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Metastability in tricritical systems

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We present a Langer-Cahn-Hilliard-like theory of some aspects of nucleation for two tricritical systems: the symmetric scalar metamagnet and ^{3}He-^{4}He mixtures. In particular, we calculate the work of formation for a tricritical droplet and the imaginary part of the free energy associated with the metastable state. In addition we obtain an explicit expression for the interface tension whose critical exponent agrees with earlier phenomenological predictions. We find that the scaling form for the work of formation exhibits a universality with respect to critical and tricritical points. In addition, we find that the singularity on the coexistence curve for the metamagnet and on the superfluid side of ^{3}He-^{4}He is of the same functional form as for Ising-like systems. However, the singularity is different on the normal side of the ^{3}He-^{4}He coexistence curve, due to the role of the phase variable of the complex superfluid order parameter.

I. INTRODUCTION

In this paper we discuss some aspects of the metastable states and associated nucleation phenomena for symmetrical tricritical systems. Our motivation is in part based on the existence of experimental studies of tricritical nucleation in ^{3}He-^{4}He mixtures[1] and Fe-Al alloys,[2] for which no satisfactory theory yet exists. In addition, a recent analysis[3] of the essential singularity at a first-order phase transition of critical systems indicates a universality of this singularity which one might also expect to hold for at least some symmetrical tricritical systems with the symmetry characteristic of Ising-like systems. We therefore present here a Langer-Cahn-Hilliard (LCH)-like theory[4–6] of metastability for models of two tricritical systems: the symmetric scalar metamagnet and ^{3}He-^{4}He mixtures. Our analysis primarily deals with three dimensions, but some results are also given in d dimensions. Our work allows us to extend the notion of the universality of the essential singularity associated with a first-order phase transition to include these tricritical as well as Ising-like critical systems. Namely, we find that the functional form of the essential singularity in the free energy on the coexistence curve is the same for the metamagnet and the superfluid phase of ^{3}He-^{4}He as for the Ising systems. However, the singularity is different on the normal side of the ^{3}He-^{4}He coexistence curve, due to the role of the phase variable. In addition, we obtain the dominant part of the contribution to the nucleation rate of these tricritical systems near the coexistence curve, although we do not calculate the so-called dynamical prefactor[5] which also contributes to the nucleation rate. Until a calculation of the dynamical prefactor is carried out, however, a detailed comparison of theory and experiment for nucleation is not possible. Since this dynamical prefactor varies from system to system (i.e., it is different for ^{3}He-^{4}He than for a metamagnet, say), we leave its calculation for a later study.

Our analysis is based on a Ginzburg-Landau Hamiltonian for tricritical systems which involves a nonconserved order parameter Ψ (such as the sublattice magnetization for an Ising-like metamagnet or the superfluid order parameter for ^{3}He-^{4}He) and a conserved "subsidiary" variable c (such as the magnetization of the metamagnet or the concentration of ^{3}He) which undergoes phase separation below the tricritical point. Although we do not present a dynamical theory of nucleation here, it should be noted that our model should be a good starting point for such a calculation and has been used in earlier studies of tricritical dynamics.[7] The fact that the Hamiltonian contains two variables leads to an interesting and complicated set of coupled equations for the mean-field saddle-point analysis which the LCH theory involves. Although the results of our approximate solution are given in the text, it is worthwhile summarizing here the physical picture which emerges from the analysis. To begin with, we first recall that the LCH approach is a spatial generalization of the classical droplet theory of nucleation. That is, the order parameter for a critical droplet which is assumed to produce the nucleation of a metastable state varies from its stable value at the center of the droplet to its metastable value in the homogeneous background in which it is embedded. The main spatial variation takes place in the region of the interface profile whose thickness is proportional to the equilibrium correlation length. The interesting feature of many tricritical models is that there are two variables, Ψ and c, which are dynamically coupled. The earlier phenomenological theories[8–10] of the surface tension for symmetrical tricritical systems are based on the assumption that there is only one correlation length and one interfacial tension for such systems. Our analysis substantiates this picture. Since we are primarily concerned with ^{3}He-^{4}He and metamagnet models in this paper (and not multicomponent fluids[11]), we summarize our results using the Ising model of a metamagnet as an example. We find from our approximate solution of the saddle-point equations for the order parameter Ψ and magnetization c that a tricritical nucleating droplet of a metastable, ordered phase, say, can be described either in terms of the spatial variation of Ψ or of c. Thus the tricritical droplet for the above case has a disordered phase value of zero for the order parameter at its center which changes to its ordered phase value over an interface width proportional to the correlation length. Since we find that the saddle-point solution for c can be given in terms of the saddle-point solution for Ψ to lowest order by a local version of the equilibrium solution, we can equally well describe the tricritical droplet by saying that the magnetization varies from its zero value at the center to its ordered phase value which the background has.

Another result of our analysis is concerned with the nature of the singularity in the free energy on the tricritical coexistence curve. Here it is important to note the difference in the basic symmetries of the two models considered. The scalar metamagnet has the same reflection symmetry as the Ising ferromagnet, whereas the ^{3}He-^{4}He model has the well-known invariance under a gauge transformation. We find that the singularity for the tricritical metamagnet has the same functional form as that predicted earlier for the Ising ferromagnet. However for the ^{3}He-^{4}He tricritical system, the situation is somewhat different. The singularity on the superfluid side of the coexistence curve is of the same form as for the metamagnet, but is modified on the normal side due to the effect of phase fluctuations. However, the work of formation of the critical droplet which enters the expression for the imaginary part of the free energy has a universal form for both Ising-like critical systems and these tricritical models.

We should also note that although our analysis is mean-field-like, certain of our results for the three dimensional case should be valid, up to logarithmic corrections, in the tricritical region. This of course is due to the fact that the borderline dimensionality above which mean-field predictions for exponents are valid is 3 for tricritical systems. The earlier analysis of critical systems does not give correct critical exponents, due to the fact that the borderline dimension is 4 in this case.

The outline of our paper is as follows: In Sec. II we define the models and summarize some relevant predictions of mean-field theory for the tricritical region. We also discuss what metastability is for this model and note that there are two types of possible metastable behavior. One corresponds to a field conjugate to the order parameter Ψ which is usually not experimentally accessible (in contrast to the critical case). The other corresponds to the field (e.g., the magnetic field) conjugate to the variable c (e.g., the magnetization). It is this type of metastability which we analyze in this paper, as it is of greater experimental relevance. Section III contains a calculation of the work of formation of the tricritical droplet, which involves a solution of the coupled saddle-point equations for Ψ and c. We solve these equations by analyzing an equivalent problem in which the saddle-point equation for Ψ is given in terms of an effective Hamiltonian for Ψ which results from exactly integrating out c in the original Boltzmann factor. This yields a nonlocal kernel in addition to the usual Ginzburg-Landau terms. We develop a perturbation solution to handle this nonlocality in which the zeroth-order effective Hamiltonian is of a Riedel-Wegner-type,[12] i.e., a sixth-order polynomial in Ψ. The perturbation scheme is essentially an expansion in powers of the inverse correlation length. To lowest order we find a critical droplet solution discussed above. There is an associated bulk and interface surface energy. The latter yields a surface tension which agrees with an earlier phenomenological theory for the surface-tension exponent,[9] but contains as well a correction term to the leading singularity, evaluated in Appendix A. A general scaling theory for the activation energy is also given for the d-dimensional case. In Sec. IV we calculate the imaginary part of the free energy for the metamagnet. This corresponds to the continuation of the stable free energy across the coexistence curve. This calculation follows the earlier analysis of Langer[4] and of Gunther *et al.*,[3] as discussed above and leads to an explicit prediction for the essential singularity in d-dimensions for this tricritical model. In Sec. V we extend this analysis to the ^{3}He-^{4}He model, where one has to deal with fluctuations of both the amplitude and the phase of the complex order parameter. In Sec. VI we present some brief concluding remarks. In Appendix A an analysis of the correction terms for the surface tension is presented. Appendix B contains some mathematical details concerning the eigenvalue problems appearing in Secs. IV and V.

II. METASTABILITY IN A TRICRITICAL MODEL

A. Mean-field statics

As a model for symmetrical tricritical systems explicit enough to study dynamical problems we consider the Hamiltonian used in earlier studies of tricritical dynamics[7, 13]

$$H[\Psi,c]=\int d\vec{x}\{\tfrac{1}{2}|\vec{\nabla}\Psi(\vec{x})|^2+\tfrac{1}{2}l_0^2[\vec{\nabla}c(\vec{x})]^2+f[\Psi(\vec{x}),c(\vec{x})]\}\ , \qquad (2.1)$$

$$f(\Psi,c)=\tfrac{1}{2}r|\Psi|^2+u|\Psi|^4+v|\Psi|^6+\tfrac{1}{2}\chi_n^{-1}c^2+\gamma c|\Psi|^2-\Delta c\ . \qquad (2.2)$$

The variable $\Psi(\vec{x})$ is the order parameter (the one associated to the order-disorder second-order phase transition) and $c(\vec{x})$ is a subsidiary order parameter which is a conserved variable and undergoes phase separation below the tricritical point. For simplicity r, u, v, χ_n, and γ are considered to depend only on the temperature and Δ is the field conjugate to c. For a metamagnet Ψ is a real scalar order parameter, the sublattice magnetization, c the magnetization, and Δ the applied magnetic field. For a ^{3}He-^{4}He mixture, Ψ is the complex superfluid order parameter, c is the local concentration of ^{3}He, and Δ is the difference in chemical potential of the two species up to an additive constant.[7]

The mean-field statics of this model has been discussed by many authors.[13, 14] We summarize the main results of this analysis in the following, as it is needed in our treatment of the nucleation problem. The properties of homogeneous equilibrium states only depend on the amplitude of the complex order parameter for ^{3}He-^{4}He mixtures. The symbol Ψ will then stand in the remainder of this section either for the real order parameter of the metamagnet or for the amplitude of the complex superfluid order parameter.

