Homogeneous nucleation of a noncritical phase near a continuous phase transition

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Homogeneous nucleation of a new phase near a second, continuous, transition, is considered. The continuous transition is in the metastable region associated with the first-order phase transition, one of whose coexisting phases is nucleating. Mean-field calculations show that as the continuous transition is approached, the size of the nucleus varies as the response function of the order parameter of the continuous transition. This response function diverges at the continuous transition, as does the temperature derivative of the free-energy barrier to nucleation. This rapid drop of the barrier as the continuous transition is approached means that the continuous transition acts to reduce the barrier to nucleation at the first-order transition. This may be useful in the crystallization of globular proteins.

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I. INTRODUCTION

When a phase transition is first order the formation of a new phase is an activated process [1]. A nucleus of the new phase must form, and overcome a free-energy barrier before it can grow into a new phase. The rate at which nuclei overcome a barrier of height ΔF^* scales as $\exp(-\Delta F^*/kT)$, and therefore this rate is very sensitive to the barrier height [2]. For definiteness consider a first-order phase transition at a temperature T_α in which the low-temperature phase is the ordered phase, and the high-temperature phase is the disordered phase. If we cool the disordered phase below T_α, but the barrier to nucleation of the ordered phase is very high, then the rate at which nuclei of the ordered-phase form will be effectively zero and the ordered phase will not form even though its free energy is lower than that of the disordered phase. The disordered phase will persist; it is said to be metastable. Here we calculate ΔF^* for nucleation near a second, continuous, transition, which we call transition β. Continuous transitions are critical points and so exhibit universal and beautiful behavior; the thermodynamic and correlation functions contain power-law terms with exponents that depend only on dimensionality and the symmetry of the order parameter [3,4]. *A priori*, we might expect that ΔF^* might also contain a power-law term with an exponent that depends only on dimensionality and the symmetry of the order parameter. This would allow us to make predictions about how ΔF^* varied near a critical point, which would apply to a whole class of systems. Below, we present the results of calculations within mean-field theory, for an Ising-like continuous transition in three dimensions. We determine the singular power law part of the free-energy barrier ΔF^*; just above T_β, it varies as ξ^{-1}, where ξ is the correlation length associated with the order parameter of transition β. This singular part means that the derivative of ΔF^* with respect to temperature diverges as the critical point is approached; the barrier to nucleation drops rapidly just above the transition. This agrees with the pioneering simulations of ten Wolde and Frenkel [5] who found an anomalously low ΔF^* near the critical point of a metastable fluid-fluid transition.

As far as the author is aware, nucleation near a critical point has only been considered for a fluid-fluid critical point within a strongly first-order fluid-crystal transition. The work was inspired by the observation that globular proteins often crystallize at temperatures close to where we might expect a metastable fluid-fluid critical point [6,7], and that the phase diagrams of some globular proteins do possess a metastable fluid-fluid transition [8,9]. But as the effect we will examine is due to the decreasing free energy cost of fluctuations near a critical point, it is universal, i.e., applies to any other system in the same universality class, that of the three-dimensional Ising model. Indeed, it is easy to show that it also applies to systems in the universality classes of the Ising model in other dimensionalities [10]. See Refs. [11–15] and references therein for recent work.

The next section briefly sets out the standard Landau theory for a continuous transition with a scalar order parameter. Section III then calculates the free energy of a nucleus within a simple mean-field theory of the square-gradient type. Derivatives with respect to temperature and external field are also found. The final section is a conclusion. (See Refs. [3,4] for an introduction to systems near critical points and Ref. [2] for an introduction to homogeneous nucleation.)

II. BULK BEHAVIOR

We have a system, which at equilibrium has one phase transition; a strongly first-order transition, transition α, which is at a temperature T_α. For definiteness we let the high-temperature phase be the disordered phase and the low-temperature phase be the ordered phase. If we consider a very pure sample [1] then we can supercool down to temperatures below T_α to obtain metastable states [2], i.e., the disordered phase is stable for long (with respect to the relaxation time of the system) periods of time over some temperature range just below T_α. It is stable because the formation of the ordered phase is an activated process, the ordered phase must nucleate, overcoming some free-energy barrier ΔF^*, which will be a strong function of temperature and that diverges as $T \to T_\alpha^-$. Here, we are interested in how ΔF^*

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behaves, if as we cool down in the metastable disordered phase, we approach a continuous transition, transition β, at some temperature $T_\beta < T_\alpha$.

