the droplet's translational eigenmodes modify the nucleation rate by the Jacobian for the change of variables to collective coordinates. We evaluate the correction in Sec. IV and we relate it to a general expression for the nucleation rate in Sec. V. In the spirit of the general formula proposed by Dillmann and Meier [13] for the droplet free energy, we show in Sec. VI that the proposed modification introduces three additional terms. It modifies

the surface-energy term, it provides an additive free energy contribution, and it gives a length scale for incorporation of the mixing entropy. The appropriate length scale becomes the interaction range of the coarse-grained attractive potential. Section VII summarizes our findings and presents our conclusions and suggestions for future work. A number of technical details have been relegated to three appendixes.

The emphasis of our work is on the translational eigenmodes and their contribution to the nucleation rate, i.e., on the calculation of the mixing entropy. Other fluctuations, for example, distortions of the droplet surface, that may be incorporated in the droplet free energy as an additional configurational-entropy term are neglected. A complete calculation of the nucleation rate requires the incorporation, or an estimate, of the effect of these additional fluctuations at least in a Gaussian approximation. This calculation, however, is beyond the scope of the present work.

II. FUNCTIONAL-INTEGRAL MEASURE

In Paper I, the quantum-mechanical grand-canonical partition function was derived under a number of approximations. The many-body wave function was decomposed according to the Bogoliubov prescription [14] into the expectation value of the field operator, which becomes the order parameter for quantum phase transitions (in particular, Bose-Einstein condensation), and a (quantum) fluctuation term, which was assumed to be small. Only two-body interactions were considered by introducing the two-body interaction potential V_{int}. The interaction potential was decomposed into a short-range repulsive part and a long-range attractive part. As in treatments of Bose-Einstein condensation, the short-range repulsive interaction was replaced by an effective local repulsion characterized by a strength g, whereas the attractive part was assumed to be nonlocal and spherically symmetric,

$$V_{int}(\mathbf{r}-\mathbf{r}') = V_{att}(|\mathbf{r}-\mathbf{r}'|) + g\,\delta(\mathbf{r}-\mathbf{r}'). \quad (1)$$

When the partition function is regularized on a lattice, the approximation of a local repulsive interaction will be effectively relaxed. Later in this section, we show the relation of g to the hard-sphere diameter of a reference fluid.

For a time-independent order parameter $\phi(\mathbf{r})$, the partition function was expressed as a functional integral over field configurations

$$\Xi_{QM} = \int D[\phi] e^{-\beta S[\phi]}, \quad (2)$$

with $\beta = (k_B T)^{-1}$, T the absolute temperature, and k_B the Boltzmann constant. The appropriate (grand-canonical) thermodynamic potential becomes

$$\beta\Omega = -\ln(\Xi). \quad (3)$$

In the partition function the "Euclidean action" was shown to be

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

where μ is the thermodynamic chemical potential, and the attractive, nonlocal term $f(\mathbf{r})$ was defined as follows:

$$f(\mathbf{r}) = \int d\mathbf{r}' V_{\text{att}}(|\mathbf{r} - \mathbf{r}'|) \phi^2(\mathbf{r}') < 0. \quad (5)$$

The local number density $\rho(\mathbf{r}) = \phi^2(\mathbf{r})$, and the total number of particles N in a volume V is

$$N = \int_V d\mathbf{r} \rho(\mathbf{r}). \quad (6)$$

In Paper I, the properties of the Euler-Lagrange equation that arises in the saddle-point evaluation of the functional integral were analyzed; in particular, the functional form of the translational eigenmodes of the nucleating droplet was related to the order parameter. Herein, we concentrate on the classical partition function and we provide a heuristic derivation of the droplet free energy of formation as described by classical nucleation theory. In doing so, we will provide an explicit correction to the nucleation rate that arises from translational invariance of the nucleating droplet center of mass, namely that the droplet may nucleate anywhere in the system volume.

The interpretation of the functional integral [Eq. (2)] becomes unequivocal in its discretized form. This discretization (which is a lattice regularization) also eliminates ultraviolet catastrophes by introducing a high wave number cutoff in k space. In the classical limit, the Euclidean action becomes a functional of the local number density and the gradient term is eliminated. It is well known [15] that two essential quantum-mechanical aspects remain in the classical partition function: the symmetry property of the many-body wave function and the h normalization of the classical partition function. The latter gives the limit of accuracy due to the uncertainty principle in assigning particle coordinates and momenta to a particular phase-space point.

We present a heuristic derivation of the discrete functional measure: the two quantum-mechanical effects are incorporated in an *ad hoc* manner in the classical partition function by considering the occupation number representation of the field operator. A formal derivation of the limiting procedure is beyond the scope of the present work (see, for example, Ref. [15]).

In the lattice regularization, the system volume is divided in M cells of linear size a. Let n_i be the number of particles within cell i; then the local density becomes $\rho_i = n_i/a^3$. Symmetry requirements for indistinguishable particles introduce a factorial term $n_i!$. The h factor arises from integration over the particle momenta to give the following discrete version of the functional integral:

$$\Xi_{cl} = \lim_{M \to \infty} \int \prod_{\{n_i\}} d\rho_i \frac{1}{\sqrt{\rho_i}} \frac{1}{N_i} \frac{1}{n_i!} \frac{1}{\bar{\Lambda}^{3n_i}} e^{-\beta S_a[\rho_i]}, \quad (7)$$

where $\bar{\Lambda} = \Lambda/a$ with $\Lambda = h/(2\pi m k_B T)^{1/2}$ the thermal de Broglie wavelength. The square root of the local density ρ_i comes from the change of variables from ϕ_i to ρ_i, N_i is a normalization constant, and the product is over all configurations $\{n_i\}$. The exponent $S_a[\rho_i]$ is the discretized version of Eq. (4) without the kinetic energy term that drops out to leading order in h.

If the measure prefactor in Eq. (7) is expressed as an exponential, the factorial terms are expanded according to the Stirling approximation, and leading-order terms are kept (the Jacobian of the ϕ_i to ρ_i change of variables drops out to leading order), we obtain

$$\exp\left\{ a^3 \sum_i \left[\rho_i \ln(\rho_i \Lambda^3) - \rho_i \right] \right\}. \quad (8)$$

A careful inspection of the measure prefactor of Eq. (7) renders intuitively clear the origin of the entropic term in Eq. (8). It is, in essence, the indistinguishability of the classical particles (their ''bosonic'' nature) which is responsible for the existence (and relevance) of such an entropic contribution in the (effective) action. Recent related discussions on the origin of such a contribution can be found in Refs. [16,17].

As discussed in Ref. [16], the properties of the interaction potential, and, in particular, the interaction potential decomposition, have to be analyzed carefully when taking the continuum limit of the classical expressions, Eqs. (7) and (8). The decomposition into a short-range (local) repulsive term and a long-range (nonlocal) attractive term implies the existence of an effective hard-sphere diameter σ. Two distinct length scales have to be considered: the lattice spacing a and the hard-sphere diameter σ. For $a \lesssim \sigma$, the occupation number of a given lattice site can be only 0,1, and the partition function becomes the lattice-gas partition function. For $\sigma \ll a$, multiple site occupation is allowed, but a coarse graining over microscopic length scales is implicitly made. Thus, the strength of the repulsive interaction g becomes a measure of an effective hard-sphere diameter and the nonlocal attractive interaction is interpreted as a coarse-grained attractive potential.

