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Instability of Alexander-McTague crystals and its implication for nucleation

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We show that the argument of Alexander and McTague, that the bcc crystalline structure is favored in those crystallization processes where the first-order character is not too pronounced, is not correct. We find that any solution that satisfies the Alexander-McTague condition is not stable. We investigate the implication of this result for nucleation near the pseudospinodal in near-meanfield systems.

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I. INTRODUCTION

Predicting the symmetry of crystalline phases from first principles and the knowledge of the intermolecular potential has eluded condensed matter physicists for years. One promising path was suggested by Alexander and McTague (AM) [1] who noted that the Landau-Ginsburg free energy indicated a particular crystalline form if the first-order nature of the transition from the liquid was not too pronounced. For systems such as those that interact with a Lennard-Jones (LJ) potential the AM argument indicated that the crystalline phase would have a triangular or hexagonal structure in $d=2$ while the same argument suggested that the bcc lattice would be favored in $d=3$. This conclusion is independent of the details of the potential as long as, like LJ, it is spherically symmetric and the fluid is monatomic. However, simulations of LJ and hard sphere systems as well as experiments on metals and rare gasses indicate that these systems freeze into an fcc structure [2,3]. This result is also obtained by the application of density functional theories [4,5].

In a related development Klein and Leyvraz [6] used the AM argument to look at nucleation of the crystal from the metastable liquid in a meanfield system near the spinodal and found a hexagonal or triangular structure for the critical droplet in $d=2$ and stacked triangular or hexagonal planes or a bcc structure in $d=3$. However, this droplet was unstable. In addition, Groh and Mulder (GM) [7] also looked at a mean-field system near a spinodal and, using bifurcation analysis, also noted that the AM argument said nothing about the nature of the stable solid but only indicated that a bifurcation to a bcc structure in $d=3$ was favored over bifurcations to other periodic structures but the stability of the bcc structure was beyond the AM or bifurcation analysis. From these results it is still unclear what the meaning or accuracy is of the AM argument. It is the purpose of this paper to perform some additional analysis of these results.

In this paper we present an argument indicating that any crystal satisfying the conditions in AM must be unstable. This argument, which uses the Landau-Ginsburg approach employed by AM does not require that the system be mean field. In addition we use the techniques of AM to investigate the nucleation process near the spinodal-like singularity in systems with long range interactions. We argue that the droplet with the structure indicated by the AM argument dominates the nucleation process. The fact that this droplet is unstable is, unlike the phases proposed by AM, physically reasonable and consistent with other results. In addition we investigate the bifurcation analysis of GM and show that the additional bifurcations to other symmetries that they find, which are not found by AM are not relevant to nucleation.

The remainder of this paper is structured as follows. In Sec. II we describe the method of AM. In Sec. III we present the argument for instability. In Secs. IV and V we discuss the implcations of this argument for nucleation of the crystal from the liquid and in Sec. VI we summarize and discuss our results.

II. ALEXANDER-McTAGUE

In this section we give a brief description of the argument of AM [1]. We will use a slightly different, but equivalent approach. We begin with the Landau-Ginzburg free energy

$$F(\rho)=\frac{1}{2}\int\int C(|\vec{x}-\vec{y}|)\rho(\vec{x})\rho(\vec{y})d\vec{x}d\vec{y}+\int f(\rho(\vec{x}),T)d\vec{x} -h\int \rho(\vec{x})d\vec{x}. \tag{1}$$

In the above we assume, following AM, that the interaction term is quadratic in ρ and that $f(\rho,T)$ can be expanded in a power series in ρ for fixed T. The quantity h is the chemical potential. The Euler-Lagrange equation that specifies the equilibrium state is obtained by functionally differentiating Eq. (1) and setting the derivative equal to zero.

$$\int C(|\vec{x}-\vec{y}|)\rho(\vec{y})d\vec{y}+\frac{\partial f(\rho,T)}{\partial \rho}-h=0. \tag{2}$$

We assume that there is a constant solution ρ_o corresponding to the stable or metastable liquid at the values of T and h we are investigating. Defining $\psi(\vec{x})$ through $\rho(\vec{x})=\rho_o+\psi(\vec{x})$ and inserting this expression in Eq. (2) we obtain

$$\int A(|\vec{x}-\vec{y}|)\psi(\vec{y})d\vec{y}+b(h,T)\psi^2(\vec{x})=0. \tag{3}$$

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Here $b(h,T)$ is the coefficient of the term quadratic in $\psi(\vec{x})$ arising out of a Taylor series expansion of $\partial f(\rho)/\partial\rho$. The dependence of $b(h,T)$ on h and T is through ρ_o. The term $A(|\vec{x}-\vec{y}|)=C(|\vec{x}-\vec{y}|)+b_1\delta(\vec{x}-\vec{y})$ where b_1 is the coefficient of the term linear in $\psi(\vec{x})$ in the Taylor expansion that also depends on h and T through ρ_o and $\delta(\vec{x}-\vec{y})$ is the Dirac δ function. Following AM we have truncated the Taylor expansion after the quadratic term using the assumption that $\psi(\vec{x})\ll 1$, i.e., the first-order nature of the transition is not too pronounced. We will see that this can be justified in a self-consistent manner.

