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Hydrodynamic Model of the Condensation of a Vapor near Its Critical Point*

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A hydrodynamic model is used to describe the condensation of a supersaturated vapor near its critical point. Calculations are based on a statistical theory of nucleation previously developed by one of the authors (J.S.L.). The method permits careful study of various statistical corrections and a quantitative treatment of the thermal nonaccommodation effect. Although the theory developed here is based on assumptions which are quite different from the classical Becker-Döring theory, numerical predictions of the critical supersaturation in Xe and CO_2 turn out to be very nearly the same as the classical results.

I. INTRODUCTION

In a previous paper,[1] one of the present authors has proposed a systematic theory of nucleation rates in metastable systems. This theory, in principle, is applicable to a broad class of statistical models of first-order phase transformations. To date, however, it has been applied only to one specific physical phenomenon, the decay of persistent current in a filamentary superconductor.[2] Our purpose in the present report is to outline a second application, specifically, to the condensation of a supersaturated vapor in the neighborhood of its critical point.

The classical theory of nucleation phenomena[3] is currently in a state of considerable uncertainty. The introduction by Lothe and Pound[3,4] of statistical corrections to the Becker-Döring formula[5,6] has called into question what was previously thought to be good qualitative agreement between the classical theory and experimental data. Most recently, Cahn and Heady[7] have confirmed earlier experimental observations by Sundquist and Oriani[8] on the nucleation of phase separation in a two-component fluid, and have concluded that the classical theory of nucleation must be seriously in error. Inasmuch as the nucleation picture is central to our understanding of the kinetics of first-order phase transformations, it seems important that the current situation be clarified by new theoretical and experimental investigations. The present work is intended as a contribution to this program of clarification.

The nucleation theory described in Ref. 1 is basically a classical theory in that the metastable state decays via thermal activation of a localized unstable fluctuation; for example, a critically large droplet. This droplet, however, may be "nonclassical" in the sense of Cahn and Hilliard.[9] That is, it need not necessarily be identifiable as a well-defined nucleus of the condensing phase. Nor, in our theory, need the probability of formation of this droplet be related in any simple mathematical way to the population of small clusters which may describe the state of metastable equilibrium. The most important distinction between the present theory and the classical one is that here we need not make any *ad hoc* assumptions regarding the over-all fluctuation rate which drives the nucleation process. This rate comes naturally out of our basic statistical formulation of the problem and, under certain circumstances, turns out to be qualitatively different from that assumed in the earlier theories.

The scheme of this paper is as follows. In Sec. II, we restate the main results of Ref. 1 and comment briefly on the meaning of certain terms which enter into the nucleation formula. In Sec. III, we introduce our hydrodynamic model for the vapor-liquid phase transition and discuss its limits of validity, especially the restriction to phenomena occurring in or near the critical region of the phase diagram. (Throughout the paper, we shall refer explicitly only to supercooling and condensation; but our theory applies equally well to superheating and boiling.) The nucleation formula is then evaluated for this model in Sec. IV and V. Section VI is devoted to an analysis of the thermal nonaccommodation effect. Apart from one important conjecture regarding the way in which fluctuations in the shape of a critical droplet are incorporated into its surface free energy, our mathematical development in Secs. IV–VI requires no assumptions other than those built into the original model. The experimental implications of these results are described in Sec. VII. Finally, there is an Appendix in which certain formal aspects of these calculations are discussed.

As we shall show in Sec. VII, the predictions of this theory are quantitatively almost identical to those of the Becker-Döring theory[5,6] for the experimentally accessible situations that we shall consider. There appear to be no analogs of the Lothe-Pound corrections[4]; and the new statistical factors that we do find turn out to have no dramatic effect on the nucleation rate. A careful experimental test of this theory seems to us to be feasible and very much needed. The critical regions of at least two substances, Xe and CO_2, have been carefully studied experimentally; and thus the numerical ingredients of our nucleation formulas are nearly all available. Moreover, we believe that homogeneous nucleation should be more easily observable near the critical point than elsewhere, because the critical droplets are so large that they should not be very sensitive to small heterogeneities in the sample. A major discrepancy of the sort found by Cahn and Heady,[7] if it exists, should therefore be clearly verifiable and extremely interesting.

II. GENERAL NUCLEATION FORMULA

The general theory of nucleation developed in Ref. 1 starts with the introduction of a set of variables η_i, $i=1,\ldots,\mathfrak{N}$, which describe $\mathfrak{N}$ degrees of freedom of the system of interest. In the system with which we are concerned, for example, the η_i will be the number densities $n(\vec{r})$ and flow velocities $\vec{u}(\vec{r})$ at positions $\vec{r}$ in the fluid. Thus, a sum over the index i represents an integration over $\vec{r}$ and a sum over each of the density and flow fields.

We next introduce a distribution function $\rho(\{\eta\},t)$, which is a probability density over configurations $\{\eta\}$ and is also a function of time t. We hypothesize that ρ satisfies a continuity equation of the form

$$\frac{\partial\rho}{\partial t}=-\sum_{i=1}^{\mathfrak{N}}\frac{\partial J_i}{\partial\eta_i}, \tag{2.1}$$

where the probability current J_i is given by

$$J_i=-\sum_{j=1}^{\mathfrak{N}}M_{ij}\left(\frac{\partial F}{\partial\eta_j}\rho+k_BT\frac{\partial\rho}{\partial\eta_j}\right). \tag{2.2}$$

Here, M_{ij} is a generalized mobility matrix, and $F\{\eta\}$ is a coarse-grained free energy. (The function F was denoted by E in Ref. 1.) Both of the latter quantities will be discussed in detail as they arise in more specific connections. For the moment, note simply that Eqs. (2.1) and (2.2) can be derived via standard statistical techniques by adding a suitable Langevin force to the equation of motion:

$$\frac{\partial\eta_i}{\partial t}=-\sum_{j}^{\mathfrak{N}}M_{ij}\frac{\partial F}{\partial\eta_j}. \tag{2.3}$$

We shall restrict all of our analysis to systems whose underlying dynamical properties can be described in the form (2.3).

The equilibrium solutions of (2.1) and (2.2) have the form

$$\rho_{eq}\{\eta\}\propto e^{-\tilde{F}\{\eta\}/k_BT}, \tag{2.4}$$

where $\tilde{F}$ is equal to F plus certain constants of motion of Eq. (2.3). For example, we shall use $\tilde{F}=F-\mu N$, where N is the total number of molecules in the system and μ is the chemical potential. The states of stable and metastable equilibrium lie at or near configurations $\{\eta\}$, which locate minima of $\tilde{F}$ and which therefore maximize ρ_{eq}. A phase transition takes place when the configuration $\{\eta\}$ starts at one such minimum, say $\{\eta_0\}$, and moves to the vicinity of another minimum of lower $\tilde{F}$. In doing this, it is most likely to pass near the lowest intervening saddle point of $\tilde{F}$, which we denote by $\{\bar{\eta}\}$. As has been argued previously,[1] $\{\bar{\eta}\}$ will describe a configuration which is everywhere the same as the initial metastable state $\{\eta_0\}$ except for the presence of a single localized fluctuation, i.e., a critically large droplet of the condensing phase. The rate of probability flow across the saddle point $\{\bar{\eta}\}$ determines the desired nucleation rate.

The formula for this nucleation rate, I, as derived in Ref. 1, can be written in the form

$$I=I_0e^{-\Delta F/k_BT}. \tag{2.5}$$

We shall write the prefactor I_0 as the product of two terms:

$$I_0=(\kappa/2\pi)\Omega_0, \tag{2.6}$$

where $\kappa/2\pi$ will be referred to as the "dynamical prefactor" and Ω_0 as the "statistical prefactor." The latter quantity can be written

$$\Omega_0=\mathcal{V}\left(\frac{2\pi k_BT}{|\bar{\lambda}_1|}\right)^{1/2}\prod_{\alpha=\alpha_0+2}^{\mathfrak{N}}\left(\frac{2\pi k_BT}{\bar{\lambda}_\alpha}\right)^{1/2}\times\prod_{\beta=1}^{\mathfrak{N}}\left(\frac{\lambda_\beta^{(0)}}{2\pi k_BT}\right)^{1/2}. \tag{2.7}$$

Each of the ingredients of Eqs. (2.5)–(2.7) will be defined in the following paragraphs.

