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Inhomogeneous nucleation in first-order phase transitions

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The Landau-Ginzburg Hamiltonian is considered as a universal model of dynamical critical behavior for a system undergoing a first-order phase transition. The resultant equation of motion is investigated for spherically symmetric solutions which obey particular boundary conditions. The solutions are found numerically and from these stationary solutions, the average order parameters and specific heats are calculated. Comparison with the results of homogeneous nucleation phenomenology and with recent experimental results is presented.

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I. INTRODUCTION

The Landau-Ginzburg Hamiltonian [1]

$$H = \int d^d x \left[\frac{D}{2} (\nabla \phi)^2 + F(\phi) \right] , \qquad (1.1)$$

where d is the dimension and $\phi(\mathbf{x}, \mathbf{t})$ denotes a scalar order parameter field for the critical system under consideration, has played an important role in the theory of phase transitions. In spite of its seeming simplicity, it has been recognized as possessing universal features for systems in the vicinity of phase transition points. In the consideration of first-order phase transitions, for systems with no sign inversion symmetry, the potential energy term $F(\phi)$ can be expanded in terms of the order parameter as

$$F(\phi) = \frac{A_2}{2}\phi^2 + \frac{A_3}{3}\phi^3 + \frac{A_4}{4}\phi^4 , \qquad (1.2)$$

where $A_3 \neq 0$ and $A_4 > 0$ are constants and $A_2 = a(T - T_0)$ depends on the temperature. We will be particularly interested in spherically symmetric order parameter patterns in three dimensions ($d = 3$). With this condition, when we minimize the Hamiltonian given in Eq. (1.1), we obtain the equation of motion,

$$D \left(\frac{d^2\phi}{dr^2} + \frac{2}{r}\frac{d\phi}{dr} \right) = A_2\phi + A_3\phi^2 + A_4\phi^3. \qquad (1.3)$$

Note that cylindrically symmetric solutions would imply a similar equation to that of Eq. (1.3) except that in the second term on the left-hand side the factor 2 would be replaced by 1. Much of the qualitative behavior of the solutions in both cases is analagous. There is ample physical motivation for our keen interest in the solutions of Eq. (1.3) since there exist numerous examples of physical systems on all length scales that favor spherical symmetry either locally or globally. Such examples range from the model of the early universe on an extremely large size scale to that of elementary particles on the microscopic length scale. A class of examples in between these two extremes is that of liquid-vapor and liquid-solid phase transitions. For both types of transitions the simplest model for the nucleation of spherical domains of the low-temperature phase is the Gibbs-Thomson model. In it, spherical particles of low-temperature phase nucleate as a result of thermal fluctuations with the free energy difference between the two phases involved given by

$$\Delta F = 4\pi^2\sigma_{12} - \frac{4}{3}\pi r^3 \frac{(g_1 - g_2)}{v_2} . \qquad (1.4)$$

where r is the radius of the frozen sphere, σ_{12} the interfacial energy between the two phases, g_1 and g_2 the high- and low-temperature phase molecular free energies, respectively, and v_2 is the molecular volume of the low-temperature phase. Assuming a homogeneous density profile within a given phase and minimizing ΔF with respect to r gives a critical radius r_c.

$$r_c = \frac{2\sigma_{12}v_2}{(g_1 - g_2)} , \qquad (1.5)$$

below which it is advantageous for the domain to shrink to a point while $r > r_c$ favors an uninhibited size expansion.

Recent experiments involving the freezing of helium, argon and oxygen in porous vessels [2–5] indicate that geometrical confinement has important effects on the physical properties of a liquid that differ from ordinary bulk substances. Such quantities as effective viscosity and pressure dependence of the critical temperature strongly depend on the pore size. This might indicate that a simple homogeneous nucleation model as described above is somewhat limited in its applicability. It is also well established that ^{4}He is a quantum system which supports the formation of radially-symmetric bubbles [6]. It appears that these bubbles play an important role in the determination of the energy spectrum of the bulk liquid ^{4}He. In addition to these examples, the nematic-isotropic phase transition in liquid crystals has displayed hysteretic behavior in confined geometries [7,8]. The following section

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will present the methodology of homogeneous nucleation. In Sec. III of this paper, we will show a possible extension of this model to inhomogeneous behavior that has similar characteristics to those observed in the above mentioned experiments.