Again following AM we consider the system in the neighborhood of a critical point associated with the fluid [1]. The critical point is characterized by $\hat{A}(|\vec{k}_o|)=0$, where $|\vec{k}_o|$ is the location of the global minimum of $\hat{C}(|\vec{k}|)$ defined in Eq. (1). Near the critical point $\hat{A}(|\vec{k}_o|)=\epsilon\ll 1$. The hat denotes the Fourier Transform and $\epsilon=(T-T_S)/T_S$ where T_S is the critical temperature. From Eq. (3) we obtain, after Fourier transform,

$$\hat{A}(|\vec{k}|)\hat{\psi}(\vec{k})+b(h,T)\int\hat{\psi}(\vec{k}-\vec{k}')\hat{\psi}(\vec{k}')d\vec{k}'=0. \qquad (4)$$

There is one solution of Eq. (4) that scales with ϵ, i.e., $\hat{\psi}(\vec{k})\sim\epsilon$ or $\psi(\vec{x})\sim\epsilon$. The scaling justifies neglecting the higher-order terms in ψ since they will be higher order in ϵ. Such scaling solutions, assuming of course that they exist, will have a free-energy cost that differs from the liquid by terms of order ϵ. What about solutions that do not scale? Unless the critical point T_S is on the coexistence curve it seems likely that there would be solutions with a lower free energy than the liquid as $\epsilon\rightarrow 0$. This existence of other solutions is what one would expect if, as we contend, the AM solution is unstable. However, here we are simply following the AM argument and do not need to consider the possibility of solutions of the Euler-Lagrange equation that do not scale and hence require higher-order terms in the Landau-Ginzburg free energy than those allowed by AM. The question of solutions for nucleation droplets that do not scale with ϵ will be addressed in Sec. V.

We now assume that the solution of Eq. (3) is of the form

$$\psi(\vec{x})=\sum_n c_n(h,T)\exp(i\vec{k}_n\cdot\vec{x}), \qquad (5)$$

where the $\vec{k}_n$ are reciprocal lattice vectors. If we now take d reciprocal lattice vectors, e.g., $\vec{k}_1\dots\vec{k}_d$ where d is the spatial dimension, to have a magnitude $|\vec{k}_o|$ then we have a solution in which $c_1\dots c_d\gg c_n$ for $n>d$ when $\epsilon\dots 1$; that is for values of h and T near the critical point.

To see this, we simply insert Eq. (5) into Eq. (3) to obtain

$$\sum_{n=1}^{\infty}c_n(h,T)\hat{A}(|\vec{k}_n|)\exp(i\vec{k}_n\cdot\vec{x})+b(h,T)\times\left[\sum_{n=1}^{\infty}c_n(h,T)\exp(i\vec{k}_n\cdot\vec{x})\right]^2=0. \qquad (6)$$

We now take $c_1(h,T)\dots c_d(h,T)\sim\epsilon$ and all other $c_n(h,T)$ to be higher order in ϵ. We can assume $\hat{A}(|\vec{k}_n|)\sim 1$ for $n\neq 1,\dots,d$. It is straightforward to generalize this argument to the case of a finite number of degenerate global minima. For $\epsilon\ll 1$ the modes with magnitude $|\vec{k}_o|$ dominate the solution. In the limit $\epsilon\rightarrow 0$ these modes are the only ones that contribute. Since these modes dominate for $\epsilon\ll 1$ they must be such that $[\Sigma_{n=1}^{d}\exp(i\vec{k}_{o,n}\cdot\vec{x})]^2$ has the same symmetry as $\exp(i\vec{k}_{o,n}\cdot\vec{x})$. Here $\vec{k}_{o,n}$ is one of the d reciprocal lattice vectors with magnitude $|\vec{k}_o|$. Note that the sum contains exponentials and their complex conjugates as the sum must be real. Therefore as in AM we must have that the reciprocal lattice vectors form equilateral triangles. In two dimensions this generates a triangular or hexagonal lattice in real space and in three dimensions either bcc or layered triangular or hexagonal structures. This result was also derived via a bifurcation analysis by GM [7]. In the following section we investigate the stability of the solutions of Eq. (3).

III. STABILITY OF THE ALEXANDER-McTAGUE SOLUTIONS

To check the stability of the solutions of Eq. (3) we perform a simple linear stability analysis. Writing $\psi(\vec{x})+\eta(\vec{x})$, where $\eta(\vec{x})$ is a small arbitrary perturbation and $\psi(\vec{x})$ is a solution to Eq. (3), and inserting this in Eq. (3) we obtain

$$\int A(|\vec{x}-\vec{y}|)\eta(\vec{y})d\vec{y}+2b(h,T)\psi(\vec{x})\eta(\vec{x})=\Phi(\eta(\vec{x})). \qquad (7)$$

The function $\Phi(\eta(\vec{x}))$ can be expanded in the eigenvectors of the operator on the left hand side of Eq. (7). If the eigenvalues of the operator are all positive then the solution is linearly stable. If there is at least one negative eigenvalue the solution is linearly unstable. We will show that there must exist at least one negative eigenvalue.

The proof makes use of the well known fact that if we have an Hermitian operator Θ defined on a Hilbert space then the average of Θ, which we will call $\overline{\Theta}$, which is defined as

$$\overline{\Theta}=\frac{\langle x|\Theta|x\rangle}{\langle x|x\rangle} \qquad (8)$$

is an upper bound for the lowest eigenvalue of the operator Θ. Here $|x\rangle$ is any vector in the Hilbert space. The derivation of this result is quite straightforward and can be found in Ref. [8] as well as most elementary books on quantum mechanics. Note that the operator in Eq. (7) is both real and symmetric and hence Hermitian. The Hilbert space we use is defined with plane wave normalization.