With these provisoes and with the correspondence $a^3 \Sigma \to \int d\mathbf{r}$ and $n_i/a^3 \to \rho(\mathbf{r})$ (see, for example, Ref. [18]), the continuum limit is taken to obtain the functional-integral representation of the classical partition function

$$\Xi_{cl} = \int D\rho \exp(-\beta S_{cl}[\rho]), \quad (9)$$

where

$$\beta S_{cl}[\rho] = \int d^3r \left\{ -\beta \mu \rho(\mathbf{r}) + \frac{1}{2} \beta f(\mathbf{r}) \rho(\mathbf{r}) + \frac{1}{2} \beta g \rho^2(\mathbf{r}) \right.$$
$$\left. + \rho(\mathbf{r}) \ln[\Lambda^3 \rho(\mathbf{r})] - \rho(\mathbf{r}) \right\}. \quad (10)$$

The normalization constant has been absorbed in the measure $D\rho$. This representation of the classical partition func-

tion is similar to the functional integral presented in Ref. [16], apart from a different treatment of the hard-core repulsive interaction. The last two terms in Eq. (10) are the Helmholtz free energy density of an ideal monoatomic classical gas. The first term may be identified as an external field coupled to the density (or the corresponding Lagrange multiplier), and the remaining two terms are nonideal corrections arising from intermolecular interactions. They are recognized as the first terms in a density expansion of the nonideal part of the classical free energy density (for an inhomogeneous system).

For a spherically symmetric (coarse-grained) attractive potential, the Euler-Lagrange equation that determines the mean-field (inhomogeneous) density profile is

$$\beta\mu = \beta f(r) + \beta g \rho(r) + \ln[\Lambda^3 \rho(r)]. \tag{11}$$

The nature of the low-density expansion becomes more transparent by considering a uniform fluid of density ρ; the extremum equation becomes

$$\beta\mu = \beta\mu_{\text{ideal}}(T,\rho) + 2B_2(T)\rho + O(\rho^2), \tag{12}$$

where we have used the ideal gas chemical potential, $\beta\mu_{\text{ideal}}(T,\rho) = \ln(\Lambda^3 \rho)$. The coefficient of the linear term $B_2(T)$ is the second virial coefficient since the density expansion of the chemical potential is [19,20]

$$\beta\mu(\rho,T) = \beta\mu_{\text{ideal}} + \sum_{k\geq 1} \frac{k+1}{k} B_{k+1} \rho^k. \tag{13}$$

In the expansion Eq. (12), the second virial coefficient is

$$B_2(T) = \tfrac{1}{2}\beta(g-\alpha), \tag{14}$$

with α the positive measure of the attractive interaction

$$\alpha = -\int_V d\mathbf{r} V_{\text{att}}(r). \tag{15}$$

The effective (renormalized) strength of the repulsive interaction g is determined by comparing $B_2(T)$ with the second virial coefficient of a van der Waals fluid. A comparison of our expressions [Eq. (11)] or (12) with those for a classical (monoatomic) van der Waals fluid is appropriate since our expressions have been obtained in the high-temperature, low-density limit. The van der Waals second virial coefficient is

$$B_2^{\text{vdW}}(T) = \frac{2\pi}{3}\sigma^3 - \frac{1}{2}\beta\alpha. \tag{16}$$

A natural way to match the attractive and repulsive parts in the virial coefficients of Eqs. (14) and (16), as per our earlier discussion, yields

$$\beta g = \frac{4\pi}{3}\sigma^3, \tag{17}$$

where σ is the diameter of the effective hard-sphere core.

It is instructive to rewrite the uniform-density limit of Eq. (11) in terms of a hard-sphere reference fluid with packing fraction $\eta = \pi\rho\sigma^3/6$,

$$\beta\mu - \ln(\Lambda^3) = \ln\rho + 8\eta - \alpha\beta\rho + O(\rho^2), \tag{18}$$

where we have used the relation of g to the hard-sphere diameter of the reference fluid, Eq. (17). The first two terms are the low-density terms of the hard-sphere chemical potential (in, for example, the Carnahan-Starling hard-sphere equation of state [19]). Thus, a density resummation of Eq. (18) gives

$$\beta\mu - \ln(\Lambda^3) = \beta\mu_{HS}(T,\rho) - \alpha\beta\rho + O(\rho^2), \tag{19}$$

where μ_{HS} is the chemical potential of a hard-sphere reference fluid. Explicit calculations with it require, of course, an approximation for the reference hard-sphere fluid. The resummed equation Eq. (19) is the uniform-fluid, extremum equation used in density-functional theory (see, for example, Ref. [21]). It differs from (12) in that only the hard-sphere (repulsive) part of the free energy has been resummed and the attractive part is treated perturbatively. On the other hand, Eq. (12) is a proper low-density expansion: both the attractive and the repulsive parts of the interaction potential contribute at every order in the density expansion. If higher-order terms in the attractive potential were incorporated in the density-functional expansion, then the two equations would become identical order by order in the perturbation expansion.

III. PHENOMENOLOGY OF CLASSICAL NUCLEATION THEORY

The free energy of formation of a nucleating droplet appears naturally in the saddle point evaluation of the partition function, Eqs. (9) and (10). It is the free energy difference corresponding to two solutions of the Euler-Lagrange equation: the (spatially) nonuniform solution and the uniform metastable vapor state

$$\beta\Delta S^\star = \beta S_{\text{drop}} - \beta S_v. \tag{20}$$

The connection to classical nucleation theory is made by performing a gradient expansion of the nonlocal term $f(r)$. The function $\rho(\mathbf{r}')$ is Taylor expanded about $\rho(\mathbf{r})$ to obtain, assuming spherical symmetry, the square-gradient approximation to the free energy

$$\beta S[\rho] = \int d\mathbf{r}\left[\frac{1}{2}\beta m_2(\nabla\rho)^2 - \beta\mu\rho(\mathbf{r}) + B_2(T)\rho^2(\mathbf{r})\right.$$
$$\left. + \rho(\mathbf{r})\ln[\Lambda^3\rho(\mathbf{r})] - \rho(\mathbf{r})\right], \tag{21}$$

where m_2 is the second moment of the attractive potential,

$$m_2 = -\frac{1}{6}\int d\mathbf{r} r^2 V_{\text{att}}(r). \tag{22}$$

Details of the gradient expansion and the derivation of Eq. (21) are presented in Appendix A. As usual, the gradient expansion assumes that the average density varies slowly over microscopic distances. Then the critical droplet free energy becomes

$$\beta \Delta S^{\star} = \int d\mathbf{r} \left\{ \frac{1}{2} \beta m_2 (\boldsymbol{\nabla}\rho)^2 - (\beta\mu + 1)[\rho_{\mathrm{drop}}(\mathbf{r}) - \rho_v] \right.$$
$$+ B_2(T)[\rho_{\mathrm{drop}}^2(\mathbf{r}) - \rho_v^2] + \rho_{\mathrm{drop}}(\mathbf{r})\ln[\Lambda^3\rho_{\mathrm{drop}}(\mathbf{r})]$$
$$\left. - \rho_v\ln[\Lambda^3\rho_v] \right\}. \tag{23}$$

Its evaluation requires the solution of the corresponding extremum equation for the nonuniform droplet-density profile: if the nonlocal attractive potential is specified, the density profile can be obtained numerically. Instead, we follow the approach taken in Paper I: since detailed information on the intermolecular interaction potential for an arbitrary system may not be available, physical intuition will be used to postulate a functional form for the density profile.

