Crystalline Nucleation in Deeply Quenched Liquids

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Employing a long-range potential model we investigate nucleation of crystalline droplets near the limit of stability of the metastable liquid. The nucleation process is found to differ considerably from what is predicted in standard models. In contrast to the classical nucleation mechanism this process provides a qualitative explanation of the results of molecular-dynamics simulations of systems undergoing deep quenches.

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Molecular-dynamics simulations of nucleation of crystalline solids from metastable liquids have often produced results which are difficult to understand from the point of view of classical nucleation theory. Three examples are the following: (i) The nucleating droplet often exhibits a bcc symmetry rather than the equilibrium fcc structure.[1,2] (ii) Nucleation is seen via the onset of a droplet with a crystalline symmetry but for some period of time no effect is noticed in the thermodynamic parameters.[1,3] (iii) Nucleation barriers calculated from the classical theory for quenches deep enough to observe (i) and (ii) are of the order[2,3] of $k_B T$; however, the lifetime of the metastable state is not consistent with such a barrier height.[3]

In contrast, nucleation in systems undergoing shallow[4] quenches appears to be similar to what one expects from the classical theory.[5-8] This suggests that the nucleation mechanism is sensitive to the details of the quench. The results obtained with the quench mechanisms used in Refs. 1-3, and their variance with the results in Ref. 4, are difficult to understand if one assumes that in all cases nucleation takes place via the mechanism described in classical nucleation theory.

In this Letter we introduce a nucleation mechanism which differs considerably from the classical and which provides a conceptual framework within which these results can be understood. The mechanism we propose is analogous to the fractal or ramified droplet nucleation found, under certain conditions, in Ising models and fluids.[9-13] In this theory, as in Ising models, the classical mechanism is modified because of the proximity of a spinodal[14,15] which has the properties of a critical point. In contrast, however, the instability we consider here is characterized by a structure factor that diverges at a *nonzero wave vector*. We stress that by "proximity of the spinodal" we do not imply that the spinodal is a singularity in the thermodynamic space which can be reached by deep quenches. Rather we are referring to the effect of spinodal-like behavior becoming more pronounced in certain limits such as long-range potentials.[9] A picture which is useful, but as yet unproved is that the spinodal is a singularity in the complex plane for finite-range potentials which moves toward the real axis as the potential range increases.[9b,9c] We introduce this nonclassical mechanism via a mean-field model consisting of particles interacting with long-range repulsive potentials. The predictions of our model are then compared with the results in Refs. 1-3. We emphasize that our purpose is to introduce a conceptual framework which can be used to obtain a qualitative understanding of the phenomena described above and to propose additional simulations which are suggested by this point of view.

We begin by obtaining the free-energy functional appropriate to a system interacting with weak, long-range repulsive potentials[14,16] of the form $\gamma^d \phi(\gamma|\mathbf{x}|)$, where γ^{-1} is the range of the potential. In the limit $\gamma \to 0$, one obtains the mean-field theory[14] with its spinodal. The free energy in the grand canonical ensemble can then be computed from the one-particle distribution function $\rho(\mathbf{x})$ as follows[14]:

$$\beta F(\rho) = \gamma^{-d} \int d^d r_1 \left[\beta\mu\rho(\mathbf{r}_1) + \frac{\beta}{2} \int d^d r_2 \phi(|\mathbf{r}_1 - \mathbf{r}_2|)\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho(\mathbf{r}_1)\ln\rho(\mathbf{r}_1) - \rho(\mathbf{r}_1) \right], \tag{1}$$

where distances are measured in units of γ^{-1}. Functionally differentiating with respect to $\rho(\mathbf{r}_1)$ we obtain

$$\rho(\mathbf{r}_1) = z \exp\left[-\beta \int \phi(|\mathbf{r}_1 - \mathbf{r}_2|)\rho(\mathbf{r}_2)\, d^d r_2 \right], \tag{2}$$

where $z = \exp(-\beta\mu)$. For repulsive potentials it is known[14] that Eq. (2) has a constant solution $\rho(\mathbf{r}_1) = \rho$ for all values of z and β which is unique for a finite range of z about $z = 0$. At a particular value of $\rho\beta$ the solution of Eq. (2) bifurcates. This is associated with the spinodal of the metastable liquid in this mean-field system.[16] It occurs at that particular value of z (or β) at which the linearization of Eq. (2) around the constant solution has nontrivial solutions. These solutions are of the form $A\cos(\mathbf{k}_0 \cdot \mathbf{x})$, with $|\mathbf{k}_0| = k_0$ with k_0 defined by $\varepsilon \equiv 1 + \beta\rho\hat{\phi}(k_0) = 0$ and ρ is the constant solution to Eq. (2) at the bifurcation point and $\hat{\phi}(k)$ is the Fourier

transform of $\phi(|\mathbf{r}|)$. The bifurcation occurs at the lowest value of z where $\varepsilon=0$ for real k_0. This means that k_0 will be given by the lowest minimum of $\hat{\phi}(k)$; $\varepsilon=0$ then defines the spinodal.