Since we are primarily interested in the situation in which the fluid phase with density ρ_o is stable or metastable we begin with this case first. Since $\hat{A}(\vec{k})$ is the $\vec{k}$ dependent susceptibility of the uniform fluid if the fluid is stable or metastable then $\hat{A}(\vec{k})>0$ for all $|\vec{k}|$. Using $\psi(\vec{x})$, the solution to Eq. (3), as the vector $|x\rangle$ in our bound we have that the bound B is given by

$$B=\frac{\int \psi^{\star}(\vec{x})A(|\vec{x}-\vec{y}|)\psi(\vec{y})d\vec{x}\,d\vec{y}+2b(h,T)\int \psi^{\star}(\vec{x})\psi^{2}(\vec{x})d\vec{x}}{\int |\psi(\vec{x})|^{2}d\vec{x}}. \tag{9}$$

Since $\psi(\vec{x})$ is a solution to Eq. (3) the bound B reduces to

$$B=\frac{-\int \psi^{\star}(\vec{x})A(|\vec{x}-\vec{y}|)\psi(\vec{y})d\vec{x}\,d\vec{y}}{\int |\psi(\vec{x})|^{2}\,d\vec{x}}. \tag{10}$$

Converting to Fourier space by using Parseval's theorem we have

$$-B\int |\hat{\psi}(\vec{k})|^{2}d\vec{k}=\int |\hat{\psi}(\vec{k})|^{2}\hat{A}(|\vec{k}|)d\vec{k}. \tag{11}$$

Since $\hat{A}(|\vec{k}|)$ is assumed to be positive definite we must have $B<0$. Hence, the upper bound of the lowest eigenvalue is less than zero that proves the result. Note the fact that $\psi(\vec{x})$ is periodic was never used in the argument that is therefore valid for any solution of Eq. (3).

Although it is not relevant for the AM argument, where the question of the structure of the solid phase near a stable or metastable liquid was considered, for the sake of completeness we demonstrate that the solutions of Eq. (3) are unstable when $\hat{A}(|\vec{k}|)<0$ for some value(s) of $|\vec{k}|$; that is, when the liquid phase is unstable. Equation (8) for the lowest eigenvalue bound can be written as

$$B\int |w(\vec{x})|^{2}\,d\vec{x}=\int w^{\star}(\vec{x})A(|\vec{x}-\vec{y}|)w(\vec{y})d\vec{x}\,d\vec{y}+2b(h,T)\int \psi(\vec{x})w^{\star}(\vec{x})w(\vec{x})d\vec{x}, \tag{12}$$

where the operator Θ is given in Eq. (7). We choose the test function $w(\vec{x})=\exp(i\vec{k}_o\cdot\vec{x})$ so that

$$BV=\hat{A}(|\vec{k}_o|)V+2b(h,T)C, \tag{13}$$

where $C=\int\psi(\vec{x})d\vec{x}$ and V is the system volume. Since $\vec{k}_o$ is the location of the global minimum of $\hat{A}(|\vec{k}|)$ and, by assumption, $\hat{A}(|\vec{k}|)<0$ for some $|\vec{k}|$, $\hat{A}(|\vec{k}_o|)<0$. Returning to Eq. (3) multiplying by $b(h,T)$ and integrating with respect to $\vec{x}$ yields

$$b(h,T)C=\frac{-b^{2}(h,T)\int |\psi^{2}(\vec{x})|d\vec{x}}{\hat{A}(0)}. \tag{14}$$

Substituting Eq. (14) into Eq. (13) we obtain

$$BV=\hat{A}(|\vec{k}_o|)V-\frac{2b^{2}(h,T)\int |\psi(\vec{x})|^{2}\,d\vec{x}}{\hat{A}(0)}. \tag{15}$$

Since $b(h,T)$ is real and $\hat{A}(|\vec{k}_o|)$ is assumed to be negative, if $\hat{A}(0)>0$ then $B<0$. If $\hat{A}(0)<0$ Eq. (3) can no longer be used to generate an equlibrium crystal. This occurs because $A(\vec{x}-\vec{y})$ and $b(h,T)$ are functions of ρ_o that is unstable to spatially constant perturbations.

The one situation left to address is the one in which $\hat{A}(|\vec{k}|)$ is positive for all $|\vec{k}|$ except for $|\vec{k}_o|$ where it is equal to zero. This is the situation in which the system is at the critical point. From Eq. (11) we now have $B=0$ if $\hat{\psi}(\vec{k})=\delta(\vec{k}-\vec{k}_o)$. This implies that $\psi(\vec{x})=\exp(i\vec{k}_o\cdot\vec{x})$. However, from our discussion in Sec. II $\psi(\vec{x})\sim\epsilon=\hat{A}(|\vec{k}_o|)=0$. Therefore the solution of Eq. (2) in this case describes the infinitely long lived fluctuations at the critical point and not a phase.

Note that the condition that we be near a critical point ($\hat{A}(|\vec{k}|)=\epsilon\ll 1$ for some $|\vec{k}|$) was necessary to argue that the AM crystals were in fact minima of the free energy. However, the critical point condition was not used to show that the solution of Eq. (3) was unstable. In addition, we have not specified the nature of the critical point. When the critical point is a spinodal then the AM argument becomes quite useful in determining the nature of the critical droplet in the nucleation process that takes place near the pseudospinodal in near-mean-field systems. We discuss this application in the following section.

Note also that the same argument that was used to show that the solutions of Eq. (3) are unstable can be used on any equation of the form

$$\int A(|\vec{x}-\vec{y}|)\psi(\vec{y})d\vec{y}+q(h,T)\psi^{n}(\vec{x})=0, \qquad (16)$$

where n in any integer greater than or equal to two.

IV. SPINODAL NUCLEATION OF A CRYSTAL FROM THE LIQUID

In this section we apply the ideas of AM to the problem of the nucleation of a crystalline solid from the liquid near a pseudospinodal in a near-mean-field system. First we note that spinodals, in the sense that one finds them in the van der Waals theory of liquids or the Curie-Weiss theory of magnetic systems, are mean-field (MF) objects. In Ising models this has been seen in Monte Carlo simulations [9] and via transfer matrix techniques [10]. A general argument using a Ginzburg criterion has also been given by Binder [11]. To study MF systems in a rigorous way Kac *et al.* [12] introduced the idea that, if a system has an interaction potential of the form $V(|\vec{x}|)=V_{ref}(|\vec{x}|)+\gamma^{d}\phi(\gamma|\vec{r}|)$ where $V_{ref}(|\vec{x})$ is a short range reference potential, γ is a parameter and $\int\gamma^{d}\phi(\gamma|\vec{x}|)d\vec{x}=D<\infty$, then in the limit $\gamma\rightarrow 0$ the system will be MF. This means that for fluids such a potential results in the van der Waals equation with the attendant MF critical exponents and spinodals. In magnetic systems the result is the Curie-Weiss description. We have assumed that the interaction is spherically symmetric for simplicity but that need not be the case.