We will assume that the nucleation barrier to transition α is so large that it is possible to start from some temperature $T > T_\alpha$ and slowly cool down past T_α, either to and below T_β, or at least to a temperature only a little above T_β, without transition α occurring. If it is possible to cool slowly down to T_β, then transition β is said to be metastable [2]; it is observable. If it is not possible to cool slowly down to T_β without transition α occurring, then clearly transition β is not observable; it is unstable not metastable with respect to transition α [2]. We will be studying nucleation of the low-temperature phase of transition α as T_β is approached from above and so we will not only be determining the effect of transition β on α but also looking at whether or not β is observable. Roughly speaking, if the proximity of a transition β acts to strongly enhance the nucleation rate of transition α, then this nucleation rate may become large thus rendering transition β unobservable. We should also mention that we are using temperature as our variable simply for definiteness, we could replace it by another field variable, e.g., pressure, without changing our conclusions.

So, starting from high temperature and cooling down below T_α, we can approach T_β. The order parameter of transition β is denoted by m and it may or may not be related to that of transition α. The external field that couples to m is h. The theory here will be mean field in nature but rather general. We only have to assume that the nucleus of the ordered phase of transition α has a core that has properties close to that of the bulk ordered phase (c.f., the assumptions that underlie classical nucleation theory [2]) and that this core couples to the order parameter of transition β. By coupling to m we mean that if there is a nucleus at the origin, then the local value of m, $m_r(r) \neq m$, where r is the distance from the center of the nucleus. Both assumptions are very reasonable; for a strongly first-order phase transition it is difficult to imagine a situation where the nucleus does not have a core with near bulk properties, and the core of the nucleus must perturb its surroundings and so, in the absence of special symmetries, will locally perturb the order parameter of transition β. Figure 1 is a schematic of the nucleus.

Near T_β we use a Landau theory for the transition β. The Landau theory of a continuous transition is simple, it is a textbook problem, see for example Chaikin and Lubensky's [4] or Kadanoff's [3]. The bulk free energy per unit volume $f(m)$ as a function of the order parameter m is

$$f(m) = \frac{1}{2} a(T - T_\beta) m^2 + m^4 - hm. \tag{1}$$

The transition is at T_β at $h = 0$. We will only examine behavior at $h = 0$ but we retain h in order to look at the response of the system to an external field that couples to m. Below, when we study the nucleus near transition β, we will find that the outermost part of the density profile of the nucleus is controlled by the response function of m, χ, defined by

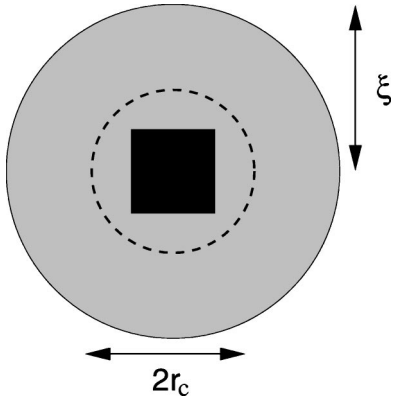

FIG. 1. Schematic of a nucleus of the ordered phase of transition α near transition β. The core of the ordered phase of transition α is solid black, and the perturbation this causes in the surroundings is the shaded circle of radius the correlation length ξ. The sphere with radius r_c, which divides the nucleus into a core and surroundings, is denoted by a dashed circle.