Before going any further, it is helpful to introduce the scalings of the independent and dependent variables according to

$$r \to \frac{\sqrt{DA_4}}{A_3} r; \qquad \phi \to \frac{A_3}{A_4}\phi \tag{1.6}$$

so that our Eq. (1.3) becomes

$$\phi'' + \frac{2}{r}\phi' = \epsilon\phi + \phi^2 + \phi^3 , \tag{1.7}$$

where we have introduced a control parameter ϵ given by

$$\epsilon = \frac{A_2 A_4}{A_3} = \frac{a A_4}{A_3}(T - T_0). \tag{1.8}$$

Thus, we see that it is completely general for us to consider the case of $a = A_3 = A_4 = D = 1$ so that

$$F(\phi) = \epsilon\phi^2 + \phi^3 + \phi^4 , \tag{1.9}$$

where now $\epsilon = (T - T_0)$. We will now work solely in our scaled variables since they have proven to be equivalent to any choice of the free parameters with the appropriate variable transformation. For a general treatment involving all free parameters we refer the reader to Ref. [9].

II. HOMOGENEOUS NUCLEATION

Here we wish to present only the key aspects of homogeneous nucleation phenomenology that will be comparable with the extensions presented in the next section. For an excellent overview on the subject, we again refer the reader to a recent review article on the subject, i.e., Ref. [10]. In the case of homogeneous nucleation, we need only to minimize the free energy given by Eq. (1.9), i.e.,

$$0 = \frac{\partial F}{\partial \phi} = 2\epsilon\phi + 3\phi^2 + 4\phi^3 \tag{2.1}$$

which gives us the possibilities that either $\phi_0 = 0$ (disordered phase) or two ordered phases arise

$$\phi_\pm = \frac{-3 \pm \sqrt{9 - 32\epsilon}}{8}. \tag{2.2}$$

In order for the above roots to be real we require that the expression under the square root be positive. Thus, the range of existence for the ordered phase is limited to