The activation energy ΔF is

$$\Delta F=F\{\bar{\eta}\}-F\{\eta_0\}. \tag{2.8}$$

This term is the same as that which has been computed in considerable detail by Cahn and Hilliard.[9]

The statistical factor Ω_0 is a measure of the volume of the saddle-point region in η space; that is, Ω_0 is a generalization of the Zeldovich factor.[6] The quantities $\lambda_\alpha^{(0)}$ which appear in Ω_0 are eigenvalues of the matrix

$$\frac{\partial^2F}{\partial\eta_i\,\partial\eta_j}$$

evaluated at the metastable minimum $\{\eta_0\}$. According to the definition of $\{\eta_0\}$, all the $\lambda_\alpha^{(0)}$ must be positive. Similarly, the $\bar{\lambda}_\alpha$ are eigenvalues of the above second-derivative matrix, in this case evaluated at the saddle point $\{\bar{\eta}\}$. Because $\{\bar{\eta}\}$ locates the highest point along the path of lowest energy leading away from $\{\eta_0\}$, there must be one and only one eigenvalue $\bar{\lambda}_\alpha$ which is negative; and this is the eigenvalue that we denote by $\bar{\lambda}_1$ in Eq. (2.7). If $F\{\eta\}$ has translational symmetry, then there must be at least three other eigenvalues $\bar{\lambda}_\alpha$ which are identically zero, corresponding to the three independent translations of the position of the symmetry-breaking fluctuation (droplet) described by $\{\bar{\eta}\}$. The product of $\bar{\lambda}$'s appearing in (2.7) starts with $\alpha = \alpha_0 + 2$, where α_0 is the total number of symmetries of F which are broken by $\{\bar{\eta}\}$. The integration over these α_0 degrees of freedom defines the factor $\mathcal{V}$ in (2.7). That is, $\mathcal{V}$ is the volume of the α_0-dimensional region of η space spanned by the set of configurations $\{\bar{\eta}\}$ which leave $F\{\bar{\eta}\}$ invariant.

The dynamical factor κ is the exponential growth rate of the unstable mode of deformation $\{\bar{\eta}\}$. To compute κ, we linearize (2.3) about $\eta_i = \bar{\eta}_i$. That is, we write

$$\frac{\partial \nu_i}{\partial t} = -\sum_{jl}^{\mathfrak{N}} M_{ij} \frac{\partial^2 F}{\partial \bar{\eta}_j \partial \bar{\eta}_l} \nu_l , \tag{2.9}$$

where $\nu_i = \eta_i - \bar{\eta}_i$. Then, setting $\nu_i \propto e^{\kappa t}$, we identify κ as the positive eigenvalue of the matrix

$$-\sum_j M_{ij} \frac{\partial^2 F}{\partial \bar{\eta}_j \partial \bar{\eta}_l} . \tag{2.10}$$

In the condensation problem, the instability described by κ is just the initial growth of a droplet which has exceeded the critical size.

III. HYDRODYNAMIC MODEL

The model of condensation of a supersaturated vapor which we shall propose here will be defined by our choice of the statistical variables η_i and the corresponding coarse-grained free energy $F\{\eta\}$. In fact, this model and its limitations are almost completely determined by our interpretation of the coarse-graining process.

The conventional formulation of classical many-body statistical mechanics in terms of molecular positions and momenta is not a very convenient one for present purposes. In the first place, it does not fit—at least not very easily—into the theory outlined in Sec. II. It is also much too detailed. We are not really interested in knowing which pair of molecules is interacting at any given time and position. Finally, the conventional formulation does not provide a very natural way of describing processes, such as condensation, which are characterized by semimacroscopic density fluctuation involving large numbers of molecules. For such processes, a hydrodynamic description in terms of local number density, flow velocity, and, perhaps, entropy density seems most appropriate.

In principle, the hydrodynamic model can be derived from the molecular model by a coarse-graining or cellular method.[10,11] That is, one divides up the macroscopic system into semimacroscopic cells of given volume and assigns specific densities and flows to each of these cells. The free energy computed by performing a partition sum subject to the cellular constraints is the coarse-grained F that we are talking about. There is no problem, in principle, in summing over the cellular densities and flows to obtain the true equilibrium free energy. Moreover, as long as each cell comes to local thermal equilibrium rapidly compared to the times required for the hydrodynamic processes that one wants to consider, then one can use the coarse-grained F for computing nonequilibrium properties of the system.

The question which arises at this point is: what is a suitable size for the coarse-graining cells? In order for the hydrodynamic description to make sense, the cell volume must be much larger than the average volume per molecule. For our purposes, however, the cells cannot have linear dimensions appreciably larger than a correlation length. If the cells are chosen to be too large, phase separation will occur within single cells, and the interesting details of the condensation mechanism will be lost in the process of taking cellular averages. To put this in another way, we expect F as a function of the average density n to be a nonconvex function with distinct minima corresponding to the vapor and liquid phases. But, if the cell size is large enough for well-defined phase separation to occur within a cell, then F must approach its convex envelope and cannot possibly have the above property. We conclude that the cell size can be neither much larger or much smaller than a correlation length.

It is this last requirement which restricts our theory to the vicinity of the critical point in the vapor-liquid system. Away from the critical point the density of the vapor phase is usually so small compared to that of the liquid that a coarse-graining cell large enough to be meaningful for the vapor must necessarily be big enough to contain a well-defined liquid droplet. Thus, the cellular approximation scheme is internally inconsistent for use in the condensation problem except near the critical point, where the densities are comparable in the two phases and correlation lengths are larger than intermolecular spacings.

With this restriction in mind, we can immediately guess a suitable form for the coarse-grained free energy F. A systematic development of this coarse-graining approximation is outlined in the Appendix. As stated above, we choose as our basic variables the local density and flow fields, $n(\vec{r})$ and $\vec{u}(\vec{r})$. (Strictly speaking, we should include local entropy or temperature fluctuations as additional independent variables, especially for purposes of discussing the thermal nonaccommodation effect in Sec. VI. Inclusion of such variables is not difficult, but raises technical questions which are not essential to the present discussion.) The free energy F must consist of a kinetic energy F_K plus an interaction term F_I. The kinetic term is simply

$$F_K\{n,\vec{u}\}=\tfrac{1}{2}m\int n(\vec{r})\vec{u}^2(\vec{r})\,d^3r. \tag{3.1}$$

We shall assume that F_I is a functional of n only, and that it can be written in the form[12,13]

$$F_I\{n\}=\int[\tfrac{1}{2}K(\vec{\nabla}n)^2+f(n)]\,d^3r, \tag{3.2}$$

where $f(n)$ is the Helmholtz free-energy density and $\frac{1}{2}K(\vec{\nabla}n)^2$ is the usual gradient energy.

The equations of motion for n and $\vec{u}$, that is, Eq. (2.3), will be

$$\frac{\partial n(\vec{r},t)}{\partial t}=-\frac{1}{m}\vec{\nabla}\cdot\frac{\delta F}{\delta\vec{u}}=-\vec{\nabla}\cdot(n\vec{u}) \tag{3.3}$$

and

$$\frac{\partial\vec{u}(\vec{r},t)}{\partial t}=-\frac{1}{m}\vec{\nabla}\frac{\delta F}{\delta n(\vec{r})}$$

$$=-\tfrac{1}{2}\vec{\nabla}\vec{u}^2-\frac{1}{m}\vec{\nabla}\frac{\delta F_I}{\delta n(\vec{r})}. \tag{3.4}$$

Equation (3.3) is the continuity equation, and (3.4) is the Euler equation. From (3.4), it is clear that we must identify the last term on the right-hand side with the gradient of the pressure. That is,

$$\frac{1}{n}\vec{\nabla}p=\vec{\nabla}\frac{\delta F_I}{\delta n}. \tag{3.5}$$

Note that when $n(\vec{r})$ is varying so slowly that the gradient energy can be neglected, Eq. (3.5) is consistent with

$$p=n\frac{\partial f}{\partial n}-f, \tag{3.6}$$

which is a standard thermodynamic relationship.

IV. STATISTICAL PREFACTOR

Our problem now is to evaluate the various quantities which enter into the nucleation formula as given in Eqs. (2.5)–(2.7). In this section we shall consider the statistical prefactor Ω_0. The dynamical prefactor κ will be discussed in Secs. V and VI.

Throughout the remainder of this paper we shall restrict our analysis to the case of classical droplets. That is, we shall consider only the limit in which the nucleating fluctuation described by $\{\bar{\eta}\}$ is, indeed, a well-defined sphere of the liquid phase with a radius R large compared to the interface thickness or the correlation length ξ. In principle, we need not make this restriction in the present theory. As we shall see, however, the classical limit is the appropriate one in cases of interest here. By going to this limit, we can do all of our calculations analytically instead of having to resort to numerical methods.

The stationary point $\{\bar{\eta}\}$ is given in our model by $\vec{u}(\vec{r})=0$ and $n(\vec{r})=\bar{n}(r)$, where $\bar{n}$ satisfies

$$\frac{\delta F_I}{\delta\bar{n}(\vec{r})}=-K\nabla^2\bar{n}+\frac{\partial f}{\partial\bar{n}}=\mu. \tag{4.1}$$

The dropletlike solutions of Eq. (4.1) have been discussed in Ref. 9 and in related papers by one of the present authors.[14,15] Everywhere outside the droplet, $\bar{n}(\vec{r})$ has the value n_v, the vapor density. Within the droplet, $\bar{n}(\vec{r})$ is equal to the liquid density n_l. If $r=|\vec{r}|$ is measured from the center of the droplet, then $\bar{n}(r)$ describes a smooth interfacial profile at $r=R$ going from n_l to n_v within a region roughly the width of the correlation length ξ.