In order to treat nucleation near the spinodal we take as our partition function

$$Z=\int \delta\rho(\mathbf{r})\exp[-\beta H(\rho(\mathbf{r}))],$$

where $\beta H(\rho(\mathbf{r}))$ is the right-hand side of Eq. (1). The interpretation is now somewhat different, as $\rho(\mathbf{r})$ is to be thought of now as a coarse-grained density in the Landau-Ginzburg sense.[17] The interaction term

$$(\beta/2)\int\int d^dr_1 d^dr_2 \phi(|\mathbf{r}_1-\mathbf{r}_2|)\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)$$

is now the interaction between two coarse-grained volumes of linear dimension γ^{-1} and the entropy term arises from integration over length scales small compared to γ^{-1}. In the limit $\gamma\to 0$ the functional integral in Z can be done by steepest-descent methods and nucleation can be described by the methods of analytic continuation.[12,18,19] The metastable state and the critical droplet are associated with saddle points of the Hamiltonian.

Since the Euler-Lagrange equation obtained by functional differentiation of Eq. (1) with respect to $\rho(\mathbf{r})$ is equivalent to Eq. (2), one has a connection (via Ref. 18) between the spatially dependent solutions of Eq. (2) and the critical droplet. Since the constant solution ρ ceases to be a minimum of the free-energy functional above its bifurcation value, it is natural to identify this point with a spinodal. We are interested in the nucleation process at $\varepsilon\sim 0$. Since we know that the solution of Eq. (2) is of the form $\rho+A\cos(\mathbf{k}_0\cdot\mathbf{r})$ at the spinodal, for small ε we expect only a slight modification to the spinodal solution. In k space then we expect the nonconstant part of the solution of Eq. (2) to be a function highly peaked around k_0. More specifically, we shall make the *Ansatz* that there are a finite number of vectors $\mathbf{k}_{0j}$, all having norm k_0, around which the solution of Eq. (2) is sharply peaked. Therefore we assume a solution to Eq. (2) of the form $\rho(\mathbf{r})=\rho+\psi(\mathbf{r})$. Since ρ is itself a solution of Eq. (2) we obtain

$$\beta\int d^dr_2\phi(|\mathbf{r}_1-\mathbf{r}_2|)\psi(\mathbf{r}_2)+\ln[1+\psi(\mathbf{r}_1)/\rho]=0. \quad (3)$$

We now assume that $\psi(\mathbf{r})$ is small and of the form $\psi(\mathbf{r})=(\sum_j a_j e^{(i\mathbf{k}_{0j}\cdot\mathbf{r})})\tilde{\psi}(r)$, where $\tilde{\psi}(r)$ is a slowly varying function on a length scale of k_0^{-1}. This will later be found to be self-consistent.

The Euler-Lagrange equation in the near-spinodal limit then becomes

$$\left[-a\beta\nabla^2\tilde{\psi}(\mathbf{r}_1)+\varepsilon\frac{\tilde{\psi}(\mathbf{r}_1)}{\rho}\right]\sum_j a_j\exp(i\mathbf{k}_{0j}\cdot\mathbf{r}_1)-\frac{\tilde{\psi}^2(\mathbf{r}_1)}{\rho^2}\left[\sum_j a_j\exp(i\mathbf{k}_{0j}\cdot\mathbf{r}_1)\right]^2+\cdots, \quad (4)$$

where $a=\phi''(\mathbf{k}_0)/2>0$ and we have expanded $\hat{\phi}(k)$ about k_0 and the logarithm about 1, keeping only the dominant nonlinear terms.

In order for Eq. (4) to have a solution when terms higher than quadratic are ignored we must choose the $\mathbf{k}_{0j}$ so that the projection of $(\sum_j a_j e^{(i\mathbf{k}_{0j}\cdot\mathbf{r}_1)})^2$ on $\sum_j a_j e^{(i\mathbf{k}_{0j}\cdot\mathbf{r}_1)}$ has norm $C\neq 0$. This can only be done in two dimensions by choice of the $\mathbf{k}_{0j}$ so that they form the reciprocal lattice basis which corresponds to a triangular or honeycomb lattice in real space.[20] In three dimensions a regular lattice structure can only be formed if the $\mathbf{k}_{0j}$ form the basis of a fcc lattice in reciprocal space and hence a bcc lattice in real space.[20]

With these choices of $\mathbf{k}_{0j}$ the function $\tilde{\psi}(r)$ is a solution of

$$-a\beta\nabla^2\tilde{\psi}(r)+\varepsilon\tilde{\psi}(r)/\rho-C\tilde{\psi}^2(r)/\rho^2=0. \quad (5)$$

This equation is of the same form as the Euler-Lagrange equation for the droplet profile in nucleation near the spinodal in Ising models and the liquid-gas transition.[12,13] The solution has the form[12] $\tilde{\psi}(r)=\varepsilon g(r/\xi)$, where $\xi\sim\varepsilon^{-1/2}$ is the correlation length at the spinodal and $g(r/\xi)\to 0$ as $r/\xi\to\infty$. When we combine the above results the critical droplet near the spinodal is of the form

$$\psi(\mathbf{r})=\sum_j a_j e^{(i\mathbf{k}_{0j}\cdot\mathbf{r})}\varepsilon g(r/\xi).$$