There exists a λ line corresponding to second-order phase transitions for

$$\tilde{r}\equiv r+2\Delta\gamma\chi_n=0\ , \qquad (2.3)$$

$$\tilde{u}\equiv u-\tfrac{1}{2}\gamma^2\chi_n>0\ . \qquad (2.4)$$

The tricritical point is characterized by

$$\tilde{r}=0\ , \qquad (2.5)$$

$$\tilde{u}=0\ , \qquad (2.6)$$

and the line of first-order transitions occurs for

$$\tilde{u}<0\ , \qquad (2.7)$$

$$\tilde{r}=\tilde{r}_0\equiv\frac{\tilde{u}^2}{2v}\ . \qquad (2.8)$$

This last equation fixes the value of $\Delta=\Delta_0$ for which, for example in the metamagnet, the ordered phases of opposite symmetry and the disordered phase coexist. The equilibrium values of Ψ and c are given by the degenerate minima of $f(\Psi,c)$:

$$\Psi=\Psi_n=0\ , \qquad (2.9)$$

for the disordered phase, and

$$c=c_n\equiv\chi_n\Delta_0\ , \qquad (2.10)$$

$$\Psi^2=\Psi_s^2\equiv-\frac{\tilde{u}}{2v}\ , \qquad (2.11)$$

$$c=c_s\equiv\chi_n(\Delta_0-\gamma\Psi_s^2)\ , \qquad (2.12)$$

for the ordered phases. The values of Ψ correspond to the three minima of the effective density $\hat{f}(\Psi)$ obtained from $f(\Psi,c)$ by setting c equal to its minimum value as a function of Ψ

$$c=\chi_n(\Delta-\gamma\Psi^2)\ , \qquad (2.13)$$

$$\hat{f}(\Psi)=\tfrac{1}{2}\tilde{r}\Psi^2+\tilde{u}\Psi^4+v\Psi^6-\tfrac{1}{2}\chi_n\Delta^2\ , \qquad (2.14)$$

and $\Delta=\Delta_0$. From Eq. (2.6) we have that $\tilde{u}\sim\epsilon$ where $\epsilon=(T_t-T)/T_t$ so that

$$\Psi_s\sim\epsilon^{1/2}\ , \qquad (2.15)$$

$$\beta_\tau=\tfrac{1}{2}\ , \qquad (2.16)$$

and

$$(c_n-c_s)\sim\epsilon\ , \qquad (2.17)$$

$$\beta_u=1\ . \qquad (2.18)$$

These and the following exponents are the well-known mean-field tricritical exponents.[12, 15, 16] (In general we shall follow Griffiths's notation.[16]) The correlation length in the disordered phase is given by

$$\xi=\left[\left.\frac{\partial^2\hat{f}}{\partial\Psi^2}\right|_{\Psi=0}\right]^{-1/2}=\tilde{r}_0^{-1/2}=\left[\frac{\tilde{u}^2}{2v}\right]^{-1/2}\sim\epsilon^{-1}\ , \qquad (2.19)$$

$$\nu_u=1\ , \qquad (2.20)$$

and in the ordered phase

$$\xi_s=\tfrac{1}{2}\xi\ . \qquad (2.21)$$

The c variable susceptibility[13] in the disordered phase is the parameter χ_n in the original Hamiltonian, while in the ordered phase,

$$\chi_s=\chi_n\left[1+2\left(\frac{u+|\tilde{u}|}{|\tilde{u}|}\right)\right]\sim\epsilon^{-1}\ , \qquad (2.22)$$

$$\gamma_u=1\ . \qquad (2.23)$$

The fact that χ_n remains finite on the disordered branch of the coexistence curve is an artifact of the mean-field approximation. A renormalization group analysis shows that the true c variable susceptibility has the same divergence, $\gamma_u=1$, on both sides of the coexistence curve.[12]

B. Mean-field analysis of metastability

In a description of a system in terms of fields (Gibbs free energy) metastable states associated with a first-order phase transition can exist for values of the fields between their coexistence and spinodal values for a given temperature. In our problem we have in principle two different kinds of metastability related to the two available fields: The field H_s conjugate to Ψ and the field Δ conjugate to c. Coexistence of phases occur for $H_s=0$ and $\Delta=\Delta_0$. Metastable states for $H_s\neq 0$ and $\Delta=\Delta_0$ are associated with a "cascade" of local minima of $\hat{f}(\Psi)$. This kind of metastability is the mathematical analog of the one studied in critical systems, in which only the field conjugate to the order parameter exists. Since H_s cannot usually be controlled experimentally we shall not discuss these metastable states; rather, we shall focus on those which originate for $\Delta\neq\Delta_0$ and $H_s=0$. These states are associated to the nonabsolute minima of $f(\Psi,c)$. These minima can be analyzed by means of $\hat{f}(\Psi)$ (with $\tilde{r}\neq\tilde{r}_0$). The value of c at the minima is then given by Eq. (2.13) with Ψ replaced by its corresponding value at the minima of $\hat{f}(\Psi)$. The extrema of $\hat{f}(\Psi)$ are located at

$$\Psi=\Psi_n=0\ , \tag{2.24}$$

$$\Psi^2=\Psi_{\pm}^2\equiv\frac{-4\tilde{u}\pm(16\tilde{u}^2-24v\tilde{r})^{1/2}}{12v}\ . \tag{2.25}$$

We thus have five different regions summarized in Fig. 1: (I) $\tilde{u}>0$, $\tilde{r}>0$; $\tilde{u}<0$, $\tilde{r}>\tilde{r}_1\equiv 2\tilde{u}^2/3v$ is the disordered stable phase. (II) $\tilde{r}<0$, is the ordered stable phases with $\Psi^2=(\Psi_+)^2$. (III) $\tilde{u}<0$, $\tilde{r}=\tilde{r}_0$ is the coexistence line discussed above. Note that $\Psi_s^2=(\Psi_+)^2$. (IV) $\tilde{u}<0$, $0<\tilde{r}<\tilde{r}_0$ represents the metastable disorderd phase and stable ordered phases with $\Psi^2=(\Psi_+)^2$. (V) $\tilde{u}<0$, $\tilde{r}_0<\tilde{r}<\tilde{r}_1$ represents the stable disordered phase and metastable ordered phases with $\Psi^2=(\Psi_+)^2$. Later on we shall use the notation Ψ^Δ and c^Δ for the values of Ψ and c in regions IV and V, so that $(\Psi_s^\Delta)^2=\Psi_+^2$, $\Psi_n^\Delta=\Psi_n=0$, $c_s^\Delta=\chi_n[\Delta-\gamma(\Psi_s^\Delta)^2]$, and $c_n^\Delta=\chi_n\Delta$. The values of Δ at $\tilde{r}=\tilde{r}_1$ and $\tilde{r}=0$ fix, respectively, the two limits of metastability or spinodal values Δ_1 and Δ_2 or Δ:

$$\Delta_1=\frac{1}{2\gamma\chi_n}\left(\frac{2}{3}\frac{\tilde{u}^2}{v}-r\right)\ , \tag{2.26}$$

$$\Delta_2=-\frac{r}{2\gamma\chi_n}\ . \tag{2.27}$$

In terms of Δ the five regions are characterized by (I) $\Delta>\Delta_1$, (II) $\Delta<\Delta_2$, (III) $\Delta=\Delta_0$, (IV) $\Delta_2<\Delta<\Delta_0$, (V) $\Delta_1>\Delta>\Delta_0$.

From this discussion we can obtain the stable, metastable, and unstable branches of Ψ with respect to Δ. These are shown in Fig. 2 by plotting Δ as a function of Ψ from $\partial\hat{\rho}(\Psi)/\partial\Psi=0$. Figure 2(a) corresponds to an isotherm below the tricritical tempera-

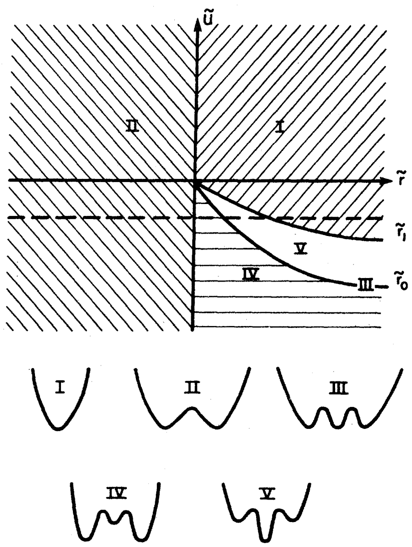

FIG. 1. Form of $\hat{\rho}(\Psi)$ in the different regions of the $\tilde{r}$, $\tilde{u}$ plane. The dashed line at fixed $\tilde{u}<0$ corresponds to the isotherm of Fig. 2(a). For ^{3}He-^{4}He mixtures the well structure displayed corresponds to a cross section of fixed phase of the complex order parameter. The same is true for Fig. 2.

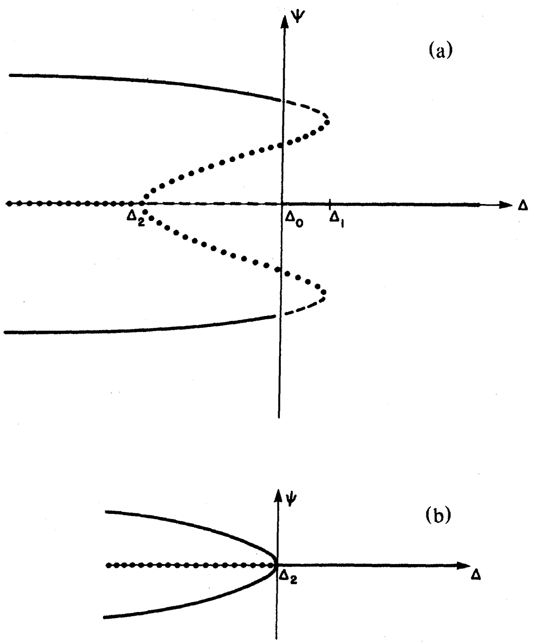

FIG. 2. Full lines represent stable states, dashed lines metastable states, and dotted lines unstable states. The $\Psi=0$ line corresponds to disordered states. (a) Isotherm below $T_t(\tilde{u}<0)$; (b) isotherm above $T_t(\tilde{u}>0)$.

ture T_t. As we approach $T_t(\tilde{u}=0)$ the values of Δ_0, Δ_1, Δ_2 approach the tricritical value Δ_t fixed by $\tilde{r}=0$ and $T=T_t$. Figure 2(b) corresponds to an isotherm above $T_t(\tilde{u}>0)$. The bifurcation value Δ_2 goes to Δ_t as we approach T_t from above. The equation of state giving the branches of c with respect to Δ can be constructed from Fig. 2 and Eq. (2.13).

In the remainder of this paper we shall discuss some features of the decay of the metastable states in regions IV and V for small deviations $(\delta\Delta)=\Delta-\Delta_0$. We shall develop a LCH[4–6] type of theory which is meant to be valid for near-equilibrium situations and which is based in part on equilibrium concepts. In particular we are using a description in terms of the fields T, Δ whereas the experimental situation often corresponds to a description in terms of T and c, since the variable c is kept constant.[17] No Legendre transformation exists between these two descriptions in the nonequilibrium situation, but they can be approximately related near equilibrium (see Sec. III E). Experimentally we can envisage three different quenches that bring the system to a nonstable state (Fig. 3). Quenches 1 and 2 correspond, respectively, to bringing the system to the ordered and disordered metastable states discussed above and shown in Fig. 2(a). Quench 3 brings the system to a disordered unstable situation. In the very early stages of the process the system will presumably decay to a metastable ordered state analogous to the one corresponding to quench 1. This decay will occur in a short time scale in which the nonconserved order parameter Ψ relaxes from Ψ_n to Ψ_s^{Δ} while the conserved c remains constant with $c=c_s$. This early time dynamical process is beyond the framework of the present near-equilibrium theory, but the real decay of this metastable state by a nucleation process occurs in a later time scale and corresponds to the description we present for the ordered metastable state. Moreover the nucleation process we describe for the three quenches is a local one and the role played by the global conservation of c, which drives the system to a coexistence final state, would appear in a later stage of droplet growth and coagulation.[22,23]

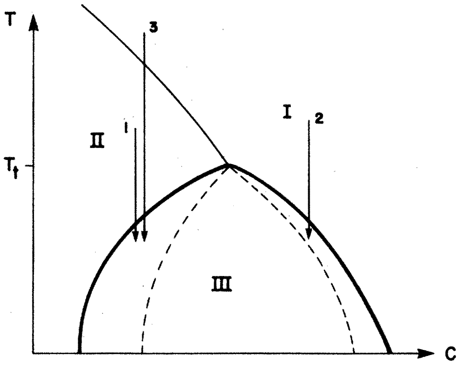

FIG. 3. Phase diagram of the system: (I) disordered states, (II) ordered states, (III) region of coexistence of phases. The dashed lines represent the spinodals. Three different quenches are shown.