In order to generate near-mean-field (NMF) systems we use the approach of Kac, however we take $\gamma\ll 1$ but finite. That is, we do not take the $\gamma\rightarrow 0$ limit. In NMF systems there is no true spinodal but, depending on the interaction range $R=\gamma^{-1}$, the system will behave as if there is a spinodal as long as one does not approach the singularity too closely [9–11]. We will refer to such apparent singularities as pseudospinodals. To study nucleation in systems with long range interactions undergoing deep quenches we adopt the techniques of saddle point evaluation of the partition function [13] to nucleation near the pseudospinodal [6,14]. We begin with a Landau-Ginzburg-Wilson Hamiltonian identical to $F(\rho)$ in Eq. (1) but with one additional requirement. We take the interaction term

$$C(|\vec{x}-\vec{y}|)=\gamma^{d}\Lambda(\gamma|\vec{x}-\vec{y}|), \qquad (17)$$

where the Λ has the properties of the long range Kac potential described above. We will take γ to be small but finite so that we are describing NMF rather than MF systems. Our Hamiltonian H is then

$$H(\rho)=\frac{1}{2}\int\gamma^{d}\Lambda(\gamma|\vec{x}-\vec{y}|)\rho(\vec{x})\rho(\vec{y})d\vec{x}\,d\vec{y}+\sum_{n=1}^{\infty}\int b_{n}(h,T)\rho^{n}(\vec{x})d\vec{x}-h\int\rho(\vec{x})d\vec{x}, \qquad (18)$$

where we have made the Taylor series expansion of $f(\rho,T)$ explicit. The partition function in the canonical ensemble is

$$Z=\int\delta\rho\exp[-\beta H(\rho)], \qquad (19)$$

where $\beta=1/K_{B}T$.

Using $R=\gamma^{-1}$ and assuming that $\rho(\vec{r})=\rho(\vec{x}/R)$ the Hamiltonian H in terms of scaled lengths becomes

$$H(\rho)=R^{d}\left[\frac{1}{2}\int\Lambda(|\vec{r}-\vec{r}\,'|)\rho(\vec{r})\rho(\vec{r}\,')d\vec{r}\,d\vec{r}\,'+\sum_{n=1}^{\infty}b_{n}(h,T)\int\rho^{n}(\vec{r})d\vec{r}-h\int\rho(\vec{r})d\vec{r}\right]. \qquad (20)$$

For $R\gg 1$ (i.e., the NMF limit) the partition function in Eq. (19) can be evaluated as a saddle point integral. The Euler-Lagrange equation that specifies the saddle point will be of the same form as Eq. (2). Identifying ρ_{o} as the constant solution that specifies the density of the liquid we write $\rho(\vec{r})=\rho_{o}+\overline{\psi}(\vec{r})$. As in AM we assume that $\overline{\psi}(\vec{r})$ is small since we are near a pseudospinodal critical point. Expanding in $\overline{\psi}(\vec{r})$ we obtain an equation for $\overline{\psi}(\vec{r})$ of the same form as Eq. (3).

$$R^{d}\left[\int\overline{A}(|\vec{r}-\vec{r}\,'|)\overline{\psi}(\vec{r}\,')d\vec{r}\,'+b(h,T)\overline{\psi}^{2}(\vec{r})\right]=0, \qquad (21)$$

where $\overline{A}(|\vec{r}-\vec{r}\,'|)=\Lambda(|\vec{r}-\vec{r}\,'|)+b_{1}\delta(\vec{r}-\vec{r}\,')$.

To obtain the nucleation droplet we assume a solution of the form

$$\overline{\psi}(\vec{r})=\sum_{n}\exp(i\vec{k}\,'_{o,n}\cdot\vec{r})\overline{\psi}'\left(\frac{\vec{r}}{L}\right), \qquad (22)$$

where $\vec{k}\,'_{o}=R\vec{k}_{o}$ and L is a length to be determined. We assume at the outset that $L\gg|\vec{k}_{o}|^{-1}$, which will be seen to be true self consistently. As before $|\vec{k}_{o}|$ is the location of the global minimum of $\overline{\hat{A}}(|\vec{k}|)$. Since $|\vec{k}_{o}|\sim R$, $\overline{\psi}'(\vec{r}/L)$ is a slowly varying function of $\vec{r}$. Consequently, we can expand $\overline{\psi}'(\vec{r}\,'/L)$ in a gradient expansion about $\vec{r}\,'=\vec{r}$. The first three terms in the expansion are

$$\overline{\psi}'\left(\frac{\vec{r}\,'}{L}\right)=\overline{\psi}'\left(\frac{\vec{r}\,'}{L}\right)+\frac{(\vec{r}-\vec{r}\,')}{L}\cdot\nabla\overline{\psi}'\left(\frac{\vec{r}\,'}{L}\right)\bigg|_{\vec{r}\,'=\vec{r}}+\frac{|\vec{r}-\vec{r}\,'|^{2}}{L^{2}}\nabla^{2}\overline{\psi}'\left(\frac{\vec{r}\,'}{L}\right)\bigg|_{\vec{r}\,'=\vec{r}}, \qquad (23)$$