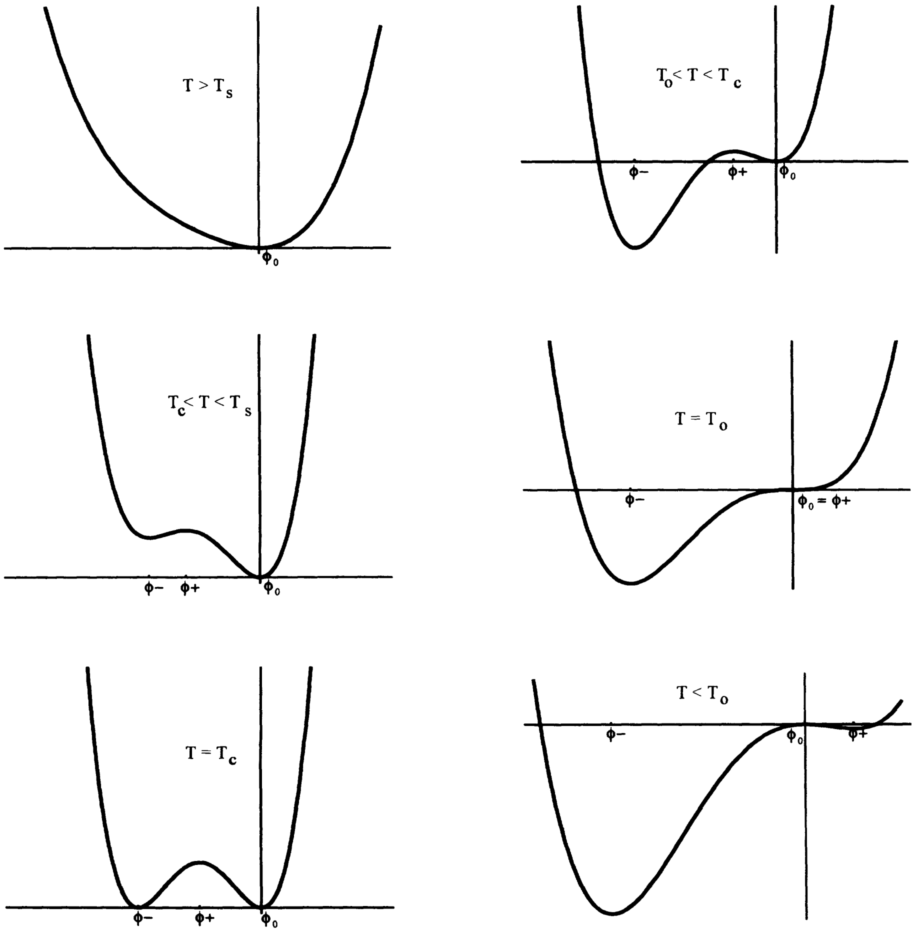

FIG. 1. Variation of the free energy $F(\phi)$ with temperature.

$$\epsilon \leq \frac{9}{32} \quad \text{or} \quad T \leq T_0 + \frac{9}{32} \equiv T_s. \tag{2.3}$$

The transition temperature T_c is found by solving the simultaneous equations

$$F(\phi) = \epsilon\phi^2 + \phi^3 + \phi^4 = 0 \tag{2.4}$$

and

$$\frac{\partial F}{\partial \phi} = 2\epsilon\phi + 3\phi^2 + 4\phi^3 = 0, \tag{2.5}$$

which gives the result

$$T_c = T_0 + \frac{1}{4}. \tag{2.6}$$

In order to have thermodynamic stability, the second variation of the free energy must be positive, i.e.,

$$0 \leq \frac{\partial^2 F}{\partial \phi^2} = 2\epsilon + 6\phi + 12\phi^2. \tag{2.7}$$

The range of thermodynamic stability for the disordered phase ($\phi_0 = 0$) is found to be $\epsilon \geq 0$ or $T \geq T_0$. For the two ordered phases $\phi_\pm$, we find that ϕ_- is metastable in the range $T_c < T < T_s$ ($\frac{1}{4} < \epsilon < \frac{9}{32}$) and absolutely stable for $T < T_c$ ($\epsilon < \frac{1}{4}$). For ϕ_+, we find that it is unstable for all temperatures $T > T_0$ ($\epsilon > 0$) and metastable in the region $T < T_0$ ($\epsilon < 0$). Figure 1 shows how the free energy $F(\phi)$ varies with temperature. Figure 2(a) depicts the hysteresis that is traced out as the order parameter varies with temperature. It is useful to point out here, that in the case of a liquid-solid transition, the order parameter corresponds to the density of the phase. Thus, ϕ_0 would correspond to the liquid phase and ϕ_- would be the solid phase. This gives us the correct behavior for bulk melting where the solid remains metastable up to T_s and for bulk freezing where likewise the liquid remains metastable down to T_0.

The specific heat is determined by

$$C = -T\frac{\partial^2 F(\phi)}{\partial T^2}, \tag{2.8}$$

and using the expansion for $F(\phi)$ given in Eq. (1.9), we find

$$C = -2T\phi\frac{\partial \phi}{\partial T}. \tag{2.9}$$

Figure 2(b) shows a plot of the specific heat. This model of homogeneous nucleation only allows for two stable or metastable states at any given time in the range of temperatures $T_0 < T < T_s$. It is the case, however, that in experiment, a much more complicated behavior is realized where many paths can be followed within this region. Homogeneous nucleation is unable to reproduce this multihysteretic behavior. In the next section, we discuss a possible extension to this model and show how the inhomogeneous solutions give rise to numerous possibilities in the behavior of the order parameter and other related quantities.