III. WORK OF FORMATION OF THE CRITICAL DROPLET

It is our aim to describe nucleation for a tricritical system in terms of a "classical" droplet picture.[4,6] In this picture of nucleation a key quantity to be discussed is the work of formation of the critical droplet nucleating the stable phase. This is given by the extrema of

$$\Delta H=H[\overline{\Psi}(\vec{x}),\overline{c}(\vec{x})]-H[\Psi^{\Delta},c^{\Delta}] \ , \tag{3.1}$$

where $[\Psi^{\Delta},c^{\Delta}]$ represent the homogeneous metastable state discussed in Sec. II in which we have prepared the system and $[\overline{\Psi}(\vec{x}),\overline{c}(\vec{x})]$ is the droplet configuration. For a metastable ordered state, with $(\Psi^{\Delta})^2=(\Psi_s^{\Delta})^2$, $c^{\Delta}=c_s^{\Delta}$, Eq. (3.1) can be written as

$$\begin{aligned}\Delta H=&\{H[\Psi_n^{\Delta},c_n^{\Delta}]-H[\Psi_s^{\Delta},c_s^{\Delta}]\}\\&+\{H[\overline{\Psi}(\vec{x}),\overline{c}(\vec{x})]-H[\Psi_n^{\Delta},c_n^{\Delta}]\} \ .\end{aligned} \tag{3.2}$$

The first bracket is associated with the bulk energy of the droplet and the second one with the interface energy. We discuss in the following the different ingredients of this expression. For simplicity we only consider in this section a real order parameter appropriate for the metamagnet and we shall show in Sec. V that our results also apply to ^{3}He-^{4}He mixtures.

A. Droplet configuration

As a first step we have to identify the droplet configuration $[\overline{\Psi}(\vec{x}),\overline{c}(\vec{x})]$. This is associated with a saddle point of the Hamiltonian and is given by the solution of the saddle-point equations

$$\left.\frac{\delta H}{\delta\Psi}\right|_{\overline{\Psi}}=\left.\frac{\delta H}{\delta c}\right|_{\overline{c}}=0 \ ,$$

i.e.,

$$\begin{aligned}0=&\vec{\nabla}^2\overline{\Psi}(\vec{x})-r\overline{\Psi}(\vec{x})-4u\overline{\Psi}^3(\vec{x})\\&-6v\overline{\Psi}^5(\vec{x})-2\gamma\overline{c}(\vec{x})\overline{\Psi}(\vec{x}) \ ,\end{aligned} \tag{3.3}$$

$$0=l_0^2\vec{\nabla}^2\overline{c}(\vec{x})-\chi_n^{-1}\overline{c}(\vec{x})-\gamma\overline{\Psi}^2(\vec{x})+\Delta \ , \tag{3.4}$$

with the boundary conditions $(r=|\vec{x}|)$

$$\overline{\Psi}^2(\vec{x})\underset{r\to\infty}{\longrightarrow}\Psi_s^2,\quad \overline{\Psi}(\vec{x})\underset{r\to0}{\longrightarrow}0,\quad \frac{d\overline{\Psi}}{dr}\underset{\substack{r\to0\\r\to\infty}}{\longrightarrow}0 \ , \tag{3.5}$$

$$\overline{c}(\vec{x})\underset{r\to\infty}{\longrightarrow}c_s,\quad \overline{c}(\vec{x})\underset{r\to0}{\longrightarrow}c_n,\quad \frac{d\overline{c}}{dr}\underset{\substack{r\to0\\r\to\infty}}{\longrightarrow}0 \ . \tag{3.6}$$

A solution with spherical symmetry of Eqs. (3.3)–(3.6) represents a droplet of disordered phase being nucleated in a homogeneous metastable phase near the ordered side of the coexistence curve. One way to analyze these equations is to consider an equivalent equation for $\vec{\Psi}(\vec{x})$ in which the coupling with $\vec{c}(\vec{x})$ is absent. Such an equation determines the saddle point of the effective Hamiltonian $\hat{H}[\Psi]$ defined by

$$e^{-\hat{H}[\Psi]}=\int Dc(\vec{x})e^{-H[\Psi,c]} \quad . \tag{3.7}$$

Since the Hamiltonian $H[\Psi,c]$ is quadratic in $c(\vec{x})$, a straightforward integration of $c(\vec{x})$ can be done and we obtain

$$\begin{aligned}\hat{H}[\Psi]=\int d\vec{x}\Big\{&\tfrac{1}{2}[\vec{\nabla}\Psi(\vec{x})]^2+\tfrac{1}{2}\tilde{r}\Psi^2(\vec{x})\\&+\Psi^2(\vec{x})\int d\vec{x}'\,\tilde{u}(\vec{x}-\vec{x}')\Psi^2(\vec{x}')\\&+v\Psi^6(\vec{x})-\tfrac{1}{2}\Delta^2\chi_n\Big\} \quad ,\end{aligned} \tag{3.8}$$

where $\tilde{r}$ is defined in Eq. (2.3) and the nonlocal kernel $\tilde{u}(\vec{x}-\vec{x}')$ is given by

$$\tilde{u}(\vec{x}-\vec{x}')=u\delta(\vec{x}-\vec{x}')-\tfrac{1}{2}\gamma^2G^0(|\vec{x}-\vec{x}'|) \quad , \tag{3.9}$$

$$G^0(|\vec{x}-\vec{x}'|)=\frac{l_0^{-2}}{4\pi}\frac{\exp(-|\vec{x}-\vec{x}'|/\chi_n^{1/2}l_0)}{|\vec{x}-\vec{x}'|} \quad . \tag{3.10}$$

An exact solution of the saddle point of the nonlocal $\hat{H}[\Psi]$ is at least as difficult as solving Eqs. (3.3)–(3.6). Nevertheless we shall argue that near the tricritical region G^0 is a rapidly decaying function so that a systematic expansion of the nonlocal term can be performed. To see this more clearly we introduce dimensionless variables

$$m(\vec{x})=\Psi(\vec{x})/\Psi_s \quad , \tag{3.11}$$

$$\vec{z}=\xi^{-1}\vec{x} \quad . \tag{3.12}$$

Furthermore we shall fix the value of $\Delta=\Delta_0$ for which phase coexistence is possible and thus according to Eq. (2.19), $\tilde{r}=\xi^{-2}$. In these circumstances

$$\begin{aligned}H[m]=\frac{1}{2\sqrt{2v}}\int d\vec{z}\Big\{&[\vec{\nabla}m(\vec{z})]^2+m^2(\vec{z})+\frac{2u\xi}{\sqrt{2v}}m^4(\vec{z})+m^6(\vec{z})\\&-\frac{\gamma^2l_0^{-2}\xi^3}{\sqrt{2v}}m^2(\vec{z})\int d\vec{z}'\,G^0(|\vec{z}-\vec{z}'|)m^2(\vec{z}')-\chi_n\xi^3\Delta_0^2\sqrt{2v}\Big\} \quad ,\end{aligned} \tag{3.13}$$

$$\tilde{G}^0(|\vec{z}-\vec{z}'|)=\frac{1}{4\pi}\frac{\exp(-|\vec{z}-\vec{z}'|/g)}{|\vec{z}-\vec{z}'|} \quad , \tag{3.14}$$

$$g=\chi_n^{1/2}l_0/\xi \quad . \tag{3.15}$$

Sufficiently near T_t we can assume that $g<<1$ and expand $m^2(\vec{z}')$ in a Taylor series around $\vec{z}'=\vec{z}$ in the nonlocal term of Eq. (3.13). Keeping the first two terms in this expansion we get to order g^4:

$$\hat{H}[m]=\frac{1}{2\sqrt{2v}}\int d\vec{z}\Big\{[\vec{\nabla}m(\vec{z})]^2+m^2(\vec{z})-2m^4(\vec{z})+m^6(\vec{z})+\frac{\gamma^2l_0^2\chi_n^2}{\xi\sqrt{2v}}[\vec{\nabla}m^2(\vec{z})]^2-\chi_n\xi^3\Delta_0^2\sqrt{2v}\Big\} \quad . \tag{3.16}$$

The quartic term comes from the m^4 term in Eq. (3.13) and from the first term of the expansion. It contains the main contribution of the nonlocal term and it is negative, corresponding to being in the coexistence region. We note that if one neglects the $(\vec{\nabla}m^2)^2$ term[18] Eq. (3.16) reduces to the Hamiltonian used to study the statics of a ternary fluid mixture with symmetrical tricritical point.[11] The saddle point corresponding to Eq. (3.16) is determined by

$$\begin{aligned}\vec{\nabla}^2\bar{m}(\vec{z})+&\frac{2\gamma^2l_0^2\chi_n^2}{\sqrt{2v}\xi}\bar{m}(\vec{z})\vec{\nabla}^2\bar{m}^2(\vec{z})\\&=\bar{m}(\vec{z})-4\bar{m}^3(\vec{z})+3\bar{m}^5(\vec{z}) \quad .\end{aligned} \tag{3.17}$$

If the $\bar{m}\vec{\nabla}^2\bar{m}^2$ term can be neglected, the solution of the one-dimensional version of Eq. (3.17) ("surface profile" problem) is known to be[19]

$$\bar{m}_0^2(z)=\tfrac{1}{2}(1+\tanh z) \quad , \tag{3.18}$$

where we have written $\bar{m}=\bar{m}_0+\bar{m}_1$, $\bar{m}_1$ being the correction arising from the $m\vec{\nabla}^2m$ term. This one-dimensional solution allows us to evaluate the surface tension of the droplet in the limit of a very large radius. It is worth noticing at this point that both Eq. (3.17) and our solution (3.18) preserves the basic symmetry of the Hamiltonian ($\Psi\to-\Psi$) and that all our subsequent results are always expressed in terms of Ψ^2. The two values $\pm\Psi_s$ represent two phases with the same thermodynamic properties that could only be distinguished by applying a field H_s. Preserving this symmetry means that we are in fact studying nucleation processes related to the two different thermodynamic phases: ordered phase characterized by Ψ_s^2 and disordered phase ($\Psi=0$).