where the gradient and Laplacian are with respect to $\vec{r}\,'/L$

Since $\overline{A}(|\vec{r}-\vec{r}\,'|)\rightarrow 0$ as $|\vec{r}-\vec{r}\,'|\rightarrow\infty$, $|\vec{r}-\vec{r}\,'|/L\ll 1$ for large L and we can truncate the series in Eq. (23) after terms of the second order. Inserting Eq. (22) and Eq. (23) into Eq. (21) we obtain

$$R^d\left[\sum_n \exp(i\vec{k}_{o,n}\cdot\vec{r})\hat{\overline{A}}(|\vec{k}_o|)\overline{\psi}'\left(\frac{\vec{r}}{L}\right) - G(h,T)\sum_n \exp(i\vec{k}_{o,n}\cdot\vec{r})\frac{1}{L^2}\nabla^2\overline{\psi}'\left(\frac{\vec{r}}{L}\right) + b(h,T) \times\left(\sum_n \exp(i\vec{k}_{o,n}\cdot\vec{r})\right)^2\overline{\psi}'^2\left(\frac{\vec{r}}{L}\right)\right]=0, \tag{24}$$

where the Laplacian is with respect to $\vec{r}/L$ and

$$G(h,T)=\int |\vec{r}-\vec{r}\,'|^2\overline{A}(|\vec{r}-\vec{r}\,'|)d(\vec{r}-\vec{r}\,')<0. \tag{25}$$

The term involving the gradient is zero as it reduces to a function proportional to $\nabla_{\vec{k}}\hat{\overline{A}}(|\vec{k}|)|_{\vec{k}=\vec{k}_o}$ and $|\vec{k}_o|$ is the global minimum of $\hat{\overline{A}}(|\vec{k}|)$. Since we are near a spinodal $\hat{\overline{A}}(|\vec{k}_o|)=\epsilon\ll 1$. We can assume [6] that $\overline{\psi}'(\vec{r}/L)\sim\epsilon$ as long as $L\sim\epsilon^{-1/2}$. Hence

$$\overline{\psi}'\left(\frac{\vec{r}}{L}\right)=\epsilon\Psi\left(\frac{\vec{x}}{R\epsilon^{-1/2}}\right), \tag{26}$$

where the scaling of $\vec{x}$ with respect to both $\epsilon^{-1/2}$ and R is explicit. For further discussion of this scaling see Sec. V. The argument of AM is now invoked to limit the $\vec{k}_{o,n}$ to lie on equilateral triangles. The critical or nucleating droplet then has the following form: In the interior it is periodic with a triangular or hexagonal structure in two dimensions and a bcc or layered hexagonal or triangular plane structure in three dimensions. These structures are modulated by an envelope that satisfies the equation

$$G(h,T)\nabla^2\overline{\psi}'(\epsilon^{1/2}\vec{r})+\hat{\overline{A}}(|\vec{k}_o|)\overline{\psi}'(\epsilon^{1/2}\vec{r}) + b(h,T)\overline{\psi}'^2(\epsilon^{1/2}\vec{r})=0, \tag{27}$$

where the Laplacian is with respect to $\vec{r}$. The boundary conditions are that $\overline{\psi}'(\epsilon^{1/2}\vec{r})\rightarrow 0$ when $|\vec{r}|\rightarrow\infty$ and that $d/d|\vec{r}|\overline{\psi}'(\epsilon^{1/2}\vec{r})=0$. at $|\vec{r}|=0$. The first condition is simply a statement that the droplet is localized. The second boundary condition assures that the droplet has no unphysical kinks at its center [13]. Note also that the structure of Eq. (27) implies that the solution is a function of $|\vec{r}|$. Since the sign of $b(h,T)$ merely sets the sign of $\overline{\psi}'(\epsilon^{1/2}|\vec{r}|)$ we lose no generality by assuming that $b(h,T)<0$.

From the discussion in Sec. III this droplet will be unstable, not just on its surface as in classical nucleation [13], but in its interior. We can see this explicitly by finding the eigenvector associated with the negative eigenvalue [13] of the operator obtained by a linear stability analysis about the critical droplet. That is, we want the solution of

$$\int \overline{A}(|\vec{r}-\vec{r}\,'|)w(\vec{r})'\,d\vec{r}\,'-2|b(h,T)|\overline{\psi}(\epsilon^{1/2}\vec{r})w(\vec{r})=\lambda w(\vec{r}), \tag{28}$$

where $\overline{\psi}(\epsilon^{1/2}\vec{r})$ is the solution to Eq. (21) given in Eq. (22).

We assume that the eigenvector has the form

$$w(\vec{r})=\sum_n \exp(i\vec{k}_o\cdot\vec{r})W(\epsilon^{1/2}\vec{r}). \tag{29}$$

Employing the same arguments we used to obtain Eq. (27) we find that the eigenvector has the same interior structure as the critical droplet and an envelope that is the solution of

$$G(h,T)\nabla^2W(\epsilon^{1/2}\vec{r})+\epsilon W(\epsilon^{1/2}\vec{r}) -2|b(h,T)|\overline{\psi}'(\epsilon^{1/2}\vec{r})W(\epsilon^{1/2}\vec{r})=\lambda W(\epsilon^{1/2}\vec{r}), \tag{30}$$

where we have set $\hat{\overline{A}}(|\vec{k}_o|)=\epsilon$.