Specifically, the density close to the center of mass of the droplet is almost constant and equal to a liquid density ρ_l. In what follows, we will assume that ρ_l is the metastable liquid density, i.e., we will be neglecting nonclassical effects (see, e.g., Ref. [21]). This is not necessary for our derivation, but it simplifies the calculations and is consistent with classical nucleation theory. Away from the droplet surface, the density approaches exponentially fast the metastable vapor density ρ_v (which is considered as an imposed boundary condition, as is usually the case in nucleation experiments). The main density variation occurs over a short interfacial length scale ξ, and is quite rapid (typically assumed to be exponential). Thus, following Langer's [9] considerations for a Landau-Ginzburg ϕ^4 free energy with a hyperbolic-tangent density profile, and accepting his arguments about universality features of the transition, we make the following density-profile ansatz:

$$\rho_{\mathrm{drop}}(r) = \frac{1}{2}(\rho_v - \rho_l)\tanh\left(\frac{r - R_c}{\xi}\right) + \frac{1}{2}(\rho_v + \rho_l). \tag{24}$$

The critical droplet radius is R_c and ξ is the interfacial correlation length. The proposed profile is a reasonable approximation for $R_c \gg \xi$, i.e., close to the coexistence curve and far way from the critical point or the spinodal. Most of the results that follow may be obtained by postulating other (similar) functional forms that respect the previously mentioned constraints (for example, the profile suggested in Paper I), including a θ-function profile. The choice of a θ-function-density variation corresponds to the capillarity approximation of classical nucleation theory. However, the hyperbolic-tangent profile has the added advantage that it depends on two length scales: the critical-droplet radius, and the interfacial correlation length. As will become apparent later, the interfacial correlation length plays an important role in the final expression for the nucleation rate.

Our analysis up to here has been fairly general under well-defined approximations. Further developments require the use of the ansatz. The previous arguments suggest that the postulated droplet profile captures the essential characteristics of the density profile of a droplet. The effect of different density-profile choices on our main results is briefly discussed in Sec. IV.

Given the ansatz for the nonuniform density the free energy expression, Eq. (23) is evaluated in the limit of classical nucleation theory, $R_c \gg \xi$ ($R_c/\xi \rightarrow \infty$). The limiting procedure is divided into two parts: the calculation of the local terms (volume contribution) and the nonlocal terms (surface contribution). For completeness we present some results for the volume part obtained with *Mathematica* [23]: an extensive discussion of the limiting procedure is given in Appendix B. In particular,

$$\lim_{R_c \gg \xi} \int d\mathbf{r}[\rho_{\mathrm{drop}}(r) - \rho_v] = \frac{4\pi}{3}R_c^3(\rho_l - \rho_v)\left\{ 1 + \frac{\pi^2}{4}\left(\frac{\xi}{R_c}\right)^2 \right.$$
$$\left. + O\left[\left(\frac{\xi}{R_c}\right)^{2n}\right] \right\}, \tag{25a}$$

$$\lim_{R_c \gg \xi} \int d\mathbf{r}[\rho_{\mathrm{drop}}^2(r) - \rho_v^2]$$
$$= \frac{4\pi}{3}R_c^3(\rho_l^2 - \rho_v^2)\left\{ 1 - \frac{3}{2}\frac{(\rho_l + \rho_v)^2}{\rho_l^2 - \rho_v^2}\frac{\xi}{R_c} + \frac{\pi^2}{4}\left(\frac{\xi}{R_c}\right)^2 \right.$$
$$\left. + O\left[\left(\frac{\xi}{R_c}\right)^3\right] \right\}, \tag{25b}$$

$$\lim_{R_c \gg \xi} \int d\mathbf{r}\{\rho_{\mathrm{drop}}(r)\ln[\Lambda^3\rho_{\mathrm{drop}}(r)] - \rho_v\ln(\Lambda^3\rho_v)\}$$
$$= \frac{4\pi}{3}R_c^3[\rho_l\ln(\Lambda^3\rho_l) - \rho_v\ln(\Lambda^3\rho_v)] + O[\exp(-R_c/\xi)]. \tag{25c}$$

Hence the local terms contribute to the volume part of the free energy as follows:

$$\beta \Delta S_{\mathrm{volume}}^{\star} \approx \frac{4\pi}{3}R_c^3[-(\beta\mu + 1)(\rho_l - \rho_v) + B_2(T)(\rho_l^2 - \rho_v^2)$$
$$+ \rho_l\ln(\Lambda^3\rho_l) - \rho_v\ln(\Lambda^3\rho_v)] + O(\rho_v^3, \rho_l^3). \tag{26}$$

According to classical thermodynamics, the low-density expansion of the Helmholtz free energy density f_H is [see, also, Eq. (13)]

$$\beta f_H(\rho) = \rho\ln(\Lambda^3\rho) - \rho + B_2(T)\rho^2 + O(\rho^3), \tag{27}$$

where $B_2(T)$ is the second virial coefficient of the fluid under consideration. Inspection of Eq. (26) shows that terms may be regrouped to obtain the low-density expansion (to order ρ^2) of the Helmholtz free energy for the (uniform)

liquid and the vapor phases. To the same order the low-density terms may be replaced by the free energy density (the density series is resummed) and with the identification of the two virial coefficients the full free energy density is obtained. Hence, Eq. (26) is rewritten as

$$\beta \Delta S^{\star}_{\text{volume}} = \beta \frac{4\pi}{3} R_c^3 [f_H(\rho_l) - \mu\rho_l] - \beta \frac{4\pi}{3} R_c^3 [f_H(\rho_v)$$
$$- \mu\rho_v] + O(\rho_l^3, \rho_v^3). \qquad (28)$$

But $f_H(\rho) - \mu\rho$ is the density of the grand-canonical potential $\omega(\rho) = -P(\rho)$ for a uniform system of density ρ and pressure $P(\rho)$ (since $\Omega = -PV$). Therefore, the volume part of free energy of formation becomes

$$\beta \Delta S^{\star}_{\text{volume}} = \beta \frac{4\pi}{3} R_c^3 [\omega(\rho_l) - \omega(\rho_v)] + O(\rho^3)$$

$$= -\beta \frac{4\pi}{3} R_c^3 [P(\rho_l) - P(\rho_v)] + O(\rho^3), \quad (29)$$

where the term multiplying the pressure is the droplet volume (leading-order term in the $R_c \gg \xi$ limit). For a careful discussion of the evaluation of the nucleation barrier in the canonical and grand-canonical ensembles see, e.g., Refs. [21,24]. Their analysis implies, as we have shown, that the volume part of droplet free energy is the difference of the grand canonical potentials in the two uniform states. For an incompressible liquid and an ideal gas vapor, the pressure difference between the center of the liquid drop and the metastable bulk vapor can be calculated to be [21]

$$\beta[P(\rho_l) - P(\rho_v)] = \rho_l \ln\left(\frac{P_v}{P_{\text{sat}}}\right), \qquad (30)$$

to give the final expression for the volume part of the droplet free energy

$$\beta \Delta S^{\star}_{\text{volume}} = -\frac{4\pi}{3} R_c^3 \rho_l \ln(S). \qquad (31)$$

The classical nucleation theory approximation for the saturation ratio $S = P_v/P_{\text{sat}}$ was used in Eq. (31), with P_{sat} the saturation pressure, and P_v the pressure of the metastable vapor. As expected, the volume part is negative (for $S > 1$). The critical radius may be replaced by the critical number of molecules (monomers, as they are usually called in nucleation studies) in the liquid droplet N_{cr}, defined as

$$N_{\text{cr}} = 4\pi \int_0^{R_c} dr \, r^2 \rho_{\text{drop}}(r). \qquad (32)$$

In the large-droplet limit with $\rho_l \gg \rho_v$, the critical number of monomers becomes

$$\lim_{R_c \gg \xi} N_{\text{cr}} = \frac{4\pi}{3} \rho_l R_c^3 \left\{ 1 - \frac{3}{2} \frac{\xi}{R_c} \ln(2) + O\left[\left(\frac{\xi}{R_c}\right)^2\right]\right\}. \qquad (33)$$

This follows from Eq. (B4) in Appendix B.