An approximate solution for $c(\vec{x})$ is obtained by comparing Eq. (3.3) [rewritten for $\bar{m}(\vec{z})$] with Eq. (3.17)

$$\bar{c}(\vec{z})=\chi_n[\Delta_0-\gamma\Psi_s^2\bar{m}^2(\vec{z})]-\frac{\gamma l_0^2\chi_n^2}{\sqrt{2v}\xi^3}\vec{\nabla}^2\bar{m}^2(\vec{z}) \ . \tag{3.19}$$

To check the consistency of this result we substitute Eq. (3.19) into Eq. (3.4). The latter equation is then satisfied if

$$(l_0^2\chi_n/\xi^2)^2\vec{\nabla}^2[\vec{\nabla}^2\bar{m}^2(\vec{z})]=0 \ . \tag{3.20}$$

Since the coefficient of the left-hand side of Eq. (3.20) is g^4, we see that our solution (3.19) is valid to order g^2. Similarly, to first approximation $\bar{c}$ and $\bar{\Psi}$ are related by the same expression as in equilibrium, i.e., Eq. (3.19) reduces to

$$\bar{c}(z)=\chi_n[\Delta_0-\tfrac{1}{2}\gamma\Psi_s^2(1+\tanh z)] \ . \tag{3.21}$$

B. Bulk energy

The bulk energy density can be evaluated in terms of the effective density $\hat{\rho}(\Psi)$

$$H[\Psi_n^\Delta,c_n^\Delta]-H[\Psi_s^\Delta,c_s^\Delta] =-\int d\vec{x}[\hat{f}(\Psi_s^\Delta)+\tfrac{1}{2}\chi_n\Delta^2] \ . \tag{3.22}$$

Since we are interested in the region near the coexistence curve we calculate $\hat{\rho}(\Psi_s^\Delta)$ to first order in $\delta\Delta$. This means that we approximate

$$\tilde{r}\simeq\tilde{r}_0+2\gamma\chi_n(\delta\Delta) \tag{3.23}$$

in both the expression for $\hat{\rho}$ and Ψ_s^Δ. To first order

$$(\Psi_s^\Delta)^2\simeq\Psi_s^2[1-\gamma\chi_n\xi^2(\delta\Delta)] \ , \tag{3.24}$$

$$-[\hat{f}(\Psi_s^\Delta)+\tfrac{1}{2}\chi_n\Delta^2]\simeq-\Psi_s^2\gamma\chi_n(\delta\Delta) =-(c_n-c_s)(\delta\Delta) \ . \tag{3.25}$$

Therefore we have obtained the classical result for the bulk energy of a droplet characterized by the subsidiary order parameter in a phase separation below a critical point.[6]

C. Surface energy

The interfacial tension is calculated under the two approximations normally made in the analysis of critical systems.[4] First we fix Δ to its coexistence region Δ_0; second, we consider a very large droplet so that we can work with a planar interface characterized by the one dimensional version of Eqs. (3.3)–(3.6). Under these circumstances it is easily seen by a formal integration of Eqs. (3.3)–(3.6) that

$$f(\bar{\Psi}(x),\bar{c}(x))=\tfrac{1}{2}l_0^2\left(\frac{d\bar{c}}{dx}\right)^2+\frac{1}{2}\left(\frac{d\bar{\Psi}}{dx}\right)^2+f(\Psi_n,c_n) \ , \tag{3.26}$$

and thus the interfacial tension becomes

$$\sigma=\int_{-\infty}^{\infty}dx\left[\left(\frac{d\bar{\Psi}}{dx}\right)^2+l_0^2\left(\frac{d\bar{c}}{dx}\right)^2\right] \ . \tag{3.27}$$

The main contribution to σ comes from the solution (3.18) which results in the value

$$\sigma=\Psi_s^2/4\xi \ . \tag{3.28}$$

Corrections to this result arising from $\bar{m}_1$ and the $\bar{c}$ solution (3.19) are discussed in Appendix A.

Equation (3.28) gives a prediction for the surface tension of a symmetrical tricritical system in agreement with the scaling law[9] derived on phenomenological grounds[8–10] and experimentally checked[20]

$$\sigma\sim\epsilon^\mu, \quad \mu=(d-1)\nu_u \ , \tag{3.29}$$

for $d=3$, $\nu_u=1$, and $\mu=2$. Equation (3.28) gives the same exponent since we have seen in the second section that $\Psi_s\sim\epsilon^{1/2}$ and $\xi\sim\epsilon^{-1}$. It should be noted that Eq. (3.28) is an expression for σ (including the amplitude) in terms of the order parameter of the problem. It represents an explicit derivation based on the model Hamiltonian Eqs. (2.1) and (2.2) and on the droplet picture. The earlier phenomenological argument[9, 10] relies on the existence of a single correlation length and applying the scaling law Eq. (3.29) derived for a critical system.[8] In our derivation the natural variable is the order parameter whereas in the phenomenological theory it is the subsidiary variable c. The first-order correction to Eq. (3.29) worked out in Appendix A gives

$$\sigma\sim A\epsilon^2(1+B\epsilon) \tag{3.30}$$

with an undetermined amplitude B.

It is worth noting that our calculation for σ follows closely that of Langer[4] for a critical system. He also finds that σ is proportional to the ratio of the square of the order parameter to the correlation length. Nevertheless as he implicitly notes, his result $\mu=\frac{3}{2}$ does not hold near the critical point since it follows from a mean-field calculation in $d=3$, while our result for μ is fortunately presumably close to correct due to the fact that $d=3$ is the border dimensionality for tricritical systems.

D. Critical radius and activation energy

For a spherical droplet of radius R, the activation energy that follows from Eqs. (3.2), (3.25), and (3.28) is

$$\Delta H = -\tfrac{4}{3}\pi R^3(\delta\Delta)\Psi_s^2\gamma\chi_n + \pi R^2\Psi_s^2/\xi \ . \tag{3.31}$$

The extremum of ΔH occurs at the critical radius

$$\begin{aligned} R_c &= \frac{2\sigma}{(\delta\Delta)(c_n-c_s)} = \frac{\Psi_s^2}{2\xi(\delta\Delta)(c_n-c_s)} \\ &= [2\xi\gamma\chi_n(\delta\Delta)]^{-1} = \frac{\tilde{u}}{2\sqrt{2}\upsilon\gamma\chi_n(\delta\Delta)} \ , \end{aligned} \tag{3.32}$$

and has the value

$$\begin{aligned} \Delta H_c &= \frac{16\pi}{3}\frac{\sigma^3}{(\delta\Delta)^2(c_n-c_s)^2} \\ &= \frac{\pi}{12}\frac{\Psi_s^6}{\xi^3[(\delta\Delta)(c_n-c_s)]^2} \ . \end{aligned} \tag{3.33}$$

The first expressions for both R_c and ΔH_c are just the classical results for a droplet described as a fluctuation in the c variable.[6] This just shows the validity of the intuitive droplet picture of nucleation, which is independent of our model of the system in terms of the order parameter Ψ and the subsidiary variable c. The equivalent expressions of R_c and ΔH_c which will be used later on, are obtained by substituting Eq. (3.28) and using the relations (2.10), (2.12), and (2.19).

Our approximation for σ restricts us to a region in which

$$R_c >> \xi \tag{3.34}$$

which according to Eq. (3.32) is

$$(\delta\Delta) << (2\gamma\chi_n\xi^2)^{-1} \ . \tag{3.35}$$

This is consistent with our approximation for the bulk energy since we have evaluated $(\Psi^\Delta)^2$ to first order in the parameter $\gamma\chi_n\xi^2(\delta\Delta)$.

E. Scaling form of the activation energy

Writing Eq. (3.33) in terms of the original parameters of the theory and recalling from Eq. (2.6) that $\tilde{u} = a\epsilon$, we have

$$\Delta H_c = \frac{\pi a^4}{48\sqrt{2}\upsilon}\left[\frac{\epsilon^2}{\upsilon\gamma\chi_n(\delta\Delta)}\right]^2 \ . \tag{3.36}$$

This result can be generalized in a straightforward way to d dimensions. In this case we will have

$$\begin{aligned} \Delta H_c &= \frac{\pi^{d/2}(d-1)^{d-1}}{\Gamma(\frac{1}{2}d+1)}\frac{\sigma^d}{[(c_n-c_s)(\delta\Delta)]^{d-1}} \\ &= \frac{\pi^{d/2}(d-1)^{d-1}}{\Gamma(\frac{1}{2}d+1)}\frac{\Psi_s^{2d}}{(4\xi)^d[(c_n-c_s)(\delta\Delta)]^{d-1}} \ , \end{aligned} \tag{3.37}$$

which in terms of the original parameters of the theory is

$$\begin{aligned} \Delta H_c &= \frac{\pi^{d/2}(1-d)^{d-1}}{2^{(5d+2)/2}\Gamma(\frac{1}{2}d+1)}\frac{\tilde{u}^{3-d}}{\upsilon^{(4-d)/2}}\left[\frac{\tilde{u}^2}{\upsilon\gamma\chi_n(\delta\Delta)}\right]^{d-1} \\ &= \frac{\pi^{d/2}a^{d+1}(1-d)^{d-1}}{2^{(5d+2)/2}\Gamma(\frac{1}{2}d+1)}\frac{\epsilon^{3-d}}{\upsilon^{(4-d)/2}}\left[\frac{\epsilon^2}{\upsilon\gamma\chi_n(\delta\Delta)}\right]^{d-1} \ . \end{aligned} \tag{3.38}$$

This expression for ΔH_c will be used in the next section.

Using the exponents introduced in Sec. II and defining unknown amplitudes by

$$\Psi_s^2 = (\Psi_s^2)_0\epsilon^{2\beta_\tau} \ , \tag{3.39}$$

$$\xi = \xi_0\epsilon^{-\nu_u} \ , \tag{3.40}$$

$$c_n - c_s = (\Delta c_0)\epsilon^{\beta_u} \ , \tag{3.41}$$

we can write Eq. (3.37) as

$$\Delta H_c = \frac{\pi^{d/2}(d-1)^{d-1}}{\Gamma(\frac{1}{2}d+1)4^d}\left[\frac{(\Psi_s^2)_0}{\xi_0}\right]^d\frac{1}{(\Delta c_0)^{d-1}}\left[\frac{\epsilon^{\beta_u\delta_u}}{(\delta\Delta)}\right]^{d-1} \ , \tag{3.42}$$

where we have used

$$2\beta_\tau + \nu_u = (d-1)\nu_u \ , \tag{3.43}$$

$$d\nu_u - \beta_u = \beta_u\delta_u \ . \tag{3.44}$$

For $d=3$, $\beta_u=1$, $\delta_u=2$ (Refs. 12, 15, and 16) and we recover the scaling form Eq. (3.36) which we deduced from our model. It is interesting to remark that Eq. (3.42) has the same scaling form as for an ordinary critical system with the appropriate choice of exponents β_u and δ_u. This result should become obvious from the first equality in Eq. (3.37) once that it has been shown that the exponent we obtain for σ coincides with $\mu = (d-1)\nu_u$. It is also worth noticing that Eqs. (3.36) and (3.42) are valid as well for metastable states near the disordered side of the coexistence curve in which an ordered droplet will nucleate the ordered stable phase out of the metastable disordered phase.