$$\chi^{-1} = \left(\frac{\partial h}{\partial m} \right) = \left(\frac{\partial^2 f}{\partial m^2} \right), \tag{2}$$

which is, using Eq. (1),

$$\chi^{-1} = a(T - T_\beta) \quad T > T_\beta. \tag{3}$$

III. THE NUCLEUS

We split the nucleus into two parts: the core and the fringe. The core is that part of the nucleus less than r_c from its center and the fringe is that part farther away than r_c. The fringe of the nucleus is assumed to be spherically symmetric. The core of the nucleus contains at its center a volume that is close to the bulk ordered phase of transition α. The fringe is essentially the region that surrounds this core and is perturbed by the core. Its radius is therefore the correlation length ξ of m and so diverges as T_β is approached. As we are concentrating on universal aspects of the nucleus and of ΔF^*, we will replace the core by a boundary condition on m_r in the fringe. We set $m_r(r = r_c) = m_c$, which is taken to be independent of temperature and of h. Also, $m_r(r \to \infty) = m$, which is just the obvious boundary condition that m must tend towards its bulk value far from the nucleus. Note that as we are above the transition and are working at zero field, $m = 0$ but we will retain an explicit m dependence in order to be able to take derivatives of ΔF^*. In the fringe and near T_β, we need only consider the order parameter for transition β and the variations in m_r will not be large. Therefore, we employ a standard Landau-Ginsburg or square-gradient functional for the excess free energy ΔF of an inhomogeneity in an otherwise homogeneous phase [2,16–18]

$$\Delta F = \Delta F_c + \int_{r \geq r_c} [\Delta f(m_r) + \kappa (\nabla m_r)^2] \mathrm{d}\mathbf{r}, \tag{4}$$

where

$$\Delta f(m_r) = f(m_r) - f(m) \tag{5}$$

is the bulk free-energy change per unit volume to go from m to m_r. The excess free energy ΔF is the free energy with a nucleus minus that without a nucleus; ΔF_c is the contribution of the core. The second term within the brackets of Eq. (4) is a gradient term; the free energy cost due to variations in space of m_r. It is proportional to the gradient squared, which is the lowest order term in a gradient expansion and so is only adequate when m is slowly varying. The coefficient κ, of this term is taken to be a constant. The total excess of m due to a nucleus is equal to the integrated value of $m_r - m$. Defining $\Delta m(\mathbf{r}) = m_r(\mathbf{r}) - m$, then the integral over all space of this function gives the total excess of the order parameter due to the nucleus

$$\Delta m = \int \Delta m(\mathbf{r})\, d\mathbf{r}. \tag{6}$$

The free-energy barrier ΔF^* is the value of ΔF for the nucleus when it is at its maximum, at the top of the barrier. The nucleus at the top of the barrier is called the critical nucleus [19]. For the critical nucleus we may set the functional derivative of ΔF with respect to the profile $m_r(\mathbf{r})$ to zero

$$\left(\frac{\partial \Delta f(m_r)}{\partial m_r}\right) - 2\kappa \nabla^2 m_r = 0 \quad r > r_c. \tag{7}$$

Once we have solved Eq. (7) we can insert the solution into Eq. (4) to obtain the excess free energy of the critical nucleus ΔF^*.

The fringe is the outermost part of the nucleus, where m_r is near the bulk value m. So we can use a Taylor expansion about $m_r = m$ for Δf

$$\Delta f(m_r) = \frac{1}{2}\chi^{-1}(\Delta m)^2 + \cdots, \tag{8}$$

$$\left(\frac{\partial \Delta f(m_r)}{\partial m}\right) = \chi^{-1}\Delta m + \cdots, \tag{9}$$

because both Δf and its first derivative are zero for $m_r = m$, and the second derivative is χ^{-1} [Eq. (2)]. Substituting Eq. (9) into Eq. (7) we have

$$\chi^{-1}\Delta m(r) - 2\kappa \nabla^2 \Delta m(r) = 0, \tag{10}$$

which has a solution of the Ornstein-Zernike form

$$\Delta m(r) = (m_c - m)\left(\frac{r_c}{r}\right)\exp[(r_c - r)/\xi], \tag{11}$$

with ξ the correlation length for m, given by

$$\xi = (2\kappa\chi)^{1/2}, \tag{12}$$

$$\xi = (2\kappa/a)^{1/2}(T - T_\beta)^{-1/2} \quad T > T_\beta, \tag{13}$$

where Eq. (12) defines ξ and we used Eq. (3) to obtain an expression for ξ near T_β, Eq. (13). To obtain Eq. (11) the boundary conditions $m_r(r \to \infty) = m$ and $m(r_c) = m_c$ were employed. It is not necessary to specify r_c or m_c beyond saying that they should be such that $m_c - m$ is small and so $\Delta m(r)$ will, as required for Eq. (10), be small for $r \geqslant r_c$. From Eq. (11) we see that the width of the fringe is, as we expected, of the order of the correlation length ξ for m.