The activation energy, in our approximation, is

$$\Delta F=\tfrac{4}{3}\pi\sigma R^2, \tag{4.2}$$

where σ is the surface energy[9,12]

$$\sigma=K\int_0^\infty\left(\frac{d\bar{n}}{dr}\right)^2dr. \tag{4.3}$$

The actual value of the critical radius R must be determined in the usual way by the degree of supersaturation. We shall quote specific formulas for R in Sec. VII. For present purposes, it will be most convenient to use R explicitly as the single variable which characterizes the size of the droplet.

We turn next to the eigenvalues λ_α. The $\lambda_\alpha^{(0)}$ are eigenvalues of the operator

$$\left.\frac{\delta^2F_I}{\delta n(\vec{r})\delta n(\vec{r}\,')}\right|_{n=n_v}=\left(-K\nabla^2+\frac{\partial^2f}{\partial n_v^2}\right)\delta(\vec{r}-\vec{r}\,'). \tag{4.4}$$

Because the right-hand side of (4.4) depends on $\vec{r}$ only through ∇^2, the eigenfunctions of (4.4) are plane waves with wave vectors, say, $\vec{q}$; and the eigenvalues are

$$\lambda_{\vec{q}}^{(0)} = K\vec{q}^{\,2} + \frac{\partial^2 f}{\partial n_v^2}. \tag{4.5}$$

There is also a set of eigenvalues, formally to be included among the $\lambda_\alpha^{(0)}$, which come from the kinetic term F_K. That is, we should include the eigenvalues of

$$\left.\frac{\delta^2 F_K}{\delta u_i(\vec{r})\delta u_j(\vec{r}\,')}\right|_{n=n_v} = m n_v \delta_{ij}\,\delta(\vec{r}-\vec{r}\,'), \tag{4.6}$$

which are all simply equal to mn_v and are counted three to a coarse-graining cell. A more careful consideration of some of the formal aspects of this calculation leads one to conclude that these eigenvalues are spurious. That is, they do not describe physically significant velocity fluctuations and, thus, do not appear in the final formula for any observable quantity. We shall discuss this point more fully in the Appendix.

At the function-space point $n(\vec{r}) = \bar{n}(\vec{r})$, the operator

$$\left.\frac{\delta^2 F_I}{\delta n(\vec{r})\delta n(\vec{r}\,')}\right|_{n=\bar{n}(\vec{r})} = \left(-K\nabla^2 + \frac{\partial^2 f}{\partial \bar{n}^2}\right)\delta(\vec{r}-\vec{r}\,') \tag{4.7}$$

is no longer translationally symmetric because of the r dependence of $\bar{n}$. As has been discussed previously,[14] the resulting spherically symmetric Schrödinger-like eigenvalue equation has an s-wave ground state with a radial eigenfunction proportional to $d\bar{n}/dr$ and a negative eigenvalue

$$\bar{\lambda}_1 \cong -2K/R^2. \tag{4.8}$$

This eigenstate is associated with the instability of the critical droplet against uniform expansions or contractions. The next states are the three p waves, with eigenvalues $\bar{\lambda} = 0$, which come about because of the broken translational symmetry. Then there are higher-order partial waves with positive $\bar{\lambda}$'s corresponding to volume-conserving deformations of the shape of the droplet. Finally, there is a continuum of nonlocalized eigenfunctions of (4.7) starting at $\bar{\lambda} = \partial^2 f/\partial n_v^2$. These eigenfunctions are similar to the states associated with the $\lambda^{(0)}$ in that they describe fluctuations in the bulk vapor; but here these fluctuations are perturbed by the presence of the droplet. As before, the eigenvalues associated with the kinetic part of F are spurious and can be disregarded.

We now can recognize the products over α and β in (2.7) as representing fluctuation corrections to the mean-field excess free energy of the droplet given by (2.8) and (4.2). These products have been evaluated explicitly for a special form of the function $f(n)$ in Ref. 14, and the result agrees with an expression given by Zittartz[16] for the free energy of a flat surface in the same model. To see this, consider Eq. (D41) of Ref. 14 in the limit of large droplet radius, and compare this expression with Zittartz's Eq. (4.7). Our conclusion is that the products over eigenvalues λ in (2.7), for the most part, must be absorbed into the quantity ΔF. That is, if we are going to evaluate ΔF using measured values of the surface energy and thermodynamic potential, it will be inconsistent to include fluctuation corrections to ΔF in the prefactor Ω_0.

There is, however, a serious gap in our logical development at this point. Strictly speaking, the nucleation formula used here requires that ΔF first be evaluated at the stationary point $\{\bar{\eta}\}$ obtained from Eq. (4.1), and then be corrected by the fluctuation terms in Ω_0. But this procedure would imply that the radius of the critical droplet be determined by the σ given in Eq. (4.3), which is not necessarily the same as the experimental surface free energy because of the fluctuation corrections. What we shall do, instead, is delete the explicit fluctuation terms in Ω_0 and interpret σ everywhere as the true surface energy; and we shall make a similar assumption concerning other thermodynamic quantities that appear. This procedure possibly can be justified formally by going beyond the Gaussian approximations for η-space integrations which were used in deriving Eq. (2.7); that is, by constructing a renormalized perturbation expansion in the neighborhood of $\{\bar{\eta}\}$. If this program can be carried out, we might also be able to compute systematically curvature corrections to the surface energy. These corrections will be omitted here, and we shall focus our attention on other ingredients of the nucleation formula, particularly, the dynamical prefactor. We hope to return, in later publications, both to the formal questions and to the more detailed description of fluctuations on a curved diffuse interface.

Note, now, that there are $n_0 + 1 = 4$ more terms in the product over the $\lambda_\beta^{(0)}$ than in that over the $\bar{\lambda}_\alpha$ in Eq. (2.7). This means that the logarithm of the combined products is not precisely a free-energy difference. To see what is happening here, it is useful to think in terms of a one-to-one pairing between the $\lambda_\beta^{(0)}$ and the $\bar{\lambda}_\alpha$. At the top of the spectra (large positive $\lambda^{(0)}$ and $\bar{\lambda}$), both kinds of eigenvalues correspond to short-wavelength fluctuations which extend throughout the volume of the system, V. We can pair these eigenvalues so that each $\bar{\lambda}$ will differ from its associated $\lambda^{(0)}$ by an amount of order R^3/V, which we can compute using Rayleigh-Schrödinger perturbation theory. Summing over the eigenvalues in this regime, we get a contribution to ΔF of order R^3, independent of V. It is only when we get down to the bottom of the continuum that a finite set of $\bar{\lambda}$'s—those corresponding to localized deformations of the droplet—fall appreciably below their associated $\lambda^{(0)}$'s. Thus, by pairing the λ's as described, the correction to ΔF remains of order R^3 in the limit $V\to\infty$, as it must. This procedure leaves four unpaired $\lambda^{(0)}$'s at the bottom of the spectrum which are not accounted for by the revised ΔF. Specifically, we have

$$\lim_{V\to\infty}\prod_{\beta=1}^{4}\left(\frac{\lambda_\beta^{(0)}}{2\pi k_BT}\right)^{1/2}=\left(\frac{1}{2\pi k_BT}\,\frac{\partial^2 f}{\partial n_v^2}\right)^2 \tag{4.9}$$

remaining as the sole explicit contribution from the complicated products over α and β in Eq. (2.7).

Having written down the value for $\bar{\lambda}_1$ in Eq. (4.8), we need only evaluate the factor $\mathcal{V}$ to complete the calculation of Ω_0. The formula for $\mathcal{V}$ relevant to our model has been given in Refs. 1 and 14. This is

$$\begin{aligned}\mathcal{V}&=V\left[\tfrac{1}{3}\int d\mathbf{r}\,(\vec{\nabla}\bar{n})^2\right]^{3/2}\\&=V\left(\frac{4\pi R^2\sigma}{3K}\right)^{3/2}.\end{aligned} \tag{4.10}$$

Here we have used (4.3) for σ; and we have assumed that $d\bar{n}/dr$ is appreciable only in a narrow region near $r=R$ for the classical droplet.