Experimental results for fluids are not given in terms of $(\delta\Delta)$ but in terms of $(\delta T)=T-T_{\text{coex}}$. By the usual argument,[21–23] near the coexistence curve we shall relate linearly these two quantities. For quenches near the ordered side of the coexistence curve (metastable ordered phase),

$$(\delta\Delta)=\chi_s^{-1}\frac{\partial c_s}{\partial T}(\delta T)\ . \tag{3.45}$$

According to Eqs. (2.22) and (2.23) we write,

$$\chi_s=(\chi_s)_0\epsilon^{-\gamma_u}\ . \tag{3.46}$$

The quantity $\partial c_s/\partial T$ is evaluated from

$$c_s-c_t=(\Delta c_0)'\epsilon^{\beta_u}\ , \tag{3.47}$$

where c_t is the tricritical value of c. We then have

$$(\delta\Delta)=-(\chi_s^{-1})_0\frac{(\Delta c_0)'}{T_t}\beta_u\epsilon^{\gamma_u+\beta_u-1}(\delta T) \tag{3.48}$$

and Eq. (3.42) becomes

$$\Delta H_c=\frac{\pi^{d/2}(1-d)^{d-1}}{\Gamma(\frac{1}{2}d+1)4^d}\left[\frac{(\Psi_s^2)_0}{\xi_0}\right]^d \times\left[\frac{(\chi_s)_0T_t}{\beta_u(\Delta c_0)'^2}\right]^{d-1}\left[\frac{\epsilon}{(\delta T)}\right]^{d-1}\ , \tag{3.49}$$

where we have used

$$\beta_u=\delta_u-1=\gamma_u\ . \tag{3.50}$$

An analogous expression holds for metastable states near the disordered side of the coexistence curve. In this case one has to use χ_n instead of χ_s. As noted earlier the normal susceptibility χ_n has the same exponent γ_u although this does not come out of the mean-field analysis of our starting model.

IV. IMAGINARY PART OF THE FREE ENERGY FOR THE METAMAGNET

The nucleation rate is thought to have the general form[5,21]

$$I=\frac{\kappa}{\pi}\,\text{Im}F\ , \tag{4.1}$$

where F represents the free energy density of the metastable state. Equation (4.1) can also be written as

$$I=\frac{\kappa}{\pi}\Omega_0e^{-\Delta H}\ . \tag{4.2}$$

From a numerical point of view the dominant factor is the exponential of the activation energy calculated in the previous section. In this section we calculate the statistical prefactor Ω_0 in d dimensions, therefore completing the calculation of the imaginary part of the free energy for the metamagnet. The dynamical prefactor κ will not be discussed. For a general Hamiltonian which depends on a set of variables $\vec\eta(\vec{x})=\{\eta_1(\vec{x}),\ldots,\eta_N(\vec{x})\}$ one can write[4,5]

$$i\,\text{Im}F\sim Z_1/Z_0\ , \tag{4.3}$$

where Z_1 and Z_0 are, respectively, the main contributions to the partition function Z at the droplet configuration $\vec\eta_d(\vec{x})$ and metastable state $\vec\eta_0(\vec{x})$, where

$$Z=\int D\vec\eta(\vec{x})\exp\{-H[\vec\eta(\vec{x})]\}\ . \tag{4.4}$$

A saddle-point integration for Z_1 and Z_0 gives

$$i\,\text{Im}F\sim\frac{\exp\{-H[\vec\eta_d(\vec{x})]\}\int D\vec\eta\exp[-\frac{1}{2}(\eta-\eta_d)_iM_{ij}(\eta-\eta_d)_j]}{\exp\{-H[\vec\eta_0(\vec{x})]\}\int D\vec\eta\exp[-\frac{1}{2}(\eta-\eta_0)_iM_{ij}(\eta-\eta_0)_j]} \tag{4.5}$$

$$=ie^{-\Delta H}\Omega_0\ , \tag{4.6}$$

where

$$i\Omega_0=V\left[\frac{\det M_0}{\det M}\right]^{1/2}\ , \tag{4.7}$$

$$M_{ij}^0=\frac{\delta^2H}{\delta\eta_i\delta\eta_j}\bigg|_{\vec\eta=\vec\eta_0},\quad M_{ij}=\frac{\delta^2H}{\delta\eta_i\delta\eta_j}\bigg|_{\vec\eta=\vec\eta_d}\ ; \tag{4.8}$$

V is the volume in $\vec\eta$ space coming from the functional integration of the eigenfunctions corresponding to the possible vanishing eigenvalue of M_0 and M, which are excluded in $(\det M_0)$ and $(\det M)$. The factor V contains the contribution of the vanishing eigenvalues corresponding to the translational modes of the droplet and $(\det M)$ contains the negative eigenvalue associated with the droplet instability giving rise to the formation of a new phase. This is the eigenvalue which introduces the imaginary part of F.

The interest in the calculation of ImF arises because of the information it gives about the singularity at the coexistence curve. Therefore we can work in the limit of vanishing field and substitute $\vec\eta_0$ by its equilibrium value in the calculation of Ω_0. In our case this means that we can work in the limit $(\delta\Delta)\rightarrow 0$ and we will evaluate the eigenvalues entering Ω_0 from the zeroth-order approximation to the Hamiltonian Eq. (3.16) which was obtained for $\Delta=\Delta_0$. This Hamiltonian reads in the original variables

$$\hat{H}[\Psi]=\int d\vec{x}\left(\tfrac{1}{2}[\vec{\nabla}\Psi(\vec{x})]^2+\frac{\tilde{u}^2}{4v}\Psi^2(\vec{x})+\tilde{u}\Psi^4(\vec{x})\right.$$
$$\left.+v\Psi^6(\vec{x})-\tfrac{1}{2}\chi_n\Delta_0^2\right) . \qquad (4.9)$$

Our calculation follows closely the one of Gunther, Nicole, and Wallace[3] for Ising-like systems: for the Hamiltonian Eq. (4.9)

$$\frac{\delta^2\hat{H}[\Psi]}{\delta\Psi^2(\vec{x})}=-\vec{\nabla}^2+\frac{\tilde{u}^2}{2v}+12\tilde{u}\Psi^2+30v\Psi^4 . \qquad (4.10)$$

Considering the ordered state to be metastable, M_0 is given by Eq. (4.10) with Ψ^2 substituted by $(\Psi_s^\Delta)^2$. In the limit we are interested in of $(\delta\Delta)\rightarrow 0$, $\Psi_s^\Delta\simeq\Psi_s$. The eigenvalues of M_0 are then given by

$$\lambda_0=k^2+\frac{2\tilde{u}^2}{v} . \qquad (4.11)$$

In the infrared limit

$$\lambda_0\simeq\frac{2\tilde{u}^2}{v}=4\xi^{-2}=\xi_s^{-2} . \qquad (4.12)$$

For a disordered metastable state

$$\lambda_0\simeq\xi^{-2} . \qquad (4.13)$$

The operator M is obtained from Eq. (4.10) by substituting Ψ by a spherical symmetrical saddle point $\overline{\Psi}$ of H which would satisfy

$$-\frac{d^2\overline{\Psi}(r)}{dr^2}-\frac{d-1}{r}\frac{d\overline{\Psi}(r)}{dr}$$
$$+\frac{\tilde{u}^2}{2v}\left(\overline{\Psi}(r)+\frac{8v}{\tilde{u}}\overline{\Psi}^3(r)+\frac{12v^2}{\tilde{u}^2}\Psi^5(r)\right)=0 . \qquad (4.14)$$

The eigenvalues of M are then determined by a Schrödinger-like equation whose radial part becomes

$$\left[-\frac{d^2}{dr^2}-\frac{d-1}{r}+\frac{l(l+d-2)}{r^2}\right.$$
$$\left.+\frac{\tilde{u}^2}{2v}\left(1+\frac{24v}{\tilde{u}}\overline{\Psi}^2(r)+\frac{60v^2}{\tilde{u}^2}\overline{\Psi}^4(r)\right)\right]\nu_{nl}(r)$$
$$=\lambda_{nl}\nu_{nl}(r) . \qquad (4.15)$$

Differentiating Eq. (4.14) it becomes obvious that $d\overline{\Psi}(r)/dr$ is an eigenfunction of Eq. (4.5) for $l=1$ (with degeneracy d) and vanishing eigenvalue. These modes are naturally associated with the translational modes of the droplet and are contained in the factor $\mathcal{V}$ which is proportional to the volume V of the system[3–5]

$$\mathcal{V}=VJ , \qquad (4.16)$$

$$J=\left(\frac{1}{d}\int d\vec{x}[\vec{\nabla}\overline{\Psi}(r)]^2\right)^{d/2}=(\Delta H_c)^{d/2} . \qquad (4.17)$$

Recalling Eq. (3.38)

$$J\sim\left(\frac{\tilde{u}^{3-d}}{v^{(4-d)/2}}\right)^{d/2}\left(\frac{\tilde{u}^2}{v\gamma\chi_n(\delta\Delta)}\right)^{(d-1)d/2} . \qquad (4.18)$$

The evaluation of the term $(\det M)$ in Eq. (4.7) requires the knowledge of the nonvanishing λ_{nl} of Eq. (4.15). Since we are concerned with bound states that have to be localized near R_c and we have assumed a large critical radius, an approximate analysis of the spectrum can be made[4] by neglecting the $(d-1)/r$ and $l(l+d-2)/r^2$ terms in Eq. (4.15) and taking for $\overline{\Psi}(r)$ the expression (3.18) with the interface at $r=R_c$

$$\overline{\Psi}^2(r)=\frac{-\tilde{u}}{4v}\left(1+\tanh\frac{r-R_c}{\xi}\right) . \qquad (4.19)$$

This leads to the following one dimensional Schrödinger-like equation with highly asymmetrical potential:

$$\left[-\frac{d^2}{dr^2}+\frac{\tilde{u}^2}{2v}\left(-\frac{5}{4}+\frac{3}{2}\tanh\frac{r-R_c}{\xi}\right.\right.$$
$$\left.\left.+\frac{15}{4}\tanh^2\frac{r-R_c}{\xi}\right)\right]\nu(r)=\lambda\nu(r) . \qquad (4.20)$$

This equation is the one appearing in the related interface profile problem[19, 24] and it is discussed in Appendix B. We show there that the only bound state is the one with $\lambda=0$ discussed above. We then argue (following Langer[4]) that the main contribution to $(\det M)$ comes from the rotational band in the neighborhood of $\lambda_{n=0,l=1}=0$. These excitations represent deformations of the critical droplet which have energies[3]

$$\lambda_{0l}\simeq\frac{(l-1)(l+d-1)}{R_c^2} . \qquad (4.21)$$

For $l=1$ we have the translational zero energy modes and for $l=0$ we have the negative eigenvalue governing the droplet instability.