Having obtained the density profile, Eq. (11), we can substitute this into Eq. (4), using Eq. (8) for Δf, and obtain an expression for the free-energy barrier to nucleation. We have

$$\begin{aligned}
\Delta F^* &= \Delta F_c + 4\pi r_c^2 (m_c - m)^2 \int_{r_c}^{\infty} dr \\
&\quad \times \left[\frac{1}{2}\chi^{-1} + \kappa\left(\frac{1}{r} + \frac{1}{\xi}\right)^2\right]\exp[2(r_c - r)/\xi] \\
&= \Delta F_c + 4\pi\kappa r_c^2 (m_c - m)^2 \int_{r_c}^{\infty} dr \\
&\quad \times \left[\frac{2}{\xi^2} + \frac{2}{\xi r} + \frac{1}{r^2}\right]\exp[2(r_c - r)/\xi] \\
&= \Delta F_c + 4\pi\kappa r_c (m_c - m)^2 [1 + r_c/\xi],
\end{aligned} \tag{14}$$

where in obtaining the second line from the first we substituted ξ for χ using Eq. (12). Finally, we can set $m = 0$ to obtain the free-energy barrier to nucleation of the ordered phase of transition α near transition β

$$\Delta F^* = \Delta F_c + 4\pi\kappa r_c m_c^2 [1 + r_c/\xi]. \tag{15}$$

As we approach transition β, $T \to T_\beta$, ΔF^* approaches the finite limit

$$\Delta F^*(T = T_\beta) = \Delta F_c + 4\pi\kappa r_c m_c^2. \tag{16}$$

The free energy ΔF^* can be written as

$$\Delta F^* = \Delta F^*(T = T_\beta) + A\left(\frac{r_c}{\xi}\right), \tag{17}$$

where $A = 4\pi\kappa r_c m_c^2$, a constant. The singular part of ΔF^* has the form the ratio r_c/ξ raised to the power 1.

A. Derivatives of ΔF^*

We can take the temperature derivative of ΔF^*. As m does not vary with T above T_β, we may use Eq. (15), and obtain

$$\frac{\partial \Delta F^*}{\partial T} = \frac{\partial \Delta F_c}{\partial T} + 4\pi\kappa r_c^2 m_c^2 \frac{\partial \xi^{-1}}{\partial T}, \tag{18}$$

which near T_β becomes

$$\frac{\partial}{\partial T}(\Delta F^* - \Delta F_c) = (2\kappa a)^{1/2}\pi r_c^2 m_c^2 (T - T_\beta)^{-1/2} \quad T > T_\beta, \tag{19}$$

where we used Eq. (13) for ξ. Just above the transition β the derivative of the barrier diverges to $+\infty$; the barrier drops very rapidly with decreasing temperature just above T_β.

Sufficiently near T_β the singular part dominates the temperature derivative of ΔF^*, because it diverges as $(T - T_\beta)^{-1/2}$. It is of interest to estimate, within the present mean-field theory, what ''sufficiently near'' means; how close to T_β do you have to be before the singular part dominates. A nonsingular contribution to the temperature dependence of ΔF^* comes from the temperature dependence of ΔF_c. If the nucleation barrier is of order a few tens of kT, which we expect to be the case when the nucleation rate is both nonnegligible and slow enough to allow a free-energy barrier to be meaningful [2], then we expect the core to contain of the order of tens of particles or spins. Assuming that each particle contributes $1k$ to the temperature derivative of ΔF_c, we have that the derivative is $O(10k)$. Thus, in order for this contribution to be dominated by the singular term we require, see Eq. (19), that $(T - T_\beta)/T_\beta$ be much less than 0.01. This assumes that once r_c, m_c, and κ have been made dimensionless, that they are all of order unity. Finally, we note that in our model we have fixed the value of m_r at $r = r_c$ to be a constant m_c, independent of temperature. In reality the value of the order parameter at a fixed distance from the center will vary with temperature, as will κ. Their variation with temperature will renormalize the temperature derivative of the singular term and contribute to the nonsingular part of the temperature derivative of the free energy. We neglect both these effects for simplicity, and because we expect them to be at most of the same order as the error we introduced when we approximated our free energy by a single quadratic term.