The resulting expression for Ω_0 is

$$\begin{aligned}\Omega_0=V&\left(\frac{4\pi R^2\sigma}{3K}\right)^{3/2}\left(\frac{\pi k_BTR^2}{K}\right)^{1/2}\\&\times\left(\frac{1}{2\pi k_BT}\,\frac{\partial^2 f}{\partial n_v^2}\right)^2.\end{aligned} \tag{4.11}$$

If we identify a correlation length ξ to be given by

$$\frac{1}{K}\,\frac{\partial^2 f}{\partial n_v^2}=\frac{1}{\xi^2}, \tag{4.12}$$

then we can write (4.11) in the form

$$\Omega_0=\left(\frac{2}{3\sqrt{3}}\right)\left(\frac{V}{\xi^3}\right)\left(\frac{\sigma\xi^2}{k_BT}\right)^{3/2}\left(\frac{R}{\xi}\right)^4. \tag{4.13}$$

The dominant factor here is V/ξ^3, which will be of order 10^{22} for $V=1\text{ cm}^3$. The other factors contribute a relatively small number of powers of 10. Thus, the statistical prefactor is essentially just the volume of the system measured in units of the correlation length cubed.

V. DYNAMICAL PREFACTOR

To compute the quantity κ, according to the prescription given in Sec. II, we must linearize Eqs. (3.3) and (3.4) about $n=\bar{n}$ and $\vec{u}=0$. The basic eigenvalue equations to be solved are therefore

$$\kappa\nu=-\vec{\nabla}\cdot(\bar{n}\vec{u}), \tag{5.1}$$

$$\kappa\vec{u}=-\frac{1}{m}\,\vec{\nabla}\left(-K\nabla^2+\frac{\partial^2 f}{\partial\bar{n}^2}\right)\nu, \tag{5.2}$$

where $\nu=n-\bar{n}$. We can immediately eliminate $\vec{u}$ by multiplying (5.2) by $\bar{n}$ and taking the divergence. This yields

$$m\kappa^2\nu=\vec{\nabla}\cdot\bar{n}\,\vec{\nabla}\left(-K\nabla^2+\frac{\partial^2 f}{\partial\bar{n}^2}\right)\nu. \tag{5.3}$$

Our problem is to find the positive eigenvalue $m\kappa^2$ of Eq. (5.3). Our strategy will be as follows. First, we find solutions of (5.3) in each of three regions: the interior liquid region, $r\lesssim R-\xi$; the exterior vapor region, $r\gtrsim R+\xi$; and the interface region, $R-\xi\lesssim r\lesssim R+\xi$. We then evaluate the relative amplitudes of these solutions by matching the values of the functions at the boundaries of the regions. Finally, we evaluate κ by applying the condition

$$\int_0^\infty r^2\nu(r)\,dr=0, \tag{5.4}$$

which is a conservation law implied by (5.1). Throughout this analysis we shall assume that κ is small and vanishes in the limit of infinitely large R. We shall check this assumption for self-consistency at the end of the calculation.

Equation (5.3) is relatively easy to solve outside of the interfacial region where $\bar{n}$ and $\partial^2 f/\partial\bar{n}^2$ are independent of r. We assume spherically symmetric solutions of the form

$$\nu(r)\propto(1/r)\,e^{\pm qr} \tag{5.5}$$

and obtain as a condition for q,

$$m\kappa^2=\bar{n}q^2\left(-Kq^2+\frac{\partial^2 f}{\partial\bar{n}^2}\right). \tag{5.6}$$

Of the two solutions to (5.6), the one of interest to us is

$$q^2\cong\frac{m\kappa^2}{\bar{n}(\partial^2 f/\partial\bar{n}^2)}\,. \tag{5.7}$$

If κ is small, then this solution will be the one in which $\nu(r)$ varies slowly over distances of the order of a correlation length ξ. The second solution of (5.6) is one in which $q^2\xi^2\cong 1$, and thus should be important only so near the interfacial region that (5.6) is no longer valid. We now write the specific interior and exterior solutions as follows. For $0<r\lesssim R-\xi$,

$$\begin{aligned}&\nu(r)=(A/r)\sinh(q_l r),\\&q_l^2\cong\frac{m\kappa^2}{n_l(\partial^2 f/\partial n_l^2)}\,.\end{aligned} \tag{5.8}$$

For $r\gtrsim R+\xi$,

$$\nu = (B/r)\, e^{-q_v(r-R)},$$

$$q_v^2 = \frac{m\kappa^2}{n_v(\partial^2 f/\partial n_v^2)} \,. \tag{5.9}$$

The interfacial region is somewhat more difficult to deal with. Our method of solution is to assume that κ is so small that we can completely neglect the left-hand side of (5.3) in order to obtain a sufficiently accurate first approximation to the solution in this region. That is, we write

$$\nu(r) = \chi(r)/r, \tag{5.10}$$

and approximate (5.3) by

$$\left(\frac{d}{dr}\,\bar{n}(r)\,\frac{d}{dr}\right)\left(-K\frac{d^2}{dr^2} + \frac{\partial^2 f}{\partial \bar{n}^2}\right)\chi \cong 0 \,. \tag{5.11}$$

In addition to dropping κ^2, we have neglected a term of order R^{-1} in the first factor on the left-hand side of (5.11).

Note now that the only intrinsic length scale remaining in (5.11) is the correlation length ξ. (Strictly speaking, there are several such lengths, ξ_v, ξ_l, etc.; but these will be all of the same order of magnitude near the critical point.) Since the exterior solutions vary only extremely slowly on this scale, we must look for solutions of (5.11) which approach constant values on either side of the interface. The most general form of such a solution is

$$\chi(r) = a\int dr'\, G(r, r'), \tag{5.12}$$

where a is some constant to be determined and G is the Green's function satisfying

$$\left(-K\frac{d^2}{dr^2} + \frac{\partial^2 f}{\partial \bar{n}^2}\right) G(r, r') = \delta(r - r'). \tag{5.13}$$

On either side of the interface, where $\partial^2 f/\partial \bar{n}^2$ becomes constant, (5.12) yields

$$\chi(r) \cong \frac{a}{(\partial^2 f/\partial \bar{n}^2)} \,. \tag{5.14}$$

Therefore, from (5.8) and (5.9), we have

$$A \sinh(q_l R) = \frac{a}{(\partial^2 f/\partial n_l^2)} \tag{5.15}$$

and

$$B = \frac{a}{(\partial^2 f/\partial n_v^2)} \,. \tag{5.16}$$

Inside the interface, we use the spectral decomposition of G:

$$G(r, r') = \sum_n \frac{\chi_n(r)\chi_n(r')}{\bar{\lambda}_n} \,, \tag{5.17}$$

where the $\bar{\lambda}_n$ are the s-wave eigenvalues $\bar{\lambda}_\alpha$ and the χ_n are the corresponding eigenfunctions. For values of r near R, the sum in (5.17) will be dominated by its first term. This is because $\bar{\lambda}_1 \cong -2K/R^2$ vanishes as R becomes large, and

$$\chi_1(r) \cong \left(\frac{K}{\sigma}\right)^{1/2} \frac{d\bar{n}}{dr} \tag{5.18}$$

is sharply peaked at the interface. Therefore,

$$\chi(r) \cong \frac{aR^2\Delta n}{2\sigma}\,\frac{d\bar{n}}{dr}\,, \quad r \cong R \tag{5.19}$$

where $\Delta n \equiv n_l - n_v$.

It remains now only to apply (5.4) to compute κ, using (5.15) and (5.16) to evaluate the constants A and B. To lowest order in the small parameter ξ/R, it turns out that one can neglect the interior region ($r<R$) altogether and neglect terms of order $q_v R \sim (\xi/R)^{1/2}$ in the exterior region. The result is $\kappa \cong \kappa_0$, where

$$\kappa_0 = \left(\frac{2\sigma n_v}{mR^3(\Delta n)^2}\right)^{1/2} . \tag{5.20}$$

With this expression for κ_0 we can go back and check the various order-of-magnitude assumptions that were made in its derivation. The quantity neglected on the right-hand side of (5.11) is of order

$$m\kappa_0^2\chi \sim \frac{K\bar{n}}{R^3\xi}\,\chi, \tag{5.21}$$

where $\bar{n} \cong n_l \cong n_v$, and we have used

$$\sigma \sim K(\Delta n)^2/\xi \tag{5.22}$$

based on Eq. (4.3). On the left-hand side of (5.11), we know that

$$\left(-K\frac{d^2}{dr^2} + \frac{\partial^2 f}{\partial \bar{n}^2}\right)\chi \sim \left(\frac{K}{R^2}\right)\chi \tag{5.23}$$

and, because ξ is the only length which is involved,

$$\frac{d}{dr}\,\bar{n}(r)\,\frac{d}{dr} \sim \frac{\bar{n}}{\xi^2} \,. \tag{5.24}$$

Thus, the neglected term is of relative order ξ/R. In a similar manner, we obtain

$$q^2 \sim \xi/R^3 < 1/R^2 \ll 1/\xi^2 \tag{5.25}$$

for both q_l and q_v.