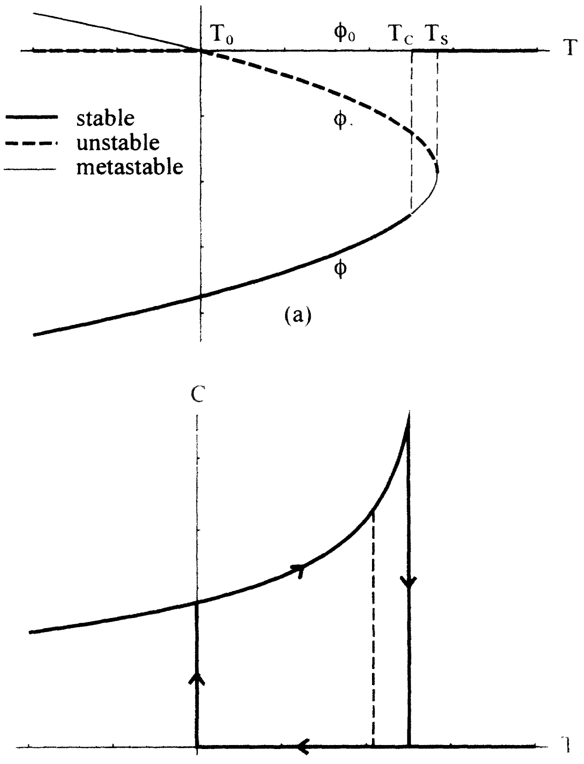

FIG. 2. (a) Variation of the order parameter with temperature and (b) the specific heat, both in the case of homogeneous nucleation.

III. INHOMOGENEOUS NUCLEATION

We wish to find solutions to Eq. (1.7) different than those in the homogeneous case. Two recent papers [12,13] have found inhomogeneous kink-type solutions that run from ϕ_0 to ϕ_-. These solutions obviously have a limited range of existence in more than one dimension since the "friction" term corresponding to the derivative $\phi_r(r)$ makes a kink solution impossible when the potential difference between ϕ_0 and ϕ_- becomes too small [e.g., at $T = T_c$ when $F(\phi_0) = F(\phi_-) = 0$]. In the range $T_0 < T < T_s$ or equivalently $0 < \epsilon < \frac{9}{32}$, it is found that the root ϕ_+ acts as an attractor for all solutions to Eq. (1.7) with initial conditions $\phi'(0) = 0$ and $\phi_- < \phi(0) < \phi_0$. We implement the requirement that $\phi'(0) = 0$ so that there is no defect in the order parameter at the center of the nucleating phase. The second boundary condition that will be imposed is that $\phi(R) = \phi_+$ for some fixed value of R. Such a condition is imposed with an eye towards trying to emulate the confined geometry of a porous glass. The choice of $\phi(R) = \phi_+$ is somewhat natural being as all solutions fulfilling the above requirements are attracted to this point. This means that starting from any value of ϕ at the center, provided it is confined by $\phi_- < \phi(0) < \phi_0$, the corresponding solution $\phi(r)$ would asymptotically tend to ϕ_+. We thus choose ϕ_+ as our boundary condition at the pore surface. With

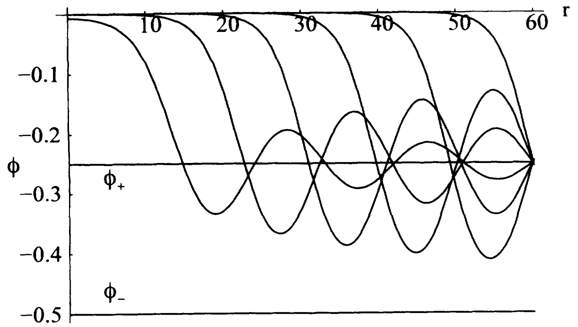

FIG. 3. Plot of the 0–5 node solutions $\phi(r)$ for $\epsilon = 0.25$. Both ϕ and r are in arbitrary (scaled) units.