From Eqs. (4.7), (4.12), (4.16), and (4.21) we have for an ordered metastable state

$$i\,\Omega_0 = iJV\frac{\xi^{-(d+1)}}{(d-1)^{1/2}}R_c$$

$$\times\exp-\left[\frac{1}{2}\sum_{l=2}^{L}a_l\ln\left(\frac{(l-1)(l+d-1)}{R_c^2\xi_s^{-2}}\right)\right] ,\quad(4.22)$$

where a_l is the degeneracy of the d-dimensional spherical harmonics

$$a_l=\frac{\Gamma(l+d)}{\Gamma(d)\Gamma(l+1)}-\frac{\Gamma(l+d-2)}{\Gamma(d)\Gamma(l-1)},\quad l>1\ ,\quad(4.23)$$

and the upper limit L is given by

$$L^2\sim\frac{R_c^2\tilde{u}^2}{v}\sim R_c^2\xi^{-2}\ ,$$

where the approximation (4.21) breaks down. An estimate of the order magnitude for L comes from considering the l-dependent term in Eq. (4.15) as a perturbation to the remaining part of the potential which is of order $\tilde{u}^2/v$, since according to Eq. (4.19) $\overline{\Psi}^2\sim\tilde{u}/v$. The precise value of L does not affect the form of the essential singularity at the coexistence curve that we wish to describe. Being in a domain in which $R_c\xi_s^{-1}>>1$ the sum over l in Eq. (4.22) can be calculated by using the Euler-MacLaurin formula.[25] One finally has[3]

$$i\,\Omega_0\sim iJV\xi_s^{-d}(R_c\xi_s^{-1})^{-d}\exp[\text{const}(R_c\xi_s^{-1})^{d-1}]\ ,\quad(4.24)$$

and for $d=3$

$$i\,\Omega_0\sim iJV\xi_s^{-3}(R_c\xi_s^{-1})^{-2/3}\exp[\text{const}(R_c\xi_s^{-1})^{2}]\ .\quad(4.25)$$

The dominant exponential term comes from the integral approximation to the sum over l and the prefactor arises from logarithmic contributions in the integral and correction terms of the Euler-MacLaurin formula.[26] The obtained form of Ω_0 has the same structure and dependence as for the critical Ising model.

From Eqs. (3.32), (4.1), (4.2), (4.12), (4.18), (4.24), and (4.25) we finally have

$$\text{Im}\,F\sim V\left(\frac{v^{1/2}}{\tilde{u}}\right)^{d}\left(\frac{\tilde{u}^{3-d}}{v^{(4-d)/2}}\right)^{d/2}\left(\frac{\tilde{u}^2}{v\gamma\chi_n(\delta\Delta)}\right)^{(d-3)d/2}$$

$$\times\exp\left[\text{const}\frac{\tilde{u}^{3-d}}{v^{(4-d)/2}}\left(\frac{\tilde{u}^2}{v\gamma\chi_n(\delta\Delta)}\right)^{d-1}\right]\ ,\quad(4.26)$$

and for $d=3$

$$\text{Im}F\sim V\left(\frac{v^{1/2}}{\tilde{u}}\right)^{3}v^{-3/4}\left(\frac{\tilde{u}^2}{v\gamma\chi_n(\delta\Delta)}\right)^{7/3}$$

$$\times\exp\left[\text{const}\,v^{-1/2}\left(\frac{\tilde{u}^2}{v\gamma\chi_n(\delta\Delta)}\right)^{2}\right]\ .\quad(4.27)$$

Likewise we can write down the scaling form of ImF in terms of the tricritical exponents in d dimensions. From the second expression in Eqs. (3.32), and (2.15)–(2.21) we have

$$R_c\xi_s^{-1}\sim\frac{\epsilon^{-\beta_u\delta_u}}{(\delta\Delta)}\ .\quad(4.28)$$

Substituting this in Eq. (4.24) and using Eqs. (3.42) and (4.17), we obtain

$$\text{Im}F\sim\epsilon^{-d\nu_u}\left(\frac{\epsilon^{\beta_u\delta_u}}{(\delta\Delta)}\right)^{(d-3)d/2}\exp\left[\text{const}\left(\frac{\epsilon^{\beta_u\delta_u}}{(\delta\Delta)}\right)^{d-1}\right]\ ,\quad(4.29)$$

and analogously in $d=3$

$$\text{Im}F\sim\epsilon^{-3\nu_u}\left(\frac{\epsilon^{\beta_u\delta_u}}{(\delta\Delta)}\right)^{7/3}\exp\left[\text{const}\left(\frac{\epsilon^{\beta_u\delta_u}}{(\delta\Delta)}\right)^{2}\right]\ ,\quad(4.30)$$

which with the appropriate values for $d=3$ ($\nu_u=1$, $\beta_u=1$, $\delta_u=2$) coincide with the result (4.27) in terms of the parameters of the model ($\tilde{u}\sim\epsilon$).

The results (4.26)–(4.30) also apply to the disordered side of the coexistence curve since the only modification needed in the above analysis is the replacement of ξ_s by ξ in Eqs. (4.24) and (4.25). Comparison of the form of Ω_0 and Eqs. (4.26)–(4.30) with the expressions[3] for Ising-like systems shows a universality of the essential singularity at a first-order phase transition. This universality for systems described by a Hamiltonian having a discrete symmetry ($\Psi\rightarrow-\Psi$) can be understood in terms of the geometrical Hamiltonian[3] for the droplet deformations which is independent of the critical or tricritical character, as becomes clear when using geometrical quantities such as R_c and ξ_s. As we shall see in the next section this universal singularity can be different for tricritical models with different symmetry properties.

V. IMAGINARY PART OF THE FREE ENERGY FOR ^{3}He-^{4}He MIXTURES

The basic difference in the model Hamiltonian for a ^{3}He-^{4}He mixture as compared with the metamagnet model is the complex nature of Ψ which introduces the phase as a new variable in the problem. As a first step in the evaluation of ImF for this case we show that the work of formation of the critical droplet calculated in Sec. III for the metamagnet applies as well to ^{3}He-^{4}He mixtures. That calculation was based on the droplet configuration solution of Eqs. (3.3) and (3.4). In this new case Eq. (3.4) remains unchanged (where we understand $\overline{\Psi}^2$ as $|\overline{\Psi}|^2$) while Eq. (3.3) has to be replaced by

$$\vec{\nabla}^2\overline{\Psi}^* - r\overline{\Psi}^* - 4u|\overline{\Psi}|^2\overline{\Psi}^* - 6v|\overline{\Psi}|^4\overline{\Psi}^* - \gamma\bar{c}\overline{\Psi}^* = 0 \tag{5.1}$$

and the complex conjugate equation. These equations can alternatively be written in terms of the modulus and the phase ϕ as

$$\vec{\nabla}^2|\overline{\Psi}| - |\overline{\Psi}|^{-3}\vec{J}^2 - r|\overline{\Psi}| - 4u|\overline{\Psi}|^3 - 6v|\overline{\Psi}|^5 - \gamma\bar{c}|\overline{\Psi}| = 0\ , \tag{5.2}$$

$$\vec{\nabla}\cdot\vec{J} = 0\ , \tag{5.3}$$

where

$$\vec{J} = |\overline{\Psi}|^2\vec{\nabla}\phi\ . \tag{5.4}$$

If we consider the particular case in which ϕ is independent of the position $\vec{x}$ (and thus constant across the interface) we reobtain Eq. (3.3) for $|\overline{\Psi}|$, with the same boundary conditions. As a consequence, all the analysis of Sec. III remains unchanged. Our particular solution corresponds to $\vec{J} = 0$. Different boundary conditions and solutions for ϕ lead to $\vec{J} \neq 0$ and they would be appropriate for studying the onset of superfluid motion[27] (or the analogous problems of superconducting states[28,29]) which is an essentially different physical problem from the one considered here. Nevertheless we shall allow for space-dependent phase fluctuations in the evaluation of Ω_0. These fluctuations are associated with local superfluid motion which is undoubtedly present in the nucleation process.

The basic, continuous symmetry of the Hamiltonian is now the invariance under a constant shift in phase. This symmetry is preserved in Eq. (5.1) and in the solution (3.18) for the normalized modulus of Ψ. Different values of the phase could only be distinguished by applying a field H_s and, as in the metamagnet case, the fact that our solutions only depend on $|\Psi|$ means that we are studying nucleation associated with the two different thermodynamic phases: normal and superfluid.

The calculation of Ω_0 follows the general formulation given in Eqs. (4.5)–(4.8), where $\vec{\eta}(\vec{x})$ stands now for the two independent variables $\Psi(\vec{x})$ and $\Psi^*(\vec{x})$. Although the results can be generalized to d dimensions we shall restrict ourselves to $d = 3$ since in the other physically interesting case of $d = 2$ no superfluid transition exists. Writing Ψ for either the droplet configuration or its metastable value and ν for the fluctuations around either of these values, the quadratic forms in Eq. (4.5) are expressed as

$$\frac{1}{2}\left(\frac{\delta^2 H}{\delta\Psi^2}\nu^2 + \frac{\delta^2 H}{\delta\Psi^{*2}}\nu^{*2} + \nu\frac{\delta^2 H}{\delta\Psi\delta\Psi^*}\nu^* + \nu^*\frac{\delta^2 H}{\delta\Psi^*\delta\Psi}\nu\right)$$
$$= \frac{1}{2}\left[(2\tilde{u}\Psi^{*2} + 6v\Psi^{*2}|\Psi|^2)\nu^2 + \left(-\tfrac{1}{2}\vec{\nabla}^2 + \frac{\tilde{u}^2}{4v} + 4\tilde{u}|\Psi|^2 + 9v|\Psi|^4\right)\nu^* + \text{c.c.}\right]\ . \tag{5.5}$$

A particular value of Ψ is characterized by its modulus and an arbitrary constant phase ϕ_0. Setting

$$\nu = \omega e^{i\phi_0} = (\omega_1 + i\omega_2)e^{i\phi_0} \tag{5.6}$$

the arbitrary phase ϕ_0 cancels out in Eq. (5.5). Upon changing variables from (ω, ω^*) to the real functions (ω_1, ω_2) the functional matrix in whose eigenvalues we are interested becomes

$$\begin{pmatrix} -\vec{\nabla}^2 + \dfrac{\tilde{u}^2}{2v} + 12\tilde{u}|\Psi|^2 + 30v|\Psi|^4 & 0 \\ 0 & -\vec{\nabla}^2 + \dfrac{\tilde{u}^2}{2v} + 4\tilde{u}|\Psi|^2 + 6v|\Psi|^4 \end{pmatrix}\ . \tag{5.7}$$

The problem is then reduced to the evaluation of the eigenvalues of the operators in the diagonal elements of the matrix. The eigenvalues associated with the first operator will give contributions to the free energy arising from fluctuations in phase with $\overline{\Psi}$. This operator coincides with Eq. (4.10) where no phase freedom existed. The eigenvalues of the second operator are associated with fluctuations $\frac{1}{2}\pi$ out of phase with $\overline{\Psi}$. These last contributions will then modify, in principle, our results of Sec. IV by some multiplicative factor.