VI. THERMAL NONACCOMMODATION EFFECT

The dynamical prefactor κ_0 that we obtained in Sec. V is an example of what was called in Ref. 1 the "limit of extreme underdamping." That is, the unstable critical droplet was presumed to expand or contract in response to purely reversible hydrodynamic forces. There are, however, two irreversible effects which require consideration—thermal dissipation and viscous damping. By means of a calculation similar to the one we shall present in this section, we have tentatively concluded that viscous forces are not very important in the present problem, and shall not discuss them further here. On the other hand, the so-called "thermal nonaccommodation effect"[4] appears to play some role in slowing the nucleation rate.

Thermal nonaccommodation occurs because the vapor surrounding the growing droplet is not a perfect heat conductor, and therefore is unable to dissipate the heat of condensation arbitrarily quickly. As a result, the temperature of the droplet rises, and its growth is retarded. To analyze this phenomenon properly, we really should reformulate our entire statistical model by including the local entropy density or the temperature among the basic field variables. For present purposes, however, we shall adopt a simpler point of view. Although we have no proof of this point, it seems reasonable to us to assume that the statistical prefactor Ω_0 is unchanged by the inclusion of thermal degrees of freedom. Accordingly, we shall focus our attention on the dynamical prefactor κ, which we shall recompute simply by adding a phenomenological equation of motion for the temperature to the hydrodynamic equations (3.3) and (3.4).

If we choose the temperature $T(\vec{r}, t)$ as the new independent field variable, then the new equation that we must include has the form[17]

$$nc\frac{\partial T}{\partial t} = -T\frac{\partial p}{\partial T}\vec{\nabla}\cdot\vec{u} - \vec{\nabla}\cdot\vec{Q}, \tag{6.1}$$

where $\vec{Q}$ is the heat flux, p is the pressure, and c is the constant-volume heat capacity per molecule. We next linearize the set of equations (3.3), (3.4) and (6.1) about the stationary configuration: $n(r) = \bar{n}(r)$, $\vec{u}(r) = 0$, and $T(r) = T = \text{const}$. We define κ and ν as before; and we let θ denote the temperature deviation. Then, eliminating $\vec{u}$ from the acceleration equation as in Eq. (5.3), we obtain

$$\kappa^2\nu = \frac{1}{m}\vec{\nabla}\cdot\bar{n}\vec{\nabla}\left(-K\nabla^2 + \frac{\partial^2 f}{\partial\bar{n}^2}\right)\nu + \frac{1}{m}\nabla^2\frac{\partial\bar{p}}{\partial T}\theta \tag{6.2}$$

and

$$\kappa\theta = -\frac{T}{\bar{n}\bar{c}}\frac{\partial\bar{p}}{\partial T}(\vec{\nabla}\cdot\vec{u}) + \frac{\lambda}{\bar{n}\bar{c}}\nabla^2\theta. \tag{6.3}$$

Here, λ is the thermal conductivity, which we shall take to be independent of n and $\vec{r}$. Barred quantities are functions of n and T evaluated at the stationary point and thus, generally, are functions of $\vec{r}$ in the interfacial region. In particular, $\partial\bar{p}/\partial T$ is a short notation for $(\partial p/\partial T)$ evaluated at $\bar{n}$, T, with p being defined in accord with Eq. (3.5).

Our procedure for solving the eigenvalue problem posed by Eqs. (6.2), (6.3), and the continuity equation (5.1) is much the same as the one we used in Sec. V. We shall solve the equations separately in the single-phase and interfacial regions, match the solutions on the boundaries, and then use (5.4) plus a similar continuity law for the heat flux to determine κ. In this case, however, we shall make a few extra simplifying assumptions at the beginning of the calculation. We shall assume that, as happened in the previous problem, the density deviation ν can be neglected in the interior of the droplet. In a similar spirit, we shall assume that the temperature deviation θ is constant throughout the interior and interfacial regions, dropping only very slowly to zero outside the droplet.

Consider first the exterior solutions. Because all of the various coefficients $\bar{n}$, $\partial\bar{p}/\partial T$, etc. become constant for $r > R + \xi$, we can look for solutions of the form

$$\nu(r) = (A/r)e^{-q(r-R)}, \tag{6.4}$$

$$\theta(r) = (B/r)e^{-q(r-R)}. \tag{6.5}$$

Moreover, because the values of q that we are interested in are very small compared to ξ^{-1}, we can neglect the gradient-energy term $K\nabla^2\nu$. The resulting determinantal equation for q is

$$\det\begin{pmatrix} \kappa^2 - \frac{1}{m}n_v q^2\left(\frac{\partial^2 f}{\partial n_v^2}\right), & -\frac{1}{m}q^2\left(\frac{\partial p_v}{\partial T}\right) \\ -\frac{T}{n_v^2 c_v}\left(\frac{\partial p_v}{\partial T}\right), & \kappa - \frac{\lambda q^2}{n_v c_v} \end{pmatrix} = 0. \tag{6.6}$$

Approximate solutions of (6.6) are $q = q_1$ and q_2, where

$$q_1^2 \cong c_v n_v \kappa b/\lambda \tag{6.7}$$

and

$$q_2^2 \cong \frac{m\kappa^2}{n_v b(\partial^2 f/\partial n_v^2)}. \tag{6.8}$$

The dimensionless quantity b is defined by

$$b = 1 + \left[T\left(\frac{\partial p_v}{\partial T}\right)^2 \Big/ c_v n_v\left(\frac{\partial^2 f}{\partial n_v^2}\right)\right]. \tag{6.9}$$

The approximations (6.7) and (6.8) are valid when

$$\frac{q_2^2}{q_1^2} = \frac{m\kappa\lambda}{c_v n_v b^2(\partial^2 f/\partial n_v^2)} \ll 1. \tag{6.10}$$

To the accuracy of this approximation, we have, for $r > R + \xi$,

$$\nu(r) \cong (A_1/r)\, e^{-q_1(r-R)} + (A_2/r)\, e^{-q_2(r-R)} \tag{6.11}$$

and

$$\theta(r) \cong \frac{T(\partial p_v/\partial T)}{c_v n_v^2}\left(\frac{A_1}{(1-b)r}\, e^{-q_1(r-R)} + \frac{A_2}{r}\, e^{-q_2(r-R)}\right). \tag{6.12}$$

Next, we must consider the interfacial region. Integrating Eq. (6.2) by the same method used in Sec. V for Eq. (5.3), we obtain the analog of (5.12),

$$\chi(r) = \int dr'\, G(r, r')\, \tilde{a}(r'), \tag{6.13}$$

where χ and G are defined in Eqs. (5.10) and (5.13), and

$$\tilde{a}(r) = a - R\theta_0 \int^r dr' \frac{1}{\bar{n}(r')} \frac{d}{dr'}\left(\frac{\partial \bar{p}}{\partial T}\right). \tag{6.14}$$

Here, θ_0 is the supposedly constant value of θ at the interface.

Using (6.13) and (6.14), we can write down the matching conditions for the exterior solutions, (6.11) and (6.12):

$$A_1 + A_2 = \frac{\tilde{a}(\infty)}{(\partial^2 f/\partial n_v^2)} \tag{6.15}$$

and

$$\frac{A_1}{(1-b)} + A_2 = n_v^2 c_v R\theta_0 \Big/ T\left(\frac{\partial p_v}{\partial T}\right). \tag{6.16}$$

This pair of equations is the analog of (5.16). We can also write the interior solution in analogy to (5.19):

$$\chi(r) \cong \frac{\tilde{A} R^2 \Delta n}{2\sigma} \frac{d\bar{n}}{dr}, \quad r \cong R \tag{6.17}$$

where

$$\tilde{A} = a + \frac{R\theta_0}{\Delta n} \int^\infty dr \frac{d\bar{n}}{dr} \int^r dr' \frac{1}{\bar{n}(r')} \frac{d}{dr'}\left(\frac{\partial \bar{p}}{\partial T}\right). \tag{6.18}$$

At this point, it is useful to apply the conservation law, Eq. (5.4). To do this we need consider only the longest-ranged part of the exterior function ν; that is, the second term on the right-hand side of (6.11). Specifically, we write

$$\int_R^\infty r^2 \nu(r)\, dr \cong A_2 q_2^{-2}. \tag{6.19}$$

In writing (6.19), we also need $q_2 R \ll 1$. The integration of (6.17) over the interfacial region is straightforward as before; and Eq. (5.4) becomes

$$-\frac{R^3 \tilde{A} (\Delta n)^2}{2\sigma} + A_2 q_2^{-2} \cong 0. \tag{6.20}$$

A_2 can be determined in terms of $\tilde{a}(\infty)$ and θ_0 by solving Eqs. (6.15) and (6.16). The quantities q_2 and b are given in Eqs. (6.8) and (6.9). It is also convenient to eliminate $\tilde{a}(\infty)$ in favor of $\tilde{A}$ by rearranging (6.18) and integrating by parts. The useful form of (6.18) is

$$\tilde{A} = \tilde{a}(\infty) + \frac{R\theta_0}{n_v}\left(\frac{\partial p_v}{\partial T}\right) + \frac{R\theta_0 n_l}{\Delta n} \int^\infty dr \left(\frac{\partial \bar{p}}{\partial T}\right) \frac{1}{\bar{n}^2} \frac{d\bar{n}}{dr}. \tag{6.21}$$

After all of these substitutions and transformations have been made, (6.20) reduces to the simple form

$$\frac{\kappa^2}{\kappa_0^2} = 1 - \frac{n_l R\theta_0}{\Delta n \tilde{A}} \int^\infty dr \left(\frac{\partial \bar{p}}{\partial T}\right) \frac{1}{\bar{n}^2} \frac{d\bar{n}}{dr}, \tag{6.22}$$

where κ_0 is the frequency defined in Eq. (5.20).