In $d=1$ the solution of Eq. (27) can easily be seen by substitution to be

$$\overline{\psi}'(\epsilon^{1/2}x)=\frac{D\epsilon^{1/2}}{\cosh^2(\alpha\epsilon^{1/2}x)}, \tag{31}$$

where α and D are constants. In $d=3$ Eq. (27) has been solved numerically [15]. The solution is radially symmetric, has its maximum at the origin and decreases to zero as $|\vec{r}|\rightarrow\infty$ Hence Eq. (30) has the form of a Schrödinger equation with a potential $V(|\vec{r}|)$ given by

$$V(|\vec{r}|)=\hat{\overline{A}}(|\vec{k}_o|)-2\overline{\psi}'(\epsilon^{1/2}|\vec{r}|). \tag{32}$$

From the discussion above, this potential is a shallow well. The lowest eigenvalue will correspond to a bound state and hence will be negative. Moreover the eigenvector corresponding to the bound state will be centered in the center of the well. From the work of Langer [13] we know that the eigenstate that corresponds to the negative eigenvalue is an unstable mode of the droplet. The fact that the bound state is centered in the center of the well is confirmation that the entire droplet is unstable consistent with the adaptation of the AM argument. This form of the eigenvector was also seen numerically in Ising models [15].

The dominant contribution to the probability of the occurrence of a critical droplet comes from inserting the solution to the Euler-Lagrange equation [Eq. (24)] into the expression for the partition function. The details of this calculation for liquid-gas and magnetic systems can be found in Langer's paper for classical nucleation [13] and in Unger and Klein for spinodal nucleation [14]. The adaptation to liquid-solid nucleation near the spinodal of the supercooled liquid of the saddle point part of the calculation is straightforward [6]. The free-energy barrier to nucleation then is given by

$$F(h,T)=R^d\int \overline{A}(|\vec{r}-\vec{r}\,'|)\,\overline{\psi}(\epsilon^{1/2}\vec{r})\,\overline{\psi}(\epsilon^{1/2}\vec{r}\,')\,d\vec{r}\,d\vec{r}\,' - |b(h,T)|\int \overline{\psi}^3(\epsilon^{1/2}\vec{r})\,d\vec{r}, \tag{33}$$

where $\overline{\psi}(\epsilon^{1/2}\vec{r})$ is the solution to Eq. (21). From Eqs. (22) and (26) we have

$$\begin{aligned}F(h,T)=R^d\epsilon^3\int \overline{A}'(|\vec{r}-\vec{r}\,'|)\left[\sum_n \exp(i\vec{k}'_{o,n}\cdot\vec{r})\Psi(\epsilon^{1/2}\vec{r})\right]\\ \times\left[\sum_n \exp(i\vec{k}'_{o,n}\cdot\vec{r}\,')\Psi(\epsilon^{1/2}\vec{r}\,')\right]d\vec{r}\,d\vec{r}\,'\\ -|b(h,T)|\int\left[\sum_n \exp(i\vec{k}'_{o,n}\cdot\vec{r})\right]^3\Psi^3(\epsilon^{1/2}\vec{r})\,d\vec{r},\end{aligned} \tag{34}$$

where $\overline{A}(|\vec{r}-\vec{r}\,'|)=\epsilon\overline{A}'(|\vec{r}-\vec{r}\,'|)$ and $\vec{k}'_{o,n}=R\vec{k}_{o,n}$.

When $|\vec{k}_{o,n}|\neq 0$

$$\int \exp(i\vec{k}_{o,n}\cdot\vec{r})\Psi(\epsilon^{1/2}\vec{r})\,d\vec{r}\sim\frac{1}{\xi^d}=\epsilon^{d/2}, \tag{35}$$

where $\xi=\epsilon^{-1/2}$ is the correlation length near the spinodal in scaled units. Therefore, the dominant contribution to the cubic term in Eq. (34) will be given by those terms in the sum $(\Sigma_n e^{i\vec{k}_{o,n}\cdot\vec{r}})^3$ that are spatial constants. The same analysis can be done for the quadratic term in Eq. (34). The dominant contribution will come from the $\vec{k}_{o,n}$ vectors that appear with opposite signs in the sums and result in exponentials of the form $\exp[\vec{k}_{o,n}\cdot(\vec{r}-\vec{r}\,')]$. These terms will be of order ξ^d and all other terms will be reduced by a factor of $1/\xi^d$ as in Eq. (35).

The free-energy barrier is then

$$F(h,T)=MR^d\epsilon^{3-d/2}, \tag{36}$$

where M is a constant. The probability of a critical droplet is

$$P_D=g(h,T)\exp(-MR^d\epsilon^{3-d/2}), \tag{37}$$

where $g(h,T)$ is small compared to the exponential [13,14].

The exponential dominates the probability of a nucleation or critical droplet. To get a feel for the magnitude of the argument of the exponential we turn to consideration of the so-called Ginzburg criterion for the validity of a mean-field treatment [11]. In MF systems fluctuations can be ignored when calculating thermodynamic quantities [11]. Ginzburg pointed out that this implies that the fluctuations of the order parameter must be small compared to its mean value. That is

$$\frac{\xi^d\chi_T}{\xi^{2d}\phi^2}\ll 1, \tag{38}$$

where ξ is the correlation length as above, χ_T is the susceptibility, and ϕ is the order parameter. Using the MF exponents for the spinodal, $\chi_T\sim\epsilon^{-1}$, $\phi\sim\epsilon$ and $\xi\sim R\epsilon^{-1/2}$, where we have made the R dependence of the correlation length explicit, we have

$$\frac{\epsilon^{-1}}{R^d\epsilon^{2-d/2}}\ll 1 \tag{39}$$

or

$$R^d\epsilon^{3-d/2}\gg 1 \tag{40}$$

for MF theory to be a good approximation. If the left hand side of Eq. (40) is infinite then MF theory is exact. Since spinodals are MF objects and pseudospinodals affect the physics only if the system is NMF we require the condition in Eq. (40) to hold if we are to see the spinodal nucleation process described above.

If $R\gg 1$ then ϵ can be small and the spinodal can be approached ($\epsilon\ll 1$) with the Ginzburg criterion $R^d\epsilon^{3-d/2}$ still valid. For Ising models the spinodal can be seen by measurements of the isothermal susceptibility that will diverge as $R\to\infty$ and $\epsilon\to 0$ [9]. In the supercooled liquid the static structure factor is known rigorously to diverge at $|\vec{k}|\neq 0$ [16]. However, in this case the situation is more complicated and the measured divergence is suppressed for $d>1$ [17].