Let us first look at the eigenvalue problem at the saddle point, or droplet configuration, when $|\Psi|$ stands for the solution of

$$\left.\frac{\delta\hat{H}[\Psi,\Psi^*]}{\delta\Psi}\right|_{\overline{\Psi}}=0$$

which becomes Eq. (4.14) for $|\overline{\Psi}|$ when $\overline{\Psi}$ is taken to have, as discussed above, a constant phase. The equation for the radial part of ω_2 reads

$$\left[-\frac{d^2}{dr^2}-\frac{2}{r}\frac{d}{dr}+\frac{l(l+1)}{r^2}+\frac{\tilde{u}^2}{2v}\left(1+\frac{8v}{\tilde{u}}|\overline{\Psi}|^2+\frac{12v^2}{\tilde{u}^2}|\Psi|^4\right)\right]\omega_2^{nl}(r)=\lambda_{nl}\omega_2^{nl}(r)\ . \tag{5.8}$$

Comparison of Eqs. (5.8) and (4.14) shows that $\omega_2=|\overline{\Psi}|$ is an exact eigenfunction for Eq. (5.8) l and $\lambda=0$. The existence of this eigenvalue is obviously related to the invariance under a phase shift. In fact writing $\overline{\Psi}=|\overline{\Psi}|e^{i\phi_0}$, we have

$$\frac{\delta\overline{\Psi}}{\delta\phi_0}=i|\overline{\Psi}|e^{i\phi_0}\ ,$$

which, according to Eq. (5.6), corresponds to $\omega_2=|\overline{\Psi}|$. Contrary to the translational modes discussed in Sec. IV, this eigenfunction is not localized and represents the bottom of a continuum of states. Since it corresponds to $l=0$ no negative eigenvalue exists in this band. The question then arises about the existence of bound states which would necessarily have negative eigenvalues. Such negative eigenvalues would have to be interpreted as phase instabilities associated with the onset of superfluid motion and would be of spurious nature for the problem at hand.[30] This question is answered following the argument of Sec. IV and considering the one dimensional equation associated with Eq. (5.8):

$$\left[-\frac{d^2}{dr^2}+\frac{\tilde{u}^2}{2v}\left(-\tfrac{1}{4}-\tfrac{1}{2}\tanh\frac{r-R_c}{\xi}+\tfrac{3}{4}\tanh^2\frac{r-R_c}{\xi}\right)\right]\omega_2(r)=\lambda\omega_2(r)\ . \tag{5.9}$$

This equation is discussed in Appendix B where it is shown that no bound state exists, and *a fortiori* we presume the result to hold for $d=3$.

We now need to consider separately the two sides of the coexistence curve.

A. Superfluid phase metastable

The matrix M_0 is given by Eq. (5.7) with Ψ replaced by Ψ_s. For the second operator, the eigenvalue problem becomes

$$-\vec{\nabla}^2\omega_2=\lambda\omega_2\ . \tag{5.10}$$

An obvious eigenvalue is $\lambda=0$ associated with $\omega_2=$ constant which should be chosen, up to normalization, as $\omega_2=|\Psi_s|$. This eigenfunction has the same meaning as the one discussed after Eq. (5.8) and it is the bottom of a continuous band with $\lambda=k^2$. This band and the one coming from M will contribute some irrelevant constant to Ω_0, while $\mathcal{V}$ in Eq. (4.16) has to be modified to take into account the two vanishing eigenvalues associated to the new variable ω_2. We shall have

$$\mathcal{V}=VJ\frac{J'}{J''}\ , \tag{5.11}$$

where J' is the volume in Ψ space swept out by $\overline{\Psi}(\vec{x})$ when ϕ_0 goes from 0 to 2π and J'' is the analogous volume swept by Ψ_s

$$J'=2\pi\left(\int_V d\vec{x}|\overline{\Psi}|^2\right)^{1/2}\simeq 2\pi|\Psi_s|(V-\tfrac{4}{3}\pi R_c^3)^{1/2}\ , \tag{5.12}$$

$$J''=2\pi\left(\int_V d\vec{x}|\Psi_s|^2\right)^{1/2}\simeq 2\pi|\Psi_s|V^{1/2}\ . \tag{5.13}$$

Neglecting the volume of the droplet with respect to the volume of the system

$$\frac{J'}{J''}\simeq 1\ , \tag{5.14}$$

and therefore the results (4.25), (4.27), and (4.30) are not modified by the existence of the phase variable.

B. Normal phase metastable

The matrix M_0 for this case is obtained by replacing Ψ by $\Psi_n=0$ in Eq. (5.7). The two operators then become identical and they have the eigenvalues Eq. (4.13). Naturally, no phase invariance appears in this case. The modifications of Ω_0 are then twofold: First we have a factor J' which is here

$$J'=2\pi\left(\int_V d\vec{x}|\overline{\Psi}|^2\right)^{1/2}\simeq 2\pi|\Psi_s|(\tfrac{4}{3}\pi R_c^3)^{1/2}\ . \tag{5.15}$$

Secondly, the continuous band Eq. (4.13) and the one coming from Eq. (5.8) will pair in Eq. (4.7) to give a multiplicative constant when an eigenvalue of

Eq. (4.13) is extracted to account for the vanishing eigenvalue of Eq. (5.8) included in J'. In summary we have a factor

$$J'\xi^{-1} \sim |\Psi_s|\xi^{-1}R_c^{3/2}\ v^{-1/4}\left[\frac{\tilde{u}^2}{v\gamma\chi_n(\delta\Delta)}\right]^{3/2}, \qquad (5.16)$$

or in terms of tricritical exponents

$$J'\xi^{-1}\left[\frac{\epsilon^{\beta_u\delta_u}}{(\delta\Delta)}\right]^{3/2}, \qquad (5.17)$$

where we have used Eqs. (2.15)–(2.20), (3.32), and (3.43)–(3.44).

Therefore we have a different singularity on the normal side of the coexistence curve which can be written from Eqs. (4.27), (4.30), (5.16), and (5.17) as

$$\mathrm{Im}F \sim V\left[\frac{v^{1/2}}{\tilde{u}}\right]^3 v^{-1}\left[\frac{\tilde{u}^2}{v\gamma\chi_n(\delta\Delta)}\right]^{23/6} \times \exp\left[\mathrm{const}\,v^{-1/2}\left[\frac{\tilde{u}^2}{v\gamma\chi_n(\delta\Delta)}\right]^2\right], \qquad (5.18)$$

$$\mathrm{Im}F \sim \epsilon^{-3\nu_u}\left[\frac{\epsilon^{\beta_u\delta_u}}{(\delta\Delta)}\right]^{23/6}\exp\left[\mathrm{const}\left[\frac{\epsilon^{\beta_u\delta_u}}{(\delta\Delta)}\right]^2\right]. \qquad (5.19)$$

Some understanding of the asymmetry of the singularities which exist on the two sides of the coexistence curve is gained by considering the different role played by the phase shift invariance. Nucleation is concerned with the process of overcoming an energy barrier and it is independent of the final stages of the decay to a coexistence regime. As such it only depends on the properties of the metastable state and of the saddle point characterizing the barrier but it does not depend on the properties of the stable state to which the system decays. On the superfluid side the metastable state and droplet configuration have the same symmetry and their contributions cancel. On the normal side only the droplet configuration possesses this symmetry. These ideas become more clear by looking at Fig. 4, where we have drawn the projection in the complex Ψ plane of $\hat{\rho}(|\Psi|)$ corresponding to the situations (IV) and (V) of Fig. 1. For a superfluid metastable state nucleation occurs at a constant phase, as implied by our solution of Eqs. (5.2)–(5.4), and the process is not essentially different from the one for the metamagnet. On the other hand no phase can be associated with the normal metastable state and it is this "phase wandering" in the nucleation process which gives rise to the additional contribution to ImF.

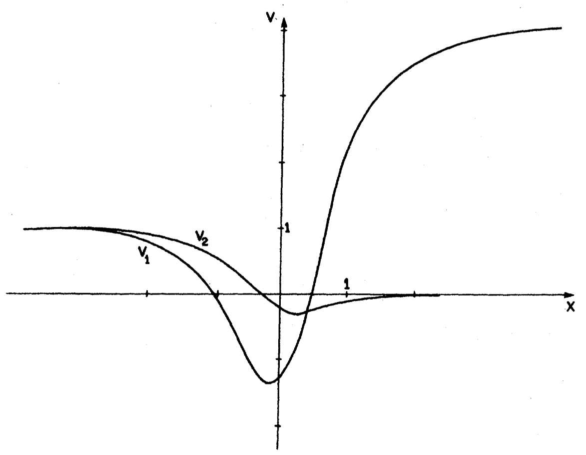

FIG. 4. Potentials in Eq. (B1). V_1 corresponds to Eq. (4.20) and V_2 to Eq. (5.9).

VI. CONCLUDING REMARKS

In this section we summarize for convenience the main approximations on which our analysis is based. To begin with, as noted in the Introduction, it is obviously a mean-field theory, in the same sense as the original work of Langer.[4,5] It would therefore be useful to supplement this work using renormalization group (RG) techniques, in order to obtain the appropriate logarithmic corrections to the three dimensional tricritical model. In addition, the domain of validity of our calculation involves three approximations. The first two are common to the Langer theory of critical nucleation, the first being that one be sufficiently close to the coexistence curve that the critical radius be large compared to the correlation length. This, of course, also justifies the discussion of the nucleation problem in terms of thermodynamic concepts. The second approximation requires that the correlation length be sufficiently small that the saddle-point evaluation of the functional integral is valid. The third assumption is particular to the way we handle the nonlocality of the exact effective Hamiltonian for Ψ. It amounts to being sufficiently close to the tricritical region so that our expansion in powers of the inverse correlation length makes sense. The overall domain of validity of our calculation is determined by a range of values of the correlation length that compromises the third approximation with the first and second ones.

As a separate matter we also would like to point out that our explicit calculation of the interfacial tension supports Widom's picture[31] based on somewhat general grounds. The main contribution to σ in the tricritical region comes from the order parameter term in Eq. (3.27). This contribution is the same as obtained from a "single-variable theory" determined by fixing a path in which $\partial f(\Psi,c)/\partial c = 0$ which amounts to considering the effective Hamiltonian Eq. (4.9). Moving away from the tricritical region, the "two-variable theory" gives rise to the contributions discussed in Appendix B.

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APPENDIX A: CORRECTIONS TO INTERFACIAL TENSION

The interfacial tension Eq. (3.27) has two different terms related, respectively, to $\overline{\Psi}(x)$ and $\overline{c}(x)$. With an obvious notation we write

$$\sigma = \sigma^{\Psi} + \sigma^{c} \ . \tag{A1}$$

We further write

$$\overline{\Psi} = \overline{\Psi}_0 + \overline{\Psi}_1 \ , \tag{A2}$$

where $\overline{\Psi}_0 = \Psi_s \overline{m}_0$, $\overline{m}_0$ being given in Eq. (3.18) and where $\overline{\Psi}_1$ is the first correction to $\overline{\Psi}_0$ obtained from Eq. (3.17) by treating the $\overline{m}\vec{\nabla}^2\overline{m}$ term as a perturbation:

$$\overline{\Psi}_1(x) = \frac{\Psi_s \gamma^2 l_0^2 \chi_n^2}{\sqrt{2\upsilon}\xi} f\left(\frac{x}{\xi}\right) \ , \tag{A3}$$

where $f(x/\xi)$ is some function of its dimensionless argument.