To complete the calculation of κ, we must go back to the thermal equation, (6.3), and use this to evaluate the ratio $\theta_0/\tilde{A}$. We shall also have to evaluate the integral on the right-hand side of (6.22).

A useful form of Eq. (6.3) is obtained by multiplying it by $\bar{n}\,\bar{c}$ and integrating over the volume of the droplet. We obtain

$$(\tfrac{4}{3}\pi R^3) n_l c_l \kappa \theta_0 \cong -4\pi \int_{\text{interface}} r^2\, dr\, T \left(\frac{\partial \bar{p}}{\partial T}\right) \vec{\nabla} \cdot \vec{\mathrm{u}} + 4\pi R^2 \lambda \left(\frac{d\theta}{dr}\right)_{R+\xi}, \tag{6.23}$$

which simply states the conservation of energy flowing across the interface. The first term on the right-hand side of (6.23) must describe the heat released by condensation of the vapor flowing into the droplet. That is, we may identify

$$4\pi \int_{\text{interface}} r^2\, dr\, T \left(\frac{\partial \bar{p}}{\partial T}\right) \vec{\nabla} \cdot \vec{\mathrm{u}} \cong 4\pi R^2 l n_v u(R+\xi), \tag{6.24}$$

where l is the latent heat per molecule and $u(R+\xi)$ denotes the velocity of the vapor just outside the interface.

Using the continuity equation (5.1) and Eq. (6.17), we can compute the flow pattern in the interfacial region. We have

$$\kappa\nu \cong \frac{\kappa\chi}{R} = \frac{\kappa \tilde{A} R \Delta n}{2\sigma} \frac{d\bar{n}}{dr} \cong -\frac{d}{dr}(\bar{n}u) \tag{6.25}$$

for r near R. Thus,

$$u(r) \cong -\frac{\kappa \tilde{A} R \Delta n}{2\sigma}\left(1 - \frac{n_l}{\bar{n}(r)}\right), \tag{6.26}$$

$$(\vec{\nabla}\cdot\vec{u}) \cong \frac{du}{dr} \cong -\frac{\kappa \tilde{A} R \Delta n n_l}{2\sigma \bar{n}^2}\,\frac{d\bar{n}}{dr}, \tag{6.27}$$

and

$$u(R+\xi) \cong \kappa \tilde{A} R (\Delta n)^2 / 2\sigma n_v . \tag{6.28}$$

Substituting (6.27) and (6.28) into (6.24), we obtain

$$l \cong -\frac{n_l T}{\Delta n}\int_{\text{interface}} dr \left(\frac{\partial \bar{p}}{\partial T}\right)\frac{1}{\bar{n}^2}\,\frac{d\bar{n}}{dr} . \qquad (6.29$$

Equation (6.23) becomes

$$\tfrac{1}{3} n_l c_l \kappa \theta_0 \cong -\frac{\kappa \tilde{A} l (\Delta n)^2}{2\sigma} - \frac{\lambda \theta_0}{R^2}, \tag{6.30}$$

where we have divided by $4\pi R^3$ and have written

$$\theta(r) \cong (R/r)\theta_0 \tag{6.31}$$

for values of $r \gtrsim R$ and $q_1 R \ll 1$.

Equation (6.30) provides us with the ratio $\theta_0/\tilde{A}$ required in (6.22); and (6.29) identifies the integral specified there. When we make these substitutions, (6.22) assumes the form

$$\frac{\kappa^2}{\kappa_0^2} = 1 - \alpha\left(\frac{\kappa}{\kappa + \tilde{\lambda}}\right), \tag{6.32}$$

where

$$\alpha = 3 l^2 (\Delta n)^2 R / 2\sigma T n_l c_l$$

and (6.33)

$$\tilde{\lambda} = 3\lambda / R^2 n_l c_l .$$

If the latent heat vanishes, then $\alpha = 0$ and (6.32) predicts $\kappa = \kappa_0$, as it should. The case of interest to us, however, is $\alpha \gg 1$ and $\kappa \ll \tilde{\lambda}$. In the latter limit, we have $\kappa \ll \kappa_0$, and thus

$$\kappa \cong \kappa_1 \equiv \frac{\tilde{\lambda}}{\alpha} = \frac{2\lambda\sigma T}{l^2 R^3 (\Delta n)^2} . \tag{6.34}$$

Note that κ is of order λR^{-3}, and is therefore smaller than $\tilde{\lambda} \sim \lambda R^{-2}$. In the next section, we shall verify explicitly for Xe and CO_2 that $\kappa_1 \ll \kappa_0$, which will confirm that the nucleation rate is limited by the thermal nonaccommodation effect for those substances.

VII. CRITICAL SUPERCOOLING

The standard test of nucleation theory is the prediction of the critical supercooling δT_c for a supersaturated vapor. In this section we shall derive a general formula for δT_c and shall discuss applications of this formula to Xe and CO_2 near their critical points.

Throughout the following analysis, we shall use conventional power-law approximations for thermodynamic quantities near the critical point, and shall assume strong-scaling relations between the critical indices. The specific quantities that we shall need are listed below as functions of $\epsilon = 1 - (T/T_c)$:

$$\Delta n = \Delta n_0 \epsilon^{\beta}, \tag{7.1}$$

$$\frac{\partial^2 f}{\partial n_v^2} = g_0 \epsilon^{\gamma'}, \tag{7.2}$$

$$\xi = \xi_0 \epsilon^{-\nu'}, \tag{7.3}$$

$$\sigma = \sigma_0 \epsilon^{2\nu'}, \tag{7.4}$$

$$l = l_0 \epsilon^{\beta}, \tag{7.5}$$

$$\lambda = \lambda_0 \epsilon^{\nu' - \gamma'} . \tag{7.6}$$

The relevant scaling relations are

$$\alpha' + 2\beta + \gamma' = 2, \tag{7.7}$$

$$3\nu' = 2 - \alpha', \tag{7.8}$$

where α' is the specific-heat index. All functions refer to $T < T_c$ and to the vapor side of the coexistence curve. The strong-scaling assumption (7.8) [which has already been used in writing (7.4)] and the mode-mode coupling scheme implied by (7.6) are probably not exact; but weak deviations from these laws will not be important in what follows.

For classical droplets, $R \gg \xi$, we have

$$R = 2\sigma / |\delta F| \tag{7.9}$$

and

$$\Delta F = 16\pi\sigma^3 / 3|\delta F|^2, \tag{7.10}$$

where

$$\delta F \cong -\Delta n \delta\mu \tag{7.11}$$

and $\delta\mu$ is the difference in chemical potential between the supersaturated vapor and the two-phase equilibrium state at the given average density. If the supersaturation is not too great,

$$\delta\mu \cong \frac{\partial^2 f}{\partial n_v^2}\,\delta n \cong \frac{\partial^2 f}{\partial n_v^2}\left(\frac{dn_v}{dT}\right)\delta T, \tag{7.12}$$

where δT is the supercooling and dn_v/dT is the slope of the coexistence curve. We can write (7.10) in the form

$$\Delta F / k_B T \cong (\tau_0 \epsilon / \delta T)^2, \tag{7.13}$$

where

$$\tau_0 = 8\left(\frac{\pi}{3}\right)^{1/2}\left(\frac{\sigma_0^3 T_c}{k_B}\right)^{1/2}\frac{1}{\beta g_0 (\Delta n_0)^2} . \tag{7.14}$$

Similarly,

$$(R/\xi) \cong \rho_0(\epsilon/\delta T), \tag{7.15}$$

with

$$\rho_0 = \frac{4\sigma_0 T_c}{\beta g_0 \xi_0 (\Delta n_0)^2}. \tag{7.16}$$

The quantities entering the prefactor I_0 can be written in analogous form. From Eq. (4.13), we have

$$\frac{\Omega_0}{V} = \left(\frac{2}{3\sqrt{3}}\right)\left(\frac{\sigma_0}{k_B T_c}\right)^{3/2} \rho_0^4 \frac{\epsilon^{4+3\nu'}}{(\delta T)^4}. \tag{7.17}$$