The nonlocal free energy term $f(\mathbf{r})$ leads to a (positive) surface contribution to the droplet free energy. This may be shown to leading order in the gradient expansion. Specifically, the gradient term becomes

$$\lim_{R_c \gg \xi} \int d\mathbf{r}(\nabla\rho)^2 = \frac{4\pi}{3}(\rho_l - \rho_v)^2 \frac{R_c^2}{\xi} \left\{ 1 + \frac{\pi^2 - 6}{12}\left(\frac{\xi}{R_c}\right)^2 \right.$$
$$\left. + O\left[\left(\frac{\xi}{R_c}\right)^{2(n+1)}\right]\right\}. \qquad (34)$$

The surface term may be reexpressed in terms of γ_R, the macroscopic surface tension for a curved interface. In the square-gradient approximation,

$$\gamma_R = m_2 \int_0^\infty dr \left|\frac{d\rho}{dr}\right|^2. \qquad (35)$$

In the large-droplet limit, the surface tension becomes

$$\lim_{R_c \gg \xi} \gamma_R = \frac{m_2}{3\xi}(\rho_l - \rho_v)^2 + O[\exp(-R_c/\xi)]. \qquad (36)$$

Hence, the correlation length may be eliminated from Eq. (34) via Eq. (36) in favor of the surface tension to obtain

$$\frac{1}{2}\beta m_2 \int d\mathbf{r}(\nabla\rho)^2 \overset{R_c \gg \xi}{=} 2\pi\beta\gamma_R R_c^2. \qquad (37)$$

Thus, the mean-field approximation of the functional integral with the proper resummation of the low-density terms, a square-gradient approximation of the nonlocal attractive term, and a physically motivated ansatz for the nonuniform density profile lead to the following expression for free energy of formation of the nucleating droplet:

$$\beta \Delta S^{\star} = -\frac{4\pi}{3}\rho_l \ln(S) R_c^3 + 2\pi\beta\gamma_R R_c^2. \qquad (38)$$

As expected from classical nucleation theory, Eq. (38) splits into a negative volume term and a positive surface term. The volume term is identical to the classical nucleation theory term, whereas the surface term becomes the classical term if we identify $\gamma_R = 2\gamma_\infty$, an identification we will use in subsequent sections. Hence, we have rederived the classical nucleation theory free energy starting from a molecular level, field-theoretic action using the density as the relevant order parameter.

IV. COLLECTIVE COORDINATES JACOBIAN

In Paper I, we showed that the contribution of the translational eigenmodes of the nucleating droplet to the nucleation rate is related to the Jacobian of the change of variables to the collective coordinates associated to these modes. As discussed in Ref. [25], translational invariance (in an infinite system) implies the existence of a zero eigenvalue of the second-order free energy operator that describes Gaussian fluctuations about the droplet configuration. Functional inte-

gration over these zero-eigenvalue translational eigenmodes leads to a divergence. This divergence is spurious and may be eliminated by changing variables to collective coordinates. Therefore, the origin of the Jacobian in the nucleation-rate expression is the functional-integral measure corresponding to the translational eigenvalues.

The Jacobian, expressed here in terms of the local density $\rho(r)$ instead of the condensate wave function $\phi(r)$ (as derived in Paper I), is

$$J_{tran} = \left[\frac{\pi}{3} \int_0^\infty dr\, r^2 \frac{1}{\rho(r)} \left(\frac{d\rho}{dr} \right)^2 \right]^{3/2}. \quad (39)$$

The division by $\rho(r)$ ensures that the Jacobian has dimensions of inverse volume.

In the spirit of this work, and of classical nucleation theory, the Jacobian is evaluated in the hyperbolic-tangent ansatz. Furthermore, if we assume that $\rho_l \gg \rho_v$, the integral may be evaluated, and in the limit $R_c \gg \xi$ [Eq. (B6)] becomes

$$J_{tran} = \left(\frac{\pi}{3} \frac{\rho_l}{\xi} \right)^{3/2} R_c^3 \left\{ 1 + \frac{3}{2} \frac{\xi}{R_c} + O\left[\left(\frac{\xi}{R_c} \right)^2 \right] \right\}$$

$$= \frac{\sqrt{3\pi}}{12} \left(\frac{\rho_l}{\xi^3} \right)^{1/2} N_{cr}. \quad (40)$$

The Jacobian depends on *two length scales*: the critical radius and the interfacial correlation length, a dependence that would have been absent had we used a θ-function density profile.

The effect of the ansatz on the Jacobian [Eq. (40)] may be estimated by comparing it with the Jacobian calculated in Paper I. There a slightly different density profile was used $[\phi_{ans}^2(r) \neq \rho_{drop}(r)]$, but the resulting Jacobian differs from the one calculated here only in the numerical prefactors. In fact, dimensional arguments and an estimate of the integral [Eq. (39)] lead to the same dependence of J_{tran} on ξ, ρ_l, and N_{cr} (up to numerical constants).

The numerical solution of the Euler-Lagrange equation [21] usually starts with an initial guess for the critical radius R_c, taken from classical nucleation theory, and then an iteration scheme is used to obtain the saddle-point solution with a (possibly) new R_c, the interfacial correlation length ξ, and the liquid density at the origin of the droplet, ρ_l. In the absence of the numerical solution for the density profile, the correlation length remains an unknown; the liquid density, as mentioned earlier, is taken to be the metastable liquid density neglecting nonclassical effects. It has been suggested [8] to relate ξ to the liquid density. Instead it is eliminated in favor of the the surface tension, cf. leading-order term in Eq. (36). Thus, consistent with the approximations made in this work, the Jacobian becomes

$$J_{tran} = \frac{3\sqrt{\pi}}{4} \left(\frac{\gamma_R}{m_2} \right)^{3/2} \rho_l^{-5/2} N_{cr}. \quad (41)$$

As mentioned in the Introduction, density-functional theory has been used to estimate the effect of the translational eigenmodes without introducing a functional integral,

see, for example, Refs. [8,10]. The calculations presented herein provide an alternative approach. Moreover, as argued in Sec. II (see also Ref. [9]), the functional integral appears naturally in field-theoretic descriptions of condensation. In the following section, we show how the saddle-point evaluation of the functional integral leads to a correction to the nucleation rate (due to translational invariance) that is consistent with classical nucleation theory.