From Eqs. (3.19) and (A2) we have

$$\overline{c}(x) = \overline{c}_0(x) + \overline{c}_1(x) + \overline{c}_2(x) + \cdots \ , \tag{A4}$$

$$\overline{c}_0(x) = \chi_n[\Delta_0 - \gamma \overline{\Psi}_0^2(x)] \ , \tag{A5}$$

$$\overline{c}_1(x) = -\gamma l_0^2 \chi_n^2 \frac{d^2\overline{\Psi}_0(x)}{dx^2} \ , \tag{A6}$$

$$\overline{c}_2(x) = -\gamma \chi_n^2 \overline{\Psi}_1^2(x) \ . \tag{A7}$$

The above corrections to $\overline{\Psi}_0(x)$ and $\overline{c}_0(x)$ lead to the following results for σ:

$$\sigma^{\Psi} = \sigma_0^{\Psi} + \sigma_1^{\Psi} + \sigma_2^{\Psi} + \cdots \ , \tag{A8}$$

$$\sigma_0^{\Psi} = \int_{-\infty}^{\infty} dx \left(\frac{d\overline{\Psi}_0(x)}{dx}\right)^2 = \frac{\Psi_s^2}{4\xi} \ , \tag{A9}$$

$$\sigma_1^{\Psi} = 2\int_{-\infty}^{\infty} dx \, \frac{d\overline{\Psi}_0(x)}{dx}\frac{d\overline{\Psi}_1(x)}{dx} \propto \frac{\Psi_s^2}{\xi}\frac{l_0^2\gamma^2\chi^2}{\sqrt{2\upsilon}\xi} \ , \tag{A10}$$

$$\sigma_2^{\Psi} = \int_{-\infty}^{\infty} dx \left(\frac{d\overline{\Psi}_1(x)}{dx}\right)^2 \propto \frac{\Psi_s^2}{\xi}\left(\frac{l_0^2\gamma^2\chi_n^2}{\sqrt{2\upsilon}\xi}\right)^2 \ , \tag{A11}$$

and also

$$\sigma = \sigma_0^{c} + \sigma_1^{c} + \sigma_2^{c} + \cdots \ , \tag{A12}$$

$$\sigma_0^{c} = \int_{-\infty}^{\infty} dx \, l_0^2 \left(\frac{d\overline{c}_0(x)}{dx}\right)^2 \propto \frac{\Psi_s^2}{\xi}\frac{l_0^2\chi_n^2\gamma^2}{\sqrt{2\upsilon}\xi} \ , \tag{A13}$$

$$\sigma_1^{c} = 2\int_{-\infty}^{\infty} dx \, l_0^2 \frac{d\overline{c}_0(x)}{dx}\frac{d\overline{c}_1(x)}{dx} \propto \frac{\Psi_s^2}{\xi}\frac{l_0^4\chi_n^3\gamma^2}{\sqrt{2\upsilon}\xi^3} \ , \tag{A14}$$

$$\sigma_2^{c} = \int_{-\infty}^{\infty} dx \, l_0^2 \left(\frac{d\overline{c}_1}{dx}\right)^2 \propto \frac{\Psi_s^2}{\xi}\frac{l_0^6\chi_n^4\gamma^2}{\sqrt{2\upsilon}\xi^5} \ . \tag{A15}$$

It should be noted that

$$\frac{\sigma_0^{c}}{\sigma_1^{c}} \propto \frac{\sigma_1^{c}}{\sigma_2^{c}} \propto g^{-2} \ . \tag{A16}$$

Nevertheless, since the expansion for $\overline{\Psi}$ is not precisely in powers of g and this is reflected in $\overline{c}$ through Eq. (3.19), the systematic expansion for σ^c breaks down when corrections arising from $\overline{\Psi}_1$ enter in $\overline{c}$. The main contribution to σ comes from σ_0^{Ψ} and the first correction term comes both σ_1^{Ψ} and σ_0^{c} which are of the same order. Thus

$$\sigma \simeq \frac{\Psi_s^2}{4\xi}\left[1 + D\frac{l_0^2\gamma^2\chi_n^2}{\sqrt{2\upsilon}\xi}\right] A\,\epsilon^2(1+B\epsilon) \ . \tag{A17}$$

The singular behavior of the second term comes only from the correlation length ξ. This can be seen by noting that the coefficient of the irrelevant[18] term $|\vec{\nabla}m^2|^2$ of the Hamiltonian Eq. (3.16) is proportional to $l_0^2\gamma^2\chi_n^2$ when this is written in terms of the original variable $\Psi(\vec{x})$.

APPENDIX B: SPECTRUM OF BOUND STATES

In this appendix we give some mathematical details concerning the spectrum of bound states of Eqs. (4.20) and (5.9) following the analysis of Ref. 32. Scaling the position variable with the correlation length both equations have the general form

$$\left[-\frac{d^2}{dx^2} + V(x)\right]\nu(x) = \lambda\nu(x) \ , \tag{B1}$$

$$V(x) = \alpha + \beta\tanh x + \gamma\tanh^2 x \ . \tag{B2}$$

The sets

$$\alpha_1 = -\tfrac{5}{4}, \quad \beta_1 = \tfrac{3}{2}, \quad \gamma_1 = \tfrac{15}{4} \ , \tag{B3}$$

$$\alpha_2 = -\tfrac{1}{4}, \quad \beta_2 = -\tfrac{1}{2}, \quad \gamma_2 = \tfrac{3}{4} \ , \tag{B4}$$

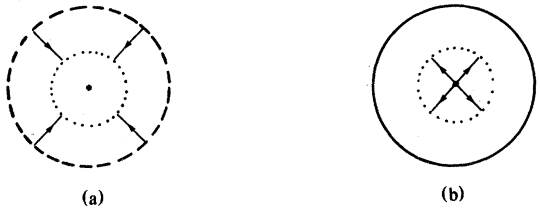

FIG. 5. Asymmetry of the superfluid (a) and normal (b) sides of the coexistence curve. The figure shows the complex Ψ plane. The radial arrowed lines represent the nucleation processes. The dotted circumference represents the unstable states or energy barrier. The dashed circumference in (a) represents the superfluid metastable states and the full line circumference in (b) represents the superfluid stable states. The center of the circumferences represents the normal stable state in (a) and the normal metastable state in (b).

correspond, respectively, to Eqs. (4.20) and (5.9). The form of the two potentials V_1 and V_2 are shown in Fig. 5. To give a simultaneous discussion of both cases it is convenient to change the variable x to $x=-x$ in the second case. This amounts to replacing β_2 by $\beta_2'=-\beta_2$. In the following x and β should be understood as x' and β' when referring Eq. (5.9). We know the eigenfunction associated to $\lambda=0$ in both cases, as discussed in the text. Both eigenfunctions can be written in the form $e^{-ax}\operatorname{sech}^b x$. The choice $a_1=\frac{1}{2}$, $b_1=\frac{3}{2}$ corresponds to Eq. (4.20) $[\nu_0=(d/dx)(1+\tanh x)^{1/2}]$ and the choice $a_2=\frac{1}{2}$, $b_2=\frac{1}{2}$ corresponds to Eq. (5.9) $[\nu_0=(1-\tanh x)^{1/2}]$. This suggests the solution

$$\nu(x)=e^{-ax}\operatorname{sech}^b x F(x) \ , \tag{B5}$$

which leads to

$$\frac{d^2F}{dx^2}-2(a+b\tanh x)\frac{dF}{dx} + [a^2+b^2-(\alpha+\gamma)+\lambda+(2ab-\beta)\tanh x - (b^2+b-\gamma)\operatorname{sech}^2 x]F(x)=0 \ . \tag{B6}$$

Choosing a, b such that

$$a^2+b^2-(\alpha+\gamma)+\lambda=0 \ , \tag{B7}$$

$$2ab-\beta=0 \ , \tag{B8}$$

and changing variables to

$$u=\tfrac{1}{2}(1-\tanh x) \ , \tag{B9}$$

we arrive at the hypergeometric equation

$$u(1-u)\frac{d^2F}{du^2}+[a+b+1-2(b+1)u]\frac{dF}{du} -[b(b+1)-\gamma]F(u)=0 \ . \tag{B10}$$

Real solutions of Eqs. (B7) and (B8) for a and b exist for the two sets of values Eqs. (B3) and (B4) for the possible bound values of λ in which we are interested: $\lambda<1$ for Eq. (B3) and $\lambda<0$ for Eq. (B4). The two independent solutions of Eq. (B10) regular at $u=0$ $(x=\infty)$ are

$$F(b+\tfrac{1}{2}-\sqrt{\gamma+1/4},\ b+\tfrac{1}{2}+\sqrt{\gamma+1/4},\ a+b+1;u) \ , \tag{B11}$$

$$u^{-(a+b)}F(b+\tfrac{1}{2}-\sqrt{\gamma+1/4},\ b+\tfrac{1}{2}+\sqrt{\gamma+1/4},\ a+b+1;u) \ . \tag{B12}$$

The corresponding solutions for $\nu(x)$ behave, respectively, as $e^{-(a+b)x}$ and $e^{(a+b)x}$ for $x\to\infty$. It follows from Eq. (B8) that a and b always have the same sign, which is not determined by Eqs. (B7) and (B8). Choosing a, $b>0$, the regular solution for $x\to\infty$ is the one associated to Eq. (B11) and it behaves for $x\to\infty$ as

$$\nu(x)\sim\frac{\Gamma(a+b+1)\Gamma(b-a)e^{(a-b)x}}{\Gamma(b+\frac{1}{2}-\sqrt{\gamma+1/4})\Gamma(b+\frac{1}{2}+\sqrt{\gamma+1/4})} + \frac{\Gamma(a+b+1)\Gamma(a-b)e^{(b-a)x}}{\Gamma(a+\frac{1}{2}-\sqrt{\gamma+1/4})\Gamma(a+\frac{1}{2}+\sqrt{\gamma+1/4})} \ . \tag{B13}$$

The equations (B7) and (B8) are symmetric under the exchange $a\leftrightarrow b$, so we can restrict ourselves to $b>a$. In this case $\nu(x)$ will only vanish for $x\to-\infty$ if the argument of one of the Γ functions in the denominator of the first term is a negative integer or zero

$$b_n+\tfrac{1}{2}-\sqrt{\gamma+1/4}=-n \ , \tag{B14}$$

and from (B8)

$$a_n=\frac{\beta}{2[\sqrt{\gamma+1/4}-(n+\frac{1}{2})]} \ . \tag{B15}$$

The existence of bound states requires the fulfillment of the assumed inequality $b_n > a_n$. For the set of values Eq. (B3) this means

$$-n+\frac{3}{2} > \frac{3}{-4n+6} . \tag{B16}$$

This is only satisfied for $n=0$ and the corresponding values of a_n and b_n are those of the $\lambda=0$ eigenfunctions. Therefore this is the only bound state that exists. For the set of values Eq. (B4) the inequality reads

$$\frac{1}{2}-n > \frac{1}{2-4n} , \tag{B17}$$

which is not satisfied for any value of n and so, no bound state exists. For $n=0$ we obtain the values of b and a corresponding to the $\lambda=0$ eigenfunction. In this case $b=a$ and according to Eq. (B13), $\nu(x)$ goes to a constant for $x \rightarrow -\infty$ ($x \rightarrow \infty$ in the original variables). The eigenfunction is the bottom of the continuum of states $\nu_\kappa(x) \rightarrow 0$ when $x \rightarrow -\infty$ for $\lambda < 1$.

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