For the isothermal case, the dynamical prefactor is

$$\kappa_0 \cong \left(\frac{2\sigma_0 n_c}{m\xi_0^2 \rho_0^3 (\Delta n_0)^2}\right)^{1/2} \epsilon^{(5/2)\nu' - \beta - 3/2} (\delta T)^{3/2}, \tag{7.18}$$

where n_c is the critical density. When thermal nonaccommodation is important, we have

$$\kappa_1 \cong \left(\frac{2\lambda_0 \sigma_0 T_c}{l_0^2 \xi_0^2 \rho_0^3 (\Delta n_0)^2}\right) \epsilon^{6\nu' - 4\beta - \gamma' - 3} (\delta T)^3. \tag{7.19}$$

As we shall see shortly, it is κ_1 rather than κ_0 which is relevant to cases of interest here. Thus, we use (7.19) in writing

$$I_0/V = \kappa\Omega_0/2\pi V \equiv J_0 \epsilon^{\phi} (T_c/\delta T), \tag{7.20}$$

where

$$\phi = 9\nu' - 4\beta - \gamma' + 1 \tag{7.21}$$

and

$$J_0 = \left(\frac{8}{3\pi\sqrt{3}}\right)\left(\frac{\lambda_0 \sigma_0^{7/2}}{\beta l_0^2 \xi_0^4 (\Delta n_0)^4 g_0 T_c^{1/2} k_B^{3/2}}\right). \tag{7.22}$$

A given nucleation rate, say, I_c nucleations per unit time, will be achieved at a $\delta T = \delta T_c$ such that

$$I_c/V = J_0 \epsilon^{\phi} (T_c/\delta T_c)\, e^{-(\tau_0 \epsilon/\delta T_c)^2}. \tag{7.23}$$

Solving for δT_c, we find

$$\delta T_c = \tau_0 \epsilon [\ln(V J_0/I_c) + \phi \ln\epsilon - \ln(\delta T_c/T_c)]^{-1/2}, \tag{7.24}$$

which is the form that we shall use for numerical analyses.

TABLE I. Values of various parameters introduced in the text for Xe and CO$_2$. Quantities marked with an asterisk (*) are rough estimates based on high-temperature data ($T > T_c$).

Quantity	Units	Xe	(Ref.)	CO$_2$	(Ref.)
T_c	°K	289.75	(18, 29)	304.12	(18, 29)
n_c	cm^{-3}	5.07×10^{21}	(18, 29)	6.38×10^{21}	(18, 29)
Δn_0	cm^{-3}	1.83×10^{22}	(18, 29)	2.53×10^{22}	(18, 29)
g_0	erg cm^3	1.63×10^{-34}	(20, 29)	1.48×10^{-34}	(19, 29)
ξ_0	cm	1.84×10^{-8}	(20)	$\sim 1\times 10^{-8}$*	(21)
σ_0	erg cm^{-2}	62.9	(19)	77	(22)
l_0	erg	2.43×10^{-13}	(23)	2.82×10^{-13}	(24)
λ_0	erg/cm sec °K	4×10^2*	(25)	$3.4\ \times 10^2$*	(26)
ν'	...	0.57	(27)	0.57	(27)
β	...	0.34		0.34	
γ'	...	1.2		1.2	

For comparison, we quote the formulas analogous to (7.23) and (7.24) in the Becker-Döring theory,

$$\frac{I_c^{\text{B.D.}}}{V} = J^{\text{B.D}} \epsilon^{\nu} e^{-(\tau_0 \epsilon/\delta T_c)^2}, \tag{7.25}$$

where

$$J^{\text{B.D}} \doteq n_c (2\sigma_0/\pi m)^{1/2}. \tag{7.26}$$

Therefore

$$\delta T_c^{\text{B.D}} \doteq \tau_0 \epsilon [\ln(V J^{\text{B.D}}/I_c) + \nu \ln\epsilon]^{-1/2}. \tag{7.27}$$

Numerical values for almost all of the quantities occurring in these formulas are available in the literature for Xe and CO$_2$. These values are quoted in Table I. The derived quantities τ_0, ρ_0, $J^{\text{B.D.}}$, J_0, and ϕ are listed in Table II. It is clear from Eq. (7.24) that the ratio $\delta T_c/\epsilon$ is only weakly dependent on ϵ, although this dependence is slightly stronger in our case than in the Becker-Döring formula, Eq. (7.27). For purposes of comparison with experiment, it is convenient to summarize both formulas in the form

$$\frac{\delta T_c}{\epsilon} = \frac{a}{(1 + b \ln\epsilon)^{1/2}}. \tag{7.28}$$

The constants a and b appear naturally in the Becker-Döring result, Eq. (7.27); and they can be chosen so as to fit the solution of Eq. (7.24) to better than 1% in the region $10^{-4} < \epsilon < 10^{-1}$. In Table III, we list values of a and b for Xe and CO$_2$ for two nucleation rates, $I_c/V = 1$ and 10^5 cm^{-3} sec^{-1}.

Given the quantities in Tables II and III, we can check various approximations and assumptions used in the derivation of the nucleation formulas. For both Xe and CO$_2$, we use (7.13) and data from Table III to find $\Delta F/kT \sim 55$ at $\delta T \cong \delta T_c$, which is certainly large enough to assure that the thermal activation picture is self-consistent. To check the

TABLE II. Values of derived quantities for Xe and CO$_2$.

Quantity	Equation	Units	Xe	CO$_2$
τ_0	(7.14)	°K	319	255
ρ_0	(7.16)	°K	215	292
J^0	(7.22)	cm^{-3} sec^{-1}	3.47×10^{32}	1.43×10^{33}
$J^{\text{B.D.}}$	(7.26)	cm^{-3} sec^{-1}	2.17×10^{33}	5.24×10^{33}
ϕ	(7.21)	...	3.57	3.57

assumption of classical droplets, we use (7.15) to deduce that, for Xe, $R_c/\xi \sim 5$; and for CO_2, $R_c/\xi \sim 10$, where R_c is the value of R at the critical supersaturation δT_c. (We give only an order-of-magnitude estimate for the latter quantity because of the lack of a value for ξ_0 for CO_2.)

The dynamical factors turn out to be, for Xe,

$$\kappa_0 = 7.9\times 10^8 (\delta T^{3/2}/\epsilon^{0.415})\ \sec^{-1} \tag{7.29}$$

and

$$\kappa_1 = 5.4\times 10^4 (\delta T^3/\epsilon^{2.14})\ \sec^{-1}. \tag{7.30}$$

Thus, if $\delta T_c/\epsilon \sim 40$,

$$\kappa_1/\kappa_0 \sim 1.7\times 10^{-2} \epsilon^{-0.22}, \tag{7.31}$$

which is much smaller than unity except for inaccessibly small values of ϵ where the approximation used in deriving (7.3) is no longer valid. Similarly, for CO_2, we have

$$\kappa_0 = 2.1\times 10^9 (\delta T^{3/2}/\epsilon^{0.415})\ \sec^{-1}, \tag{7.32}$$

$$\kappa_1 = 6.5\times 10^4 (\delta T^3/\epsilon^{2.14})\ \sec^{-1}; \tag{7.33}$$

and, for $\delta T_c/\epsilon \sim 30$,

$$\kappa_1/\kappa_0 \sim 5\times 10^{-3} \epsilon^{-0.22}. \tag{7.34}$$

It follows that the left-hand side of (6.32) is completely negligible, in accord with the assumption made in the derivation of (6.34).

The most important feature of the results shown in Table III is that, despite all of the statistical and hydrodynamical corrections, the nucleation rates computed here turn out to be only very little different from the Becker-Döring values. It is conceivable that, with very careful measurements, one might detect the slight variation of $\delta T_c/\epsilon$ as a function of $\ln\epsilon$, which is predicted here. To the best of our knowledge, no really systematic study of nucleation near the critical point of a vapor-to-liquid phase transition has yet been attempted. Sengers and Chen[28] have observed metastable states in CO_2, and their data appear to be consistent with our estimated limits of metastability. That is, their vapor-pressure curves end near or somewhat earlier than where we predict they should. But these experiments were not meant to constitute a serious test of the nucleation theory. In view of the uncertainties surrounding the theory of nucleation phenomena, it seems to us that such a test would be extremely worthwhile.

APPENDIX: COARSE-GRAINING APPROXIMATION

The nucleation theory developed in Ref. 1 requires that the system of interest be described in an essentially field-theoretic language. As implied in Sec. III of this paper, serious problems arise in trying to formulate such a description for classical many-body statistical mechanics. The quasihydrodynamic "cellular" or "coarse-graining" approximation solves—or at least circumvents—some of these difficulties. In this Appendix, we shall outline a more formal development of the cellular method than was presented in Sec. III. Some aspects of this development are directly relevant to the analysis in Sec. IV.