V. NUCLEATION RATE

The determination of the nucleation rate from the functional-integral expression has been discussed extensively in the past [9,12,26–28]. Under some general assumptions (coarse-grained free energy, small supersaturation, and Gaussian approximation of the functional integral), the nucleation rate may be written as

$$I_{nuc} = \frac{\kappa}{2\pi} V J_{tran} \Omega' e^{-\beta \Delta \Omega^\star}, \quad (42)$$

where $\Delta \Omega^\star$ is the free energy of formation of the critical droplet, κ the dynamical prefactor, and Ω' the contribution of Gaussian fluctuations about the (uniform) metastable and the (spatially nonuniform) saddle-point density profiles. The term Ω', a generalization of the Zeldovich factor, may be viewed as the leading-order correction to the droplet excess free energy arising from the configurational entropy of the droplet. The prime denotes that fluctuations corresponding to the translational eigenmodes of the nucleating droplet have been excluded: they have been treated separately, as summarized in the preceding section. The complete expression for Ω' may be found in, for example, Ref. [29], whereas an intriguing suggestion to relate the nucleation rate to the imaginary part of the true system free energy is presented in Ref. [27]. The dynamical prefactor κ, a quantity that depends on the dynamics of the system, is the initial growth rate of a droplet larger than the critical size.

In previous sections, we showed that the mean-field approximation of the classical partition function gives a droplet free energy that may be cast in terms of a volume plus a surface term. Hence, the exponent $\beta \Delta \Omega^\star$ is identified with the critical droplet free energy as given by the capillarity approximation. The Jacobian J_{tran} becomes the consistent correction to classical nucleation theory due to translational invariance. The lengthy derivations of Secs. III and IV are thereby justified in that they show that *the Jacobian becomes a correction to the nucleation rate that is consistent with classical nucleation theory (CNT)*. The self-consistent derivation of this correction from an order parameter based, field-theoretic point of view (at the level of molecular interactions) is one of the main findings of this work.

The remaining unknowns, κ and Ω', are determined by comparing Eq. (42) to the classical nucleation rate. The classical rate, without the factor $1/S$ frequently introduced *ad hoc* to ensure consistency with the one-monomer limit (see, however, Ref. [5]), is [30]

$$I_{\text{CNT}} = \rho_v \left(\frac{2\gamma_\infty}{\pi m} \right)^{1/2} \frac{\rho_v}{\rho_l} V \, e^{-\beta\Delta\Omega^\star_{\text{CNT}}}, \qquad (43)$$

which for the purposes of the comparison is expressed as

$$I_{\text{CNT}} = \beta_g(N_{\text{cr}}) Z_{cr}(N_{\text{cr}}) V \rho_v e^{-\beta\Delta\Omega^\star_{\text{CNT}}}. \qquad (44)$$

The classical prefactor naturally separates into the product of three terms: the growth rate (impingement factor) $\beta_g(N_{\text{cr}})$, the classical Zeldovich factor $Z_{cr}(N_{\text{cr}})$, and the vapor density ρ_v times the exponential of the droplet free energy of formation. The last factor is the equilibrium concentration of critical clusters containing N_{cr} molecules. The growth rate is the rate at which the critical cluster grows by one monomer: it is calculated from kinetic theory of gases to be (the accommodation coefficient has been set to unity)

$$\beta_g(N_{\text{cr}}) = 9^{1/3} \left(\frac{2}{\pi} \right)^{1/6} \left(\frac{\beta}{m} \right)^{1/2} P(\rho_v)(N_{\text{cr}} v_l)^{2/3}, \qquad (45)$$

where $v_l = 1/\rho_l$ is the molecular volume. The Zeldovich factor gives the contribution to the nucleation rate of number fluctuations in the critical droplet as

$$Z_{cr}(N_{\text{cr}}) = (\beta\gamma_\infty)^{1/2} \left(\frac{2}{9\pi\rho_l N_{\text{cr}}^2} \right)^{1/3}. \qquad (46)$$

The ideal gas law has been used to relate vapor quantities, $\beta P(\rho_v) = \rho_v = 1/v_v$.

Comparison of the two nucleation-rate expressions, Eqs. (42) and (43), suggests the identification of the dynamical prefactor $\kappa/(2\pi)$ with the growth rate $\beta_g(N_{\text{cr}})$ and the fluctuations correction Ω' with the Zeldovich factor $Z_{cr}(N_{\text{cr}})$. These identifications imply that the growth rate is given by the kinetic-theory result for the number of collisions between two molecules in a gas, and that the only critical-droplet fluctuations incorporated are number fluctuations. Thus, the modified nucleation rate becomes

$$I_{\text{nuc}} = \beta_g(N_{\text{cr}}) Z_{cr}(N_{\text{cr}}) V J_{\text{tran}} e^{-\beta\Delta\Omega^\star_{\text{CNT}}} \qquad (47a)$$

$$= \frac{3}{\sqrt{m}} \frac{\gamma_\infty^2}{m_2^{3/2}} \left(\frac{\rho_v^2}{\rho_l^7} \right)^{1/2} V N_{\text{cr}} e^{-\beta\Delta\Omega^\star_{\text{CNT}}}. \qquad (47b)$$

In writing the last equality the correlation length was eliminated in favor of the macroscopic surface tension. Since the product of the growth rate times the Zeldovich factor is dimensionless, inspection of Eq. (47a) shows that the Jacobian ensures that the nucleation rate per unit volume has the correct dimensions. In the classical rate [Eq. (44)], the vapor density ensures that the rate has correct dimensions.

VI. CLASSICAL NUCLEATION THEORY MODIFIED

The modified classical nucleation rate [Eq. (47b)] is rewritten in a more suggestive form so that it may be compared to previous proposals for the incorporation of translational corrections. Following the suggestion that these additional degrees of freedom contribute to the leading-order correction

to $\beta\Delta\Omega_{\text{CNT}}$, we rewrite the nucleation rate as

$$I_{\text{nuc}} = \left(\frac{2\gamma_\infty}{\pi m} \right)^{1/2} \frac{\rho_v}{\rho_l} e^{-\beta\Delta\Omega^\star_{\text{mod}}}, \qquad (48)$$

where the prefactor is the product of the classical growth rate times the Zeldovich factor (both evaluated at the critical monomer number N_{cr}), and the other terms have been exponentiated to give

$$\beta\Delta\Omega^\star_{\text{mod}} = -N_{\text{cr}}\ln S + \theta N_{\text{cr}}^{2/3} - \ln(V J_{\text{tran}}). \qquad (49)$$

For notational simplicity we introduced the dimensionless surface tension $\theta = (36\pi)^{1/3} \beta\gamma_\infty / \rho_l^{2/3}$. The first two terms in Eq. (49) are the free energy of formation of an N_{cr}-monomer cluster according to classical nucleation theory; the last term is

$$-\ln(V J_{\text{tran}}) = -\frac{3}{2} \ln(\theta N_{\text{cr}}^{2/3}) - \ln\left[\frac{V}{(\beta\alpha\lambda^2\rho_l)^{3/2}} \right]. \qquad (50)$$

The second moment of the attractive potential m_2 was eliminated from Eq. (50) in terms of the range of the attractive potential λ defined as

$$\lambda^2 = \frac{1}{3} \frac{\displaystyle\int d\mathbf{r}\, r^2 V_{\text{att}}(r)}{\displaystyle\int d\mathbf{r}\, V_{\text{att}}(r)} = \frac{2m_2}{\alpha}. \qquad (51)$$

Thus, the final expression for the modified droplet free energy of formation becomes

$$\beta\Delta\Omega^\star_{\text{mod}} = -N_{\text{cr}}\ln S + \theta N_{\text{cr}}^{2/3} - \frac{3}{2} \ln(\theta N_{\text{cr}}^{2/3}) + \frac{3}{2} \ln(\beta\alpha\rho_l)$$

$$- \ln\left(\frac{V}{\lambda^3} \right). \qquad (52)$$

A decomposition of the correction to the classical expression has been chosen such that each term may be interpreted physically. The first correction term is a logarithmic correction to the surface-free energy term. The second is an additive (logarithmic) contribution to the free energy of formation: the argument of the logarithm is the (dimensionless) average attractive energy in the condensed phase. The last term defines a length scale (or equivalently a volume scale) necessary for a correct counting of translational states and the calculation of the corresponding entropy term, as summarized in the Introduction. For completeness we calculate the relevant parameters (such as λ and α) for a Lennard-Jones-type potential in Appendix C.