this boundary condition, this can be viewed as forming an inhomogeneous nucleus of a fixed size. We chose a value of $R = 60$, but this number is completely arbitrary. With this choice, we looked for solutions starting near $\phi(0) \lesssim \phi_0$, i.e., near the liquid phase. Now our solutions will not begin at ϕ_0, but due to thermal fluctuations (as in the case of homogeneous nucleation), at some point with slightly higher energy. We found solutions from 0 to 5 nodes and have plotted a sample of the full set of solutions for $\epsilon = 0.25$ in Fig. 3. Solutions with a higher number of nodes will also exist, but the energy required to achieve such solutions becomes increasingly higher, and soon the starting point $\phi(0)$ lies closer to ϕ_- than to ϕ_0. Solutions were able to be found for almost the entire range $0 < \epsilon < \frac{9}{32}$ although near the points $\epsilon = 0$ and $\epsilon = \frac{9}{32}$ it sometimes became difficult to find the lower node solutions. It was found that the 0 node solution only existed up to $\epsilon \approx 0.255$ and at higher values of ϵ would become unconfined. There was a similar finding for the 1 and 2 node solutions, disappearing at progressively higher values of ϵ, but all other higher node solutions were found throughout the entire range. For each of the solutions, the average value of the order parameter σ was calculated using

$$\sigma = \langle\phi\rangle = \frac{\int_0^R \phi r^2 dr}{R^3} , \tag{3.1}$$

and the plots of the σ for the 0 to 5 node solutions along with the homogeneous solutions are shown in Fig. 4. We see immediately that the possibility now exists for the system to follow several distinct paths in the region $T_0 < T < T_s$. The specific heat is found in a similar fashion to Eq. (2.9), except that ϕ is replaced with $\sigma = \langle\phi\rangle$ yielding

$$C = -2T\sigma\frac{\partial\sigma}{\partial T}. \tag{3.2}$$

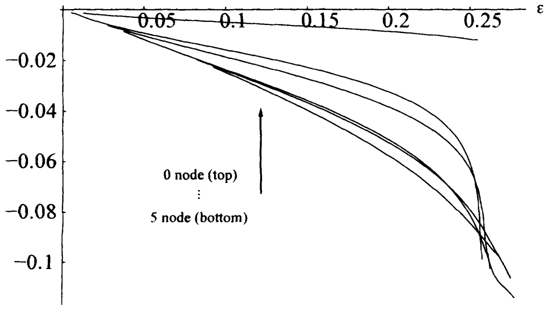

FIG. 4. Plot of σ as a function of ϵ from Eq. (3.1) for the 0–5 node solutions. Both σ and ϵ are in arbitrary (scaled) units.

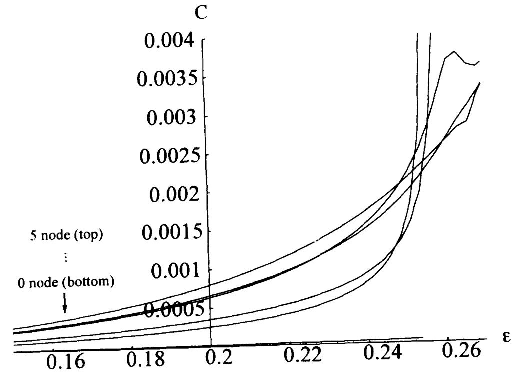

FIG. 5. Plot of the specific heats C as a function of ϵ for each of the 0–5 node solutions. Both C and ϵ are in arbitrary (scaled) units.

The plots of the specific heats associated with the various solutions are shown in Fig. 5. The behavior of the order parameter and the specific heat are very different from those that came about in the homogeneous model. We now need to compare our theoretical model and its results with experiment.