We start by defining cellular basis functions $\psi_\alpha(\vec{r})$ which are unity inside cells of volume Δ and vanish everywhere else. Our statistical variables will be

$$n_\alpha = \sum_{A=1}^{N} \psi_\alpha(\vec{r}_A) \tag{A1}$$

and

$$\vec{j}_\alpha = \sum_{A=1}^{N} \left(\frac{\vec{p}_A}{m}\right) \psi_\alpha(\vec{r}_A), \tag{A2}$$

where $A = 1, \ldots, N$, and N is the number of particles in the system. The canonical partition function for this system can be written in the form

$$Z_N = \int \delta n \delta \vec{j}\, e^{-F\{n,\vec{j}\}/k_B T} \delta^K \left(N - \sum_\alpha n_\alpha\right), \tag{A3}$$

where

$$\int \delta n \delta \vec{j} \equiv \prod_\alpha \sum_{n_\alpha=0}^{\infty} \int d^3 j_\alpha \approx \prod_\alpha \int dn_\alpha \int d^3 j_\alpha \tag{A4}$$

and

$$e^{-F/k_B T} \equiv \int \delta r \delta p\, e^{-H\{r,p\}/k_B T} \times \prod_\alpha \delta^K \left(n_\alpha - \sum_A \psi_\alpha(\vec{r}_A)\right) \times \prod_\alpha \delta \left(\vec{j}_\alpha - \sum_A \frac{\vec{p}_A}{m} \psi_\alpha(\vec{r}_A)\right). \tag{A5}$$

TABLE III. Values of the parameters a and b appearing in the formula $\delta T_c/\epsilon = a/(1 + b \ln\epsilon)^{1/2}$. (a) Becker-Döring theory, Eq. (7.27); (b) present theory, Eq. (7.24).

	Xe		CO_2	
I_c/V	1	10^5	1	10^5
(a) Becker-Döring theory, Eq. (7.27)				
a (°K)	36.41	39.49	28.97	31.39
b	0.007 43	0.008 74	0.007 34	0.008 62
(b) Present theory, Eq. (7.24)				
a (°K)	36.35	39.43	28.77	31.16
b	0.0334	0.0393	0.0326	0.0383

In Eq. (A5), $H\{\vec{r},\vec{p}\}$ is the conventional many-body Hamiltonian; δ^K denotes a Kronecker δ function; and

$$\int \delta r \delta p \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \prod_{A=1}^{N} d^3 r_A d^3 p_A . \tag{A6}$$

The final form of (A4) is valid in the limit of large Δ.

From (A5), we see that the coarse-grained F is defined by the canonical average of the exact joint-probability distribution in the space of coarse-grained variables $n_\alpha, \vec{j}_\alpha$. We can simplify (A5) by the following sequence of operations. First, we replace the δ functions in (A5) by their integral representations. Next, we integrate over the momenta $\vec{p}_A$. The remaining integrations over configuration space can be performed either by a perturbation method (Mayer graphical expansion) or by a simple occupation-number approximation.[10] We shall choose the latter method because we are mainly interested only in the general shape of the functional F.

Inserting integral representations in (A5) yields

$$e^{-F/k_BT} = \prod_\alpha \oint \frac{dz_\alpha}{2\pi i z_\alpha} \int_{-\infty}^{+\infty} \frac{d^3\xi_\alpha}{(2\pi)^3} \times \exp\left(i \sum_\alpha (n_\alpha \ln z_\alpha + \vec{\xi}_\alpha \cdot \vec{j}_\alpha)\right) e^{\Phi\{z, \vec{\xi}\}} , \tag{A7}$$

where the z integrations are performed around a closed contour surrounding the origin, and

$$e^{\Phi} = \int \delta r \delta p e^{-H/k_BT} \times \exp\left(-i \sum_A [\ln z(\vec{r}_A) + \vec{\xi}(\vec{r}_A) \cdot \vec{p}_A/m]\right) . \tag{A8}$$

The functions $z(\vec{r})$ and $\vec{\xi}(\vec{r})$ are

$$\ln z(\vec{r}) \equiv \sum_\alpha \ln z_\alpha \psi_\alpha(\vec{r}); \tag{A9}$$

$$\vec{\xi}(\vec{r}) \equiv \sum_\alpha \vec{\xi}_\alpha \psi_\alpha(\vec{r}). \tag{A10}$$

The momentum integration in (A8) is straightforward as long as there are no velocity-dependent interactions in H. The result is

$$e^{\Phi\{\zeta\}} = (2\pi m k_B T)^{3N/2} \int \delta r \times \exp\left(- U\{r\}/k_BT - i \sum_A \ln \zeta(\vec{r}_A)\right) , \tag{A11}$$

where $U\{\vec{r}\}$ is the interaction part of H and

$$\zeta(\vec{r}) = z(\vec{r}) \exp[-k_BT \vec{\xi}^2(\vec{r})/m] . \tag{A12}$$

Thus, the quantity $-k_BT\Phi$ is the free energy for a system of interacting particles in a random external field whose activity is $\zeta(r)$.

Once we transform from z to ζ in (A12), the integration over the ξ's becomes trivial in (A7). We find

$$e^{-F/k_BT} = \prod_\alpha \oint \left(\frac{m}{2\pi k_B T n_\alpha}\right)^{3/2} \frac{d\xi_\alpha}{2\pi i \xi_\alpha} \times \exp\left(i \sum_\alpha n_\alpha \ln\zeta_\alpha - \frac{m}{k_BT} \sum_\alpha \frac{\vec{j}_\alpha^2}{\bar{n}_\alpha} + \Phi\{\zeta\}\right) . \tag{A13}$$

The important point to note is that F contains the term

$$F_K = \frac{m}{2} \sum_\alpha \frac{\vec{j}_\alpha^2}{n_\alpha} = \frac{m}{2} \sum_\alpha n_\alpha \vec{u}_\alpha^2 \rightarrow \frac{m}{2} \int d^3 r n(\vec{r}) \vec{u}^2(\vec{r}), \tag{A14}$$

where we have defined the velocity field $\vec{u}$ by writing

$$n_\alpha \vec{u}_\alpha = \vec{j}_\alpha, \tag{A15}$$

and have used the continuum limit,

$$\frac{n_\alpha}{\Delta} \rightarrow n(\vec{r}); \;\; \vec{u}_\alpha \rightarrow \vec{u}(\vec{r}); \;\; \sum_\alpha \rightarrow \Delta^{-1} \int d^3 r. \tag{A16}$$

If we integrate over the $\vec{j}_\alpha$ in (A13), as we must in computing the partition function, the Gaussian integrals exactly cancel the factors $(m/2\pi n_\alpha k_BT)^{3/2}$. It is this cancellation which enabled us to neglect the eigenvalues of $\delta^2 F_K/\delta u_i \delta u_j$ in Sec. IV.

So far we have made no approximations. To make further progress, however, we have to evaluate the interaction term. The simplest thing to do is just to go backwards. That is, we write

$$\prod_\alpha \oint \frac{d\zeta_\alpha}{2\pi i \zeta_\alpha} \exp\left(i \sum_\alpha n_\alpha \ln\zeta_\alpha + \Phi\{\zeta\}\right) = (2\pi m k_B T)^{3N/2} \int \delta r e^{-U/k_BT} \times \prod_\alpha \delta^K \left(n_\alpha - \sum_A \psi_\alpha(\vec{r}_A)\right) = (2\pi m k_B T)^{3N/2} e^{-F_U\{n\}/k_BT}. \tag{A17}$$

The conventional occupation-number approximation is:

$$e^{-F_U\{n\}/k_BT} \cong \prod_\alpha \frac{\Delta^{n_\alpha}}{n_\alpha !} e^{-\overline{U}\{n\}/k_BT}, \tag{A18}$$

where $\overline{U}\{n\}$ denotes some effective interaction energy. If all the n_α are large, we have

$$\begin{aligned} F_U/k_BT &\cong \frac{\bar{U}}{k_BT} + \sum_\alpha \left[n_\alpha \ln(n_\alpha/\Delta) - n_\alpha - \tfrac{1}{2}\ln(2\pi n_\alpha) + \cdots \right] \\ &\cong \frac{\bar{U}}{k_BT} + \int d^3r \left[n \ln n - n - \tfrac{1}{2\Delta}\ln(2\pi\Delta n) + \cdots \right]. \end{aligned} \tag{A19}$$

In the continuum limit, $\bar{U}$ will have an expansion of the form

$$\bar{U}\{n\} = \int d^3r \left[f_0(n) + \tfrac{1}{2}K(n)(\vec{\nabla} n)^2 + \cdots \right]. \tag{A20}$$

Collecting terms back through Eq. (A13), we recover a coarse-grained free energy $F\{n, \vec{u}\}$ of the form hypothesized in Sec. III.

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