The decomposition presented in Eq. (52) suggests that there is a "natural" proper scale for the definition of an effective volume, necessary to treat translational degrees of freedom (equivalently, the length scale to be used to distinguish different states or configurations). This length scale is defined at the molecular level and is related to the range of the attractive interaction potential.

The proposed free energy may be compared to the frequently used general formula for an N cluster

$$\beta\Delta\Omega(N) = -N\ln S + k_N\theta N^{2/3} + \tau\ln N - \ln(q_0 V). \quad (53)$$

The quantity k_N describes N-dependent deviations of the cluster surface energy from that of a macroscopic liquid droplet, whereas τ and q_0 are adjustable parameters. The first two terms are the volume and surface contributions considered in classical nucleation theory, the others are terms like positional and configurational entropies.

Equation (53) is based on the droplet model proposed by Fisher [31] and reelaborated by Dillmann and Meier [13]. Droplet models may be expressed in this form: $\tau=0$ yields the classical theory (no mechanical degrees of freedom), $\tau=-4$ yields the theory of Lothe-Pound [1] (translational and rotational degrees of freedom), $3/2<\tau<-1/2$ yields versions of the Reiss-Katz-Cohen [3] theories (center-of-mass fluctuations). Dillmann and Meier proposed $\tau\sim2.2$, whereas Fisher [31] argued that the nonclassical contribution arose from the droplet configurational entropy to obtain $\frac{57}{26}\lesssim\tau\lesssim\frac{11}{2}$. Each theory has its own value for q_0, and $k_N=1$ is common to all of them. The functional form of the N term suggests that it is an entropic contribution. Note that Eq. (53) is a general expression for an N-cluster, whereas the modified expression [Eq. (52)] has been evaluated at the extremal configurations (i.e., at N_{cr}).

The modified formula expressed in this form yields

$$k_N = 1 - \frac{3}{2}\frac{\ln\theta}{\theta}N_{cr}^{-2/3}, \quad (54)$$

and $\tau=-1$.

Recently Reiss, Kegel, and Katz (RKK) [5] proposed an intuitively appealing correction. They argued that a droplet can be defined up to volume fluctuations: their expression for the correction to classical nucleation theory is

$$\beta\Delta\Omega_{RKK} = -\ln\left[V\left(\frac{\beta\rho_l}{N\kappa_T}\right)^{1/2}\right], \quad (55)$$

where κ_T is the isothermal compressibility. The compressibility equation is [32]

$$\frac{\partial\rho}{\partial P} = \beta + \beta\rho\int d\mathbf{r}[g(r)-1], \quad (56)$$

where $g(r)$ is the radial distribution function of the fluid, may be used to replace κ_T in terms of molecular quantities. Substitution yields

$$\beta\Delta\Omega_{RKK} = -\ln\frac{V}{v_l} + \frac{1}{2}\ln N + \ln\left\{1+\rho_l\int_V d\mathbf{r}[g(r)-1]\right\}. \quad (57)$$

In the low-density limit, the logarithm may be expanded, $g(r)\rightarrow\exp[-\beta V_{12}(r)]$, and the integral may be related to the second virial coefficient

$$B_2(T) = -\frac{1}{2}\int d\mathbf{r}[e^{-\beta V_{12}(r)}-1] \quad (58)$$

to obtain

$$\lim_{\rho\rightarrow0}\beta\Delta\Omega_{RKK} = -\ln\frac{V}{v_l} + \frac{1}{2}\ln N - 2\rho_l B_2(T). \quad (59)$$

Thus, if the same decomposition is made for the RKK theory, the molecular volume in the condensed phase becomes the scaling volume, and $\tau=+1/2$. A similar dependence on the molecular volume in the liquid phase has been proposed by Barrett [8], but with a dependence on N_{cr} that is similar to the one derived in this work, $\tau=-1$.

VII. SUMMARY AND CONCLUSIONS

The contribution of a nucleating droplet's translational degrees of freedom to classical nucleation rate was addressed in this work. Our calculation was based on a field-theoretic description of a cluster of condensed-phase molecules in terms of a nonuniform density profile of a liquid-state droplet. This approach, originally proposed in Ref. [12], was motivated by its successful use in quantum phase transitions (and, in particular, in Bose-Einstein condensation). Starting from the many-body Hamiltonian for a system of interacting Bose particles, a functional-integral representation of the classical partition function was obtained. The symmetry properties of the many-body Bose wave function and the h normalization factor of the classical partition function were introduced in the functional-integral measure. The classical entropy term ($\rho\ln\rho$) in the partition-function action was directly related to the symmetry properties of the many-body wave function, and in particular to particle indistinguishability. Only two-body interactions were considered, an approximation that leads to a low-density expansion of the appropriate classical thermodynamic potential.

The intermolecular interaction potential was decomposed into a short-range (local) repulsive part and a long-range (nonlocal) attractive part. This decomposition naturally led to the identification of two different length scales: the lattice spacing a, a length scale introduced in the lattice regularization of the functional integral, and an effective hard-sphere diameter σ. It was argued that for $\sigma\ll a$, the continuum limit of the partition function implies a coarse graining of the initial attractive interaction potential. In that limit, the parameter that characterizes short-range repulsive interactions was specified in terms of an effective hard-sphere diameter.

The free energy of formation of the nucleating droplet was obtained in the saddle-point evaluation of the functional integral as the free energy difference of two extremal configurations: the (spatially) nonuniform field configuration and the uniform metastable configuration. This free energy difference was related to the capillarity approximation of classical nucleation theory by postulating a physically motivated nonuniform density profile. The density ansatz was used to resum the low-density expansion to obtain the Helmholtz free energy density of a uniform fluid (be it vapor or liquid). The nonlocal attractive term was expanded in gradi-

ents, retaining only the leading-order square-gradient term.

In the limit of a droplet radius much larger than the interfacial correlation length, a limit consistent with the capillarity approximation, we showed that the local free energy term gives a negative volume contribution to the droplet free energy (for saturation ratios greater than unity) and the gradient term a positive surface contribution. Thus, the expression for the droplet free energy in the capillarity approximation was obtained in the mean-field approximation of the functional integral. This argument provides a (valid in the appropriate low-density limit, yet not rigorous) justification of the frequently postulated classical expression starting from microscopic (i.e., molecular level) considerations. It was noted that in the classical density-functional theory of nucleation, only the hard-sphere part is resummed, whereas the attractive part of the interaction potential is kept as a leading-order perturbation.

As discussed in the past, see, for example, Refs. [12,27,29] the nucleation-rate prefactor was expressed as the product of a dynamical prefactor times a statistical prefactor. We argued that the exponential term in the nucleation rate reduces to the classical nucleation theory expression. The statistical prefactor was split into a contribution of the translational eigenmodes and a contribution of all other Gaussian fluctuations about the saddle and metastable configurations. The translational eigenmodes were treated as described in Paper I and summarized herein, whereas the dynamical prefactor was approximated by the droplet growth rate as given by kinetic theory. Furthermore, only critical-number fluctuations were considered. This approximation corresponds to keeping only the negative eigenvalue of the saddle-point Gaussian-fluctuations matrix, an approximation that reduces to the so-called Zeldovich factor in classical nucleation theory.