We can also take the derivative of ΔF^* with respect to the field h conjugate to m. Using Eq. (14), and taking note of the definition of χ, Eq. (2),

$$\frac{\partial \Delta F^*}{\partial h} = \frac{\partial \Delta F_c}{\partial h} - 8\pi\kappa r_c m_c \chi [1 + r_c/\xi], \tag{20}$$

where after taking the derivative we set $m = 0$. Note that $\partial\xi/\partial h = 0$. As transition β is approached, the rate of change of ΔF^* with respect to the field conjugate to the order parameter diverges as the response function χ. Also, if we substitute our solution for $m(r > r_c)$, Eq. (11), with $m = 0$, into Eq. (6), we obtain the size of the nucleus

$$\Delta m^* = \Delta m_c^* + 8\pi\kappa r_c m_c \chi [1 + r_c/\xi] \tag{21}$$

with

$$\Delta m_c = \int_{r \le r_c} \Delta m(\mathbf{r})\, d\mathbf{r}, \tag{22}$$

the contribution of the core, and we used Eq. (12) to substitute χ for ξ^2. Comparing Eqs. (20) and (21), we see that

$$\frac{\partial}{\partial h}(\Delta F^* - \Delta F_c) = -(\Delta m^* - \Delta m_c). \tag{23}$$

For the fringe, the derivative of the free energy with respect to h is equal to minus the excess m. This result is essentially what is called the nucleation theorem [20–22] in studies of nucleation in fluids. It states that the larger the nucleus, the larger Δm^* is, the more rapidly the nucleation barrier varies with h. In fluids m is a number density difference and h is the chemical potential.

Returning to Eq. (21) for Δm^* we see that although the core can only contribute a finite amount to Δm^* as its volume is finite, the contribution of the fringe diverges as transition β is approached. The size of the nucleus diverges as χ as the continuous transition is approached. This result was first derived by the author in Ref. [15]. See also the earlier work of Talanquer and Oxtoby [11] who first suggested that the size of the nucleus diverges as a critical point is approached. In Refs. [11,15] the critical point is that of a fluid-fluid or vapor-liquidlike transition. Assuming as before that the core contains of the order of tens of particles or spins, then as the contribution of the fringe to Δm^* is varying as $(T - T_\beta)^{-1}$, then the fringe should dominate Δm^* for $(T - T_\beta)/T_\beta$ much less than 0.1. This is a less strict requirement than required for the temperature derivative, so it is necessary to get much closer to the critical point to see the singular part in ΔF_c than is required to see the singular part of Δm^*.

IV. CONCLUSION

We have considered the effect of a continuous transition, transition β, on the homogeneous nucleation of a new phase at a first-order transition, transition α. We found that the temperature derivative of the free-energy barrier to nucleation ΔF^*, diverged as $(T - T_\beta)^{-1/2}$ within our mean-field theory, and that the size of the critical nucleus, the nucleus at the top of the free-energy barrier to nucleation, diverged as the response function $\chi \sim (T - T_\beta)^{-1}$. The presence of a critical point makes the nucleus very large, its diameter is the correlation length ξ, and causes the free-energy barrier to nucleation to decrease rapidly with decreasing temperature. It reduces the barrier and so facilitates nucleation. This is just what was first demonstrated by ten Wolde and Frenkel [5] for nucleation of a crystalline phase near the critical point of a fluid-fluid transition. It is a rather general phenomenon and applies to any continuous transition with a scalar order parameter, i.e., any Ising-like transition. Whether or not the same effect appears near a continuous transition in a system which is anisotropic or in which the order parameter is not a simple scalar, is an interesting open question.

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[1] Here we consider only homogeneous nucleation, nucleation in the bulk, far from any interface. Heterogeneous nucleation, nucleation at an interface, either with a wall or an impurity, is in fact more common, and is not always an activated process.
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