The implications of these investigations is that the argument of AM, while it does not predict the structure of stable crystals, can be adapted to determine the structure of at least one kind of nucleation droplet near the pseudospinodal in liquids with long range interactions. Questions have been raised in the work of GM about the possibility of other forms of nucleation droplets near the spinodal. In the following section we will address this question.

V. UNIQUENESS OF CRITICAL DROPLET

The question of the uniqueness of a critical droplet, given the thermodynamic parameters that specify the metastable state, has not been fully resolved. This is true even in phase transitions, such as gas liquid, where there is no spatial symmetry breaking. The resolution of this problem is even more difficult when, as in the nucleation of the crystal from the liquid, the spatial symmetry changes. To completely answer this question for a given T and h, all solutions of the Euler-Lagrange equation resulting from setting the functional derivative of $H(\rho)$ found in Eq. (20) would have to be found and the free-energy cost of each solution evaluated. This is a formidable task that has yet to be done either analytically or numerically.

In the simpler liquid-gas nucleation process, although it has not been proven, the idea that there is only one saddle point separating the metastable and stable state seems quite reasonable. In the liquid-solid transition multiple saddle points with different spatial symmetries seems more plausible. In this regard GM [7] have performed a bifurcation analysis of supercooled liquids near the spinodal. They found that the first-order bifurcation analysis yields only a bcc solution but that the second-order analysis results in a solution with an fcc symmetry. They also found that within the mean-field Landau theory the bcc structure has a lower maximum of the free energy than the fcc structure. The word structure was used rather than phase since, as we have seen in Sec. III, these structures are unstable. Groh and Mulder however, do not consider nucleation. It is the purpose of this section to provide an argument, unfortunately not a proof, that as the spinodal is approached the bcc nucleation droplet found in the preceding section dominates the nucleation process.

We begin by noting that it is necessary to have the linear size of the critical or nucleation droplet equal to or larger than the correlation length. Particles separated by a scale smaller than the correlation length are highly correlated. Therefore, the statistical fluctuations that begin the evolution up a saddle point hill should involve regions that are at least of the correlation length size. The converse is not true. Critical droplets can be large compared to the correlation length since critical droplets are rare compared to the fluctuations that set the scale for correlations. It has been the case in all simulations that have looked at nucleation that the critical droplet size is either equal to or larger than the correlation length [18,19]. This being the case then the critical droplet profile $\psi(\vec{x})$ can be approximated by the form

$$\psi(\vec{x})=\sum_n \exp(i\vec{k}_n\cdot\vec{r})\Phi\left(\left|\frac{\vec{r}}{L}\right|\right), \tag{41}$$

where the $\vec{k}_n$ are the entire set of reciprocal lattice vectors and $L\geqslant\xi$. This form of the droplet clearly is not exact. We would expect some effect of the fact that the envelope will decay to zero as $|\vec{r}/L|\to\infty$ on the symmetry. However, that will be in the tail of the droplet, which is expected to have exponential decay [14,6,19] [also see Eq. (31)] and will have negligible effect on the interior symmetry. Near the spinodal where the correlation length ξ diverges, the interior of the droplet will be unaffected by the envelope. In addition any scaling should also be unaffected by the approximation made at the edge of the droplet.

With arguments essentially identical to those of Sec. IV the envelope obeys an equation similar to Eq. (24).

$$\begin{aligned}&\sum_n \exp\left[(i\vec{k}_n\cdot\vec{r})\hat{A}(|\vec{k}_n|)\Phi\left(\frac{\vec{r}}{L}\right)\right]\\&-|G(h,T)|\sum_n \exp(i\vec{k}_n\cdot\vec{r})\nabla^2\Phi\left(\frac{\vec{r}}{L}\right)\\&+b(h,T)\left[\sum_n \exp(i\vec{k}_n\cdot\vec{r})\right]^2\Phi^2\left(\frac{\vec{r}}{L}\right)\\&+c(h,T)\left[\sum_n \exp(i\vec{k}_n\cdot\vec{r})\right]^3\Phi^3\left(\frac{\vec{r}}{L}\right)=0,\end{aligned} \tag{42}$$

where the Laplacian is with respect to $\vec{r}$ and $G(h,T)$, $b(h,T)$ and $c(h,T)$ are independent of $\vec{r}$ and $\vec{k}$. The Laplacian term is of order $1/L^2$ and $L\geqslant\xi\sim\epsilon^{-1/2}$. We have restricted our considerations to Hamiltonians that include terms up to $\Phi^4(\vec{r}/L)$ neglecting higher orders in Φ. These higher-order terms can be included with no essential change in the argument. If the term

$$\sum_n \exp(i\vec{k}_n\cdot\vec{r})\hat{A}(|\vec{k}_n|)\to 0 \tag{43}$$

slower than $1/L^2$ as the spinodal is approached, then the Laplacian term can be ignored. This would result, assuming that symmetry constraints could be satisfied, in $\Phi(\vec{r}/L)$ being a spatial constant. Since nucleation droplets are, almost by definition, localized this result would clearly be unsatisfactory. The only way that the term in Eq. (43) can go to zero at all is if the sum is limited to terms in which $|\vec{k}_n|=|\vec{k}_o|$ where $\vec{k}_o$ has the same meaning as in previous sections. [See Eq. (24).]