The consistent incorporation of the effect of translational eigenmodes in the nucleation rate along with the connection of the classical droplet free energy to the evaluation of the partition function are the main results of our work.

The modification of the classical nucleation rate was formally viewed as a modification of the droplet free energy The resulting expression was discussed in terms of the general formula proposed by Dillmann and Meier [13] for the droplet free energy of formation. We showed that the additional terms modify the surface energy and contribute an additive (logarithmic) contribution. More importantly, we showed that the proper length scale for the calculation of the entropy associated to droplet's translational states is related to the interaction range of the coarse-grained, attractive interaction potential.

It should be mentioned that our expression for the droplet free energy neglects the contribution of all other fluctuations (e.g., distortion of the droplet surface that would lead to an additional droplet configurational entropy). Such a calculation involves the determination of the contribution of Gaussian fluctuations about the two extremal configurations. Our analysis of the nucleation rate in terms of a functional integral suggests that previously developed techniques for saddle-point evaluations of functional integrals may be profitably used for the calculation of the additional configurational-entropy term. This exercise is left as future work, as is the numerical solution of the Euler-Lagrange equation that will provide a numerical justification for the density-profile ansatz. An additional topic of interest that will be addressed in future work is a detailed comparison of results of the corrected (to account for translations) predictions of our self-consistent revision of classical nucleation theory with experimental results on homogeneous nucleation of gases that can be described well by approximate intermolecular potentials (such as the Lennard-Jones potential; see e.g., Appendix C).

APPENDIX A: GRADIENT EXPANSION

As argued in the main text, the action in the classical partition function Eq. (10) is a function of the local density $\rho(\mathbf{r})$,

$$\beta S_{cl}[\rho] = \int d\mathbf{r} \left\{ -\beta\mu\rho(\mathbf{r}) + \frac{1}{2}\beta f(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\beta g\rho^2(\mathbf{r}) \right.$$
$$\left. + \rho(\mathbf{r})\ln[\Lambda^3\rho(\mathbf{r})] - \rho(\mathbf{r}) \right\}, \tag{A1}$$

where the nonlocal, attractive term $f(\mathbf{r})$, defined in Eq. (5), is

$$f(\mathbf{r}) = \int d\mathbf{r}' V_{\text{att}}(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}'). \tag{A2}$$

The attractive potential is assumed spherically symmetric. The local density $\rho(\mathbf{r}')$ in Eq. (A2) is expanded in a Taylor expansion about $\mathbf{r}$, and its substitution in $f(\mathbf{r})$ introduces the following terms in $S_{cl}[\rho]$:

$$\int d\mathbf{r}\, d\mathbf{r}' f(\mathbf{r})\rho(\mathbf{r}) = f_0 + f_1 + f_2 + \cdots, \tag{A3}$$

where f_i are defined to be

$$f_0 = \int d\mathbf{r}\, d\mathbf{r}' \rho(\mathbf{r}) V_{\text{att}}(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}), \tag{A4a}$$

$$f_1 = \int d\mathbf{r}\, d\mathbf{r}' \rho(\mathbf{r}) V_{\text{att}}(|\mathbf{r}-\mathbf{r}'|)\frac{d\rho}{d\mathbf{r}_i}\bigg|_{\mathbf{r}} (\mathbf{r}-\mathbf{r}')_i, \tag{A4b}$$

$$f_2 = \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}' \rho(\mathbf{r}) V_{\text{att}}(|\mathbf{r}-\mathbf{r}'|)\frac{d^2\rho}{d\mathbf{r}_i d\mathbf{r}_j}\bigg|_{\mathbf{r}} (\mathbf{r}-\mathbf{r}')_i (\mathbf{r}-\mathbf{r}')_j. \tag{A4c}$$

Only leading-order terms in the gradient expansion were retained. The expansion, which assumes long-wavelength variations of the density, can be made more formal by introducing a scale parameter as described in Ref. [33].

For an infinite system with α the strength of the attractive interaction, defined in Eq. (15),

$$f_0 = -\alpha \int d\mathbf{r}\rho^2(\mathbf{r}). \tag{A5}$$

Symmetry arguments (spherically symmetric attractive potential) show that the linear-gradient term f_1 vanishes. The third term may be reexpressed in term of $\mathbf{x} = \mathbf{r} - \mathbf{r}'$ as follows:

$$f_2 = \frac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})\frac{d^2\rho}{d r_i d r_j}\bigg|_{\mathbf{r}}\int d\mathbf{x}V_{\text{att}}(|\mathbf{x}|)x_i x_j \tag{A6a}$$

$$= \frac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})\frac{d^2\rho}{d\mathbf{r}\cdot d\mathbf{r}}\bigg|_{\mathbf{r}}\left\{\frac{1}{3}\int d\mathbf{x}\,V_{\text{att}}(|\mathbf{x}|)\mathbf{x}^2\right\} \tag{A6b}$$

$$= m_2\int d\mathbf{r}\left(\frac{d\rho}{d\mathbf{r}}\right)^2_{\mathbf{r}}, \tag{A6c}$$

where the term $\mathbf{x}_i \cdot \mathbf{x}_j$ was replaced by $\mathbf{x}_i^2$ because the cross terms are odd functions, $\mathbf{x}_i^2 = \mathbf{x}\cdot\mathbf{x}/3$ since all three directions are equivalent (spherical symmetry), the surface term was dropped in the integration by parts, and the second moment of the attractive potential m_2 was defined in Eq. (22).

Thus, the gradient approximation to the classical action becomes

$$\beta S[\rho] = \int d\mathbf{r}\left\{\frac{1}{2}\beta m_2(\boldsymbol{\nabla}\rho)^2 - \beta\mu\rho(\mathbf{r}) + \frac{1}{2}\beta(g-\alpha)\rho^2(\mathbf{r})\right.$$
$$\left. + \rho(\mathbf{r})\ln[\Lambda^3\rho(\mathbf{r})] - \rho(\mathbf{r})\right\}. \tag{A7}$$

This derivation justifies Eq. (21) in the main text.

APPENDIX B: LARGE-DROPLET LIMIT

We present exact and limiting values for integrals that appear in the main text as calculated by *Mathematica* [23]. The $R_c \gg \xi$ limiting values were obtained by first evaluating the integrals for a given droplet radius (the integrals usually evaluate to polylogarithm functions) and then the large-droplet limit was taken. In some (explicitly mentioned) cases, the limit $\rho_l \gg \rho_v$ was taken before the large-droplet limit to avoid indeterminate limits.