IV. COMPARISON WITH EXPERIMENT: FREEZING OF CRYOGENIC FLUIDS IN POROUS GLASSES

We will now attempt to form our results to this point into a model that qualitatively describes the very recent experimental results of the freezing of cryogenic fluid in porous glasses such as Vycor and silica xerogel [5]. As previously mentioned, the order parameter in the case of a liquid-solid transition represents the density. With this in mind, measurements made ultrasonically, as done by Molz *et al.* [5], provide a sensitive measurement of the density of the sample.

The transverse sound velocity of a system is known to be a direct function of the density [5]. The crossover seen in Fig. 4 in the region of $\epsilon = 0.25$ is very similar to that found by Molz *et al.* (see Fig. 8 in Ref. [5]). It is unlikely that the system would find itself in a state with only solutions of one type (1 node, or 2 node, etc.), but it is feasible that as the system's temperature is decreased, the contribution of each solution to the entire ensemble would change producing the same type of result. Because of our choice of parameters, T_c is much closer to T_s than to T_0 and the plots become crowded above T_c. To compare these plots further, the correct parameter values for the case being studied (Ar, He, etc.) would be required, but the overall behavior would remain the same. It is important to note that as the pore radius is increased

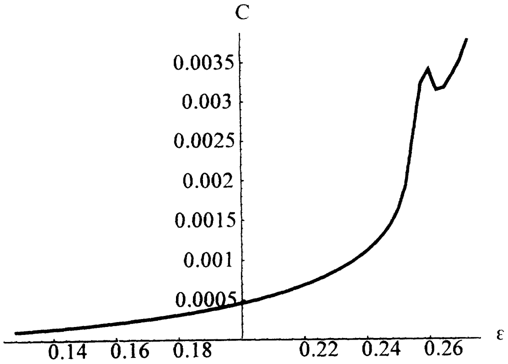

FIG. 6. Plot of the specific heat C as a function of ϵ upon freezing with inhomogeneous solutions present. Both C and ϵ are in arbitrary (scaled) units.

($R \rightarrow \infty$) the plots of σ for the various solutions would merge into one line and we would again be left with the homogeneous case.

The hysteretic behavior of the specific heat was stated in Ref. [5] to be consistent with the ultrasonic data, although we have no plot to directly compare with Fig. 5. If we make some assumptions about the contribution of each solution to the overall state of the system, we could construct a plot of the specific heat upon freezing. As we lower the temperature below T_s, the higher node solutions are the first to enter, with the lower node (0,1 and 2) solutions existing only at lower temperatures. If we assume that the system would distribute itself evenly over all possible solutions at a given temperature, we see that the specific heat has a jump as shown in Fig. 6 when the lowest node solutions become valid. This again compares very well with the situation observed experimentally.

A remark should be made in regard to the chosen dimensionality of our solutions. The geometry of pores used in the experiment discussed is certainly not precisely spherical. Nor is it cylindrical. Recent experiments on the filling and draining of Vycor pores suggest a fractal dimension of 2.6 for the pores [11]. With this fact in mind, we believe the assumption about the spherical nature of the solutions approximates the reality better. However, the effect of dimensionality (including a possibly fractal dimension) on the behavior of the solutions should be investigated in a separate study.

V. CONCLUSIONS

We have presented, in this paper, a model for inhomogeneous nucleation in a prototypic spherically symmetric system undergoing a first-order phase transition. These solutions enable us to describe some of the experimental results that remained largely unexplained by the homogeneous nucleation model. They are also an improvement on recent inhomogeneous kink-type solutions [12,13] since they exist over the entire region $T_0 < T < T_s$ and produce a many path hysteresis in the variation of the order parameter with temperature. The qualitative results seem to agree very well with experiment, but for further comparison accurate parameter values for the model are required. One further improvement would also be to find these inhomogeneous solutions starting in the region of ϕ_+ in order to emulate the system under the process of melting with a solid nucleus at $r = 0$. The effect of the symmetry of the confining surface on the behavior of inhomogeneous solutions merits another investigation.

ACKNOWLEDGMENTS

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