Therefore, we must have

$$\sum_n \exp(i\vec{k}_n\cdot\vec{r})\hat{A}(|\vec{k}_n|)=\sum_n \exp(i\vec{k}_{o,n}\cdot\vec{r})\hat{A}(|\vec{k}_{o,n}|)\sim\epsilon \tag{44}$$

as this is the only possible way that this term can go to zero as $\epsilon\to 0$. Since the terms linear in Φ must scale the same way this implies that $1/L^2\sim\epsilon$ so that $L\sim\epsilon^{-1/2}$ or $L\sim\xi$. If $b(h,T)$ is not zero in Eq. (42) then $\Phi(\vec{r}/L)$ must scale as ϵ. If it were to scale as ϵ^x with $x>1$ then the nonlinear terms in Φ in Eq. (42) can be ignored relative to the linear terms. This results in a solution of the form

$$\Phi\left(\frac{\vec{r}}{L}\right)=\Phi(\epsilon^{1/2}\vec{r})=C_1\exp(\epsilon^{1/2}\hat{n}\cdot\vec{r})+C_2\exp(-\epsilon^{1/2}\hat{n}\cdot\vec{r}), \tag{45}$$

where $\hat{n}$ is a unit vector whose direction is arbitrary. For the droplet to be localized the constant C_1 must be set to zero. This results in a violation of the boundary condition that the derivative with respect to $|\vec{r}|$ is zero at $|\vec{r}|=0$. Hence this droplet is physically ruled out. If $x<1$ then the linear terms in Φ, including the Laplacian term, can be ignored resulting again in a nonlocal solution. In general nucleation from the liquid to the solid is described by Hamilitonians in which $b(h,T)\neq 0$ and hence the AM argument can be used to fix the spatial symmetry in the interior of the critical droplet. Note that $b(h,T)$ is a function of h and T and is therefore specified only by the parameters that define the metastable state.

Suppose that $b(h,T)=0$. In this case, arguments similar to the ones above imply that $\Phi(\vec{r}/L)\sim\epsilon^{1/2}$. The Φ^4 term in the Hamiltonian is now relevant and the nucleation barrier will now scale as $R^d\epsilon^{2-d/2}$. In addition a simple extension of AM indicates that the droplet symmetry will now be a square lattice in $d=2$ and an fcc lattice, or stacked layers of square lattices, in $d=3$.

It is interesting to ask why, except for a particular symmetry of the Hamiltonian, the critical droplet has a bcc symmetry in $d=3$ when the bifurcation analysis of GM indicates that an fcc bifurcation is also allowed even when the coefficient $[b(h,T)]$ of the cubic term in the Hamiltonian is nonzero. Repeating the GM analysis is beyond the scope of this paper however, the key to their construction of the fcc bifurcation is the use of lattice vectors for which $|\vec{k}| \neq |\vec{k}_o|$. The argument we used made use of (1) the requirement that the droplet be localized, (2) the droplet has no kinks at its center, and (3) the assumption that the linear droplet size L was greater than or equal to the correlation length ξ. These conditions taken together resulted [see Eqs. (43) and (44)] in a restriction of the reciprocal lattice vectors to those for which $|\vec{k}| = |\vec{k}_o|$. These conditions, while necessary for specifying the nucleation problem are not needed in the bifurcation analysis of GM. Hence, even though the fcc bifurcation is allowed it will not occur in a critical droplet as the spinodal is approached.

It is important to emphasize that we have restricted our consideration to Hamiltonians that are in the same class as that considered by AM. In density functional language this implies that all direct correlation functions higher than the pair are zero. Whether the inclusion of higher-order correlation functions changes the result remains to be seen.

VI. SUMMARY AND DISCUSSION

We have argued that the prediction of a stable bcc phase near a spinodal, or pseudospinodal, of a supercooled liquid by AM is not correct. The predicted bcc phase is unstable for any value of the thermodynamic parameters. This is different from the analysis of GM that used the spinodal as a bifurcation point and examined the structure of the AM solutions near the bifurcation. In addition, the requirement that the spinodal be a bifurcation point imposes the condition that it can be approached arbitrarily closely. From the Ginzburg criterion of Eq. (40) this implies that $R \rightarrow \infty$ and the system is MF. The result obtained for the instability of these solutions is not restricted to MF systems in this work. In addition this result is valid away from a spinodal should the system be MF.

However, we have used the AM argument to show that the nucleation or critical droplet near a spinodal does have triangular structure in two dimensions and a possibly bcc-like structure in three dimensions. As discussed in Sec. IV there is also a possible droplet structure consisting of stacked planes in three dimensions, each of which has a triangular structure. There is some simulation [23,24] and experimental evidence [25] that such a droplet may form. The same argument that was used to show that the AM ‘‘crystal’’ was unstable is also used to show that the critical droplet is unstable. This is, however, physically reasonable for a critical droplet near a spinodal [6,14]. It is important to stress that the bcc droplet structure here does not refer to a stable bcc phase in the interior of the droplet as one would expect from classsical nucleation [21]. The bcc structure simply means that the density variation in the critical droplet, which is inherently unstable, has a bcc symmetry.

It should also be noted that droplets like the ones predicted in this paper were found in molecular dynamics simulations of supercooled Lennard-Jones fluids even though the stable crystal has a fcc structure [20]. In addition it is known from theoretical studies of the liquid-gas transition that as one moves away from the pseudospinodal the droplet develops a core that appears almost classical [15]. This phenomenon is consistent with the results of a density functional calculation of liquid solid nucleation by Shen and Oxtoby [21].

Many systems of technological importance have long range, or effective long range interactions. These include polymers [11], neutral plasmas, and metals [22]. Since critical droplets are at least the size of the correlation length and all statistical lengths, such as the droplet diameter, are measured in units of the interaction range R, classical nucleation, where the surface tension is assumed to remain nonzero [13] will be strongly suppressed. In these systems, spinodal nucleation will dominate the metastable state decay. Since the structure of the interior of a spinodal nucleation droplet is not the stable crystal as would be expected in the classical process the evolution of this droplet as it grows will be an important step in determining the structure of the stable or metastable crystal.

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