The integrals that follow are necessary for the evaluation of the volume term of the droplet free energy

$$\lim_{R_c\to\infty}\int_0^\infty dr r^2[\tanh(r-R_c)-1]$$

$$= \lim_{R_c\to\infty}\frac{F(3,-z)}{2}$$

$$= -\frac{2}{3}R_c^3 - \frac{\pi^2}{6}R_c + O(R_c^{-2n+1}), \tag{B1a}$$

$$\lim_{R_c\to\infty}\int_0^\infty dr\, r^2\text{sech}^2(r-R_c)$$

$$= \lim_{R_c\to\infty} -F(2,-z)$$

$$= 2R_c^2 + \frac{\pi^2}{6} + O(R_c^{-2n}), \tag{B1b}$$

where $n = 1,2,3,\ldots$, $z = \exp(2R_c)$, and the polylogarithm function $F(n,z)$ is

$$F(n,z) = \sum_{k=1}^\infty \frac{z^k}{k^n}. \tag{B2}$$

It is relatively easy to note that the following general result holds:

$$\lim_{R_c\to\infty}\int_0^\infty dr\, r^2[\tanh(r-R_c)-1]^n = \frac{(-2)^n}{3}R_c^3. \tag{B3}$$

A limit required for the expression of the number of monomers in the critical cluster N_{cr} in terms of the critical radius, with the additional assumption that $\rho_l \gg \rho_v$, is

$$\lim_{R_c\to\infty}\int_0^{R_c} dr\, r^2[1-\tanh(r-R_c)] = \frac{2}{3}R_c^3 - R_c^2\ln(2). \tag{B4}$$

The integrals that lead to the surface-energy term and the square-gradient surface tension evaluate to

$$\lim_{R_c\to\infty}\int_0^\infty dr\,\text{sech}^4(r-R_c) = \lim_{R_c\to\infty}\left\{\frac{4z^2(3+z)}{3(1+z)^2}\right\}$$

$$= \frac{4}{3} + O[\exp(-R_c)], \tag{B5a}$$

$$\lim_{R_c\to\infty}\int_0^\infty dr\, r^2\,\text{sech}^4(r-R_c)$$

$$= \lim_{R_c\to\infty}\left\{-\frac{2[z+(1+z)F(2,-z)]}{3(1+z)}\right\}$$

$$= \frac{4}{3}R_c^2 + \frac{\pi^2-6}{9} + O(R_c^{-2n}). \tag{B5b}$$

Finally, the limiting value of the exact integral (in the spirit of Eq. (31a) of Ref. [12]) that appears in the evaluation of the Jacobian Eq. (39) in the limit $\rho_l \gg \rho_v$ is

$$
\lim_{R_c \to \infty} \int_0^\infty dx \, x^2 \frac{\text{sech}^4(x - R_c)}{1 - \tanh(x - R_c)}
$$

$$
= \lim_{R_c \to \infty} \{\ln(1 + z) - F(2, -z)\}
$$

$$
= 2R_c^2 + 2R_c . \tag{B6}
$$

APPENDIX C: INTERACTION POTENTIAL

The numerical evaluation of the modified classical nucleation rate requires, apart from the density profile, the evaluation of the strength and the interaction range of the coarse-grained attractive potential V_{att}. For completeness, we present these parameters for the (modified, fully attractive) Lennard-Jones (LJ) potential, decomposed as described in Ref. [34], namely,

$$
V_{\text{att}}(r) = -\epsilon \quad \text{for} \quad r < 2^{1/6}\sigma, \tag{C1a}
$$

$$
V_{\text{att}}(r) = 4\epsilon \left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right) \quad \text{for} \quad r \geq 2^{1/6}\sigma. \tag{C1b}
$$

Then, one finds that the strength of the attractive potential is

$$
\alpha_{\text{LJ}} = \frac{32\pi}{9}\sqrt{2}\epsilon\sigma^3, \tag{C2}
$$

the second moment of the attractive potential evaluates to

$$
m_2 = -\frac{1}{6}\int d\mathbf{r} \, r^2 V_{\text{att}}(r) = \frac{48}{35}2^{5/6}\epsilon\pi\sigma^5, \tag{C3}
$$

and the corresponding interaction range λ_{LJ} is

$$
\lambda_{\text{LJ}} = \left(\frac{27}{35} \right)^{1/2} 2^{1/6}\sigma. \tag{C4}
$$

Caution has to be exercised in using these formulas when comparing theoretical predictions with experimental results. The approximation of the intermolecular interaction potential by a Lennard-Jones potential is expected to be reasonable for nonpolar, almost spherical molecules but not for small polar molecules such as water. Moreover, the choice of the hard-sphere diameter, i.e., the mapping of the Lennard-Jones potential to a hard-sphere fluid is not unique [22]. Alternatively, the Lennard-Jones parameters may be determined by a fitting procedure that ensures that bulk thermodynamic properties or the macroscopic surface tension are obtained [34].

[1] J. Lothe and G.M. Pound, J. Chem. Phys. **36**, 2080 (1962).

[2] R.H. Heist and H. He, J. Phys. Chem. Ref. Data **23**, 781 (1994).

[3] H. Reiss, J.L. Katz, and E.R. Cohen, J. Chem. Phys. **48**, 5553 (1968).

[4] H. Reiss and W.K. Kegel, J. Phys. Chem. **100**, 10428 (1996).

[5] H. Reiss, W.K. Kegel, and J.L. Katz, Phys. Rev. Lett. **78**, 4506 (1997); **102**, 8548 (1998).

[6] J.G. Kirkwood, J. Chem. Phys. **18**, 380 (1950).

[7] I.J. Ford, Phys. Rev. E **56**, 5615 (1997).

[8] J. Barrett, J. Chem. Phys. **107**, 7989 (1997).

[9] J.S. Langer, Ann. Phys. (N.Y.) **41**, 108 (1967).

[10] V. Talanquer and D.W. Oxtoby, J. Chem. Phys. **100**, 5190 (1994).

[11] D. Reguera and J.M. Rubí, J. Chem. Phys. **115**, 7100 (2001).

[12] Y. Drossinos, P.G. Kevrekidis, and P.G. Georgopoulos, Phys. Rev. E **63**, 036123 (2001).

[13] A. Dillmann and G.E.A. Meier, J. Chem. Phys. **94**, 3872 (1991).

[14] F. Dalfovo, S. Giorgini, L.P. Pitaevskii, and S. Stringari, Rev. Mod. Phys. **71**, 463 (1999).

[15] K. Huang, *Statistical Mechanics* (Wiley, New York, 1963).

[16] H.-J. Woo and X. Song, J. Chem. Phys. **114**, 5637 (2001).

[17] H. Frusawa and R. Hayakawa, Phys. Rev. E **60**, R5048 (1999).

[18] G. Parisi, *Statistical Field Theory* (Addison-Wesley, Reading, MA, 1998).

[19] J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1976).

[20] T.L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, New York, 1986).

[21] D.W. Oxtoby and R. Evans, J. Chem. Phys. **89**, 7521 (1989).

[22] X.C. Zeng and D.W. Oxtoby, J. Chem. Phys. **94**, 4472 (1991).

[23] S. Wolfram, *The Mathematica Book*, 4th ed. (Cambridge University Press, Cambridge, 1999).

[24] D.J. Lee, M.M. Telo de Gama, and K.E. Gubbins, J. Chem. Phys. **85**, 490 (1985).

[25] Y. Drossinos and D. Ronis, Phys. Rev. B **39**, 12 078 (1989).

[26] J.S. Langer, Ann. Phys. (N.Y.) **54**, 258 (1969).

[27] J.S. Langer, Physica (Amsterdam) **73**, 61 (1974).

[28] N.J. Günther, D.A. Nicole, and D.J. Wallace, J. Phys. A **13**, 1755 (1980).

[29] J.S. Langer and L.A. Turski, Phys. Rev. A **8**, 3230 (1973).

[30] J.H. Seinfeld and S.N. Pandis, *Atmospheric Chemistry and Physics* (Wiley, New York, 1998).

[31] M.E. Fisher, Physics (Long Island City, N.Y.) **3**, 255 (1967).

[32] D.A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).

[33] R. Evans, Adv. Phys. **28**, 143 (1979).

[34] R. Nyquist, V. Talanquer, and D.W. Oxtoby, J. Chem. Phys. **103**, 1175 (1995).