The interpretation of this result is that the critical droplet near the spinodal will be a small-amplitude fluctuation with a specific symmetry (bcc in $d=3$). Since the $\mathbf{k}=\mathbf{0}$ part of $\psi(\mathbf{r})$ is of second order in ε, the critical droplet will produce almost no effect in the thermodynamics. For example, we predict the appearance of a droplet with crystalline symmetry and no latent heat release. This is in contrast to the classical nucleation theory and in agreement with the results in Refs. 1 and 3.

The early-growth phase of the spinodal droplets can be studied with the methods of Langer.[18] The details will be given in a later publication.[21] The results are that the initial stage of growth involves a relatively rapid increase in the amplitude of the $\mathbf{k}_{0j}$ modes with a comparatively slow growth in the density. This would appear in simulations[1,3] as an initial period of structure-factor growth centered about k_0 with very little change in the thermodynamic parameters, followed by a thermodynamically measurable change, again agreeing with Refs. 1–3.

Another result relevant to the simulations is that the rate of droplet growth goes to zero as the spinodal is approached. This implies that critical slowing down affects the growth rate.[12] This would appear in the simulations as an increase in time lag between the appearance of

crystalline order and the release of the latent heat as $\varepsilon \rightarrow 0$. This may have been observed in Ref. 3 and will be discussed in detail below.

It is of considerable interest with regards to comparison with the simulations and other theoretical calculations to determine the properties of critical droplets when one is close to the spinodal but not in the asymptotic limit. This is facilitated by the fact that Eq. (5) is of the same form as found in the liquid-gas and Ising transitions. One can, therefore, adapt the results of Ref. 13. We describe the results here and leave the details for a later publication.[21]

As the quench at which nucleation takes place is moved away from the spinodal, the barrier to nucleation of a fcc lattice (which is infinite relative to the bcc barrier height at the spinodal) is reduced but remains large. Therefore in a large sample, in which many nucleating events take place, fcc droplets occur but would be rare. This is consistent with simulations[2] on a system of soft spheres with a fcc stable crystal phase. The nucleation and growth characteristics of the bcc droplet are qualitatively the same as those *at* the spinodal, with one difference. As the quench becomes shallower the droplet density increases. This increase takes the form of a denser core in the center of the droplet. The prediction of the theory as embodied in Eqs. (4) and (5) is that the droplet (for these slightly shallower quenches) will have a core in which the density is higher than that of the surrounding "halo" which is still at the liquid density. The structure of the droplet, both core and halo, will be bcc.

The final point we make about the properties of this type of nucleation concerns barrier heights. The free energy barrier is simple to obtain[11,12] and is proportional to $\gamma^{-d}[1+\beta\rho\hat{\phi}(k_0)]^{3-d/2}$. This is *not* obtained via the classical assumption of a surface tension which is independent of quench depth. In fact, the surface tension vanishes as the spinodal is approached. The implication is that the classical calculations of free-energy barriers in Refs. 2 and 3 which obtain barrier heights $\sim k_B T$ will not apply if the systems have been quenched into the spinodal region as we have been suggesting.

Our approach also provides a possible explanation of the finite size effects which seem to plague molecular dynamics simulations of crystal nucleation. This phenomenon has been explicitly discussed in a very interesting paper by Honeycutt and Andersen[3] who compare simulations done on Lennard-Jones systems of 500 and 1300 particles. They find that the critical droplet is not independent of the system size up to the 1300-particle systems they measure. They also find that both the time elapsed until the appearance of the critical droplet as well as the time between the droplet's appearance and the temperature elevation increase with system size. They offer as a possible explanation that a diffuse interface[7a,22] makes the effective size of the droplet larger than the size obtained by their methods. Our results would also support this interpretation. We can also understand the increase in the elapsed times cited above from our point of view. If, as we suggest, Honeycutt and Andersen are near a spinodal, critical slowing down should be an important factor in the dynamical evolution of the droplets.[12] Small system size will interfere with the critical aspects and cause a speeding up of the droplet evolution. As the system size is increased the finite size effects should be lessened and time scales would naturally increase. The effect we are describing depends on the proximity of a spinodal. It is not, in our view, a general characteristic of crystalline nucleation but will be sensitive to quench depth and rate. This suggests that the results of Refs. 1–3 may not be in conflict with Ref. 4 and that more attention should be paid to these factors in future simulations.

We have outlined a set of "experimental" facts and discussed the nucleation theory applicable to a system of particles interacting with weak long-range repulsive forces. The properties observed in the simulations are consistent with the predictions of our model. Such properties are not predicted in the classical theories which assume a clear distinction between the bulk crystalline part of the droplet and its surface. Some of the characteristics of the nucleation process we propose are similar to the properties of droplets found near the spinodals of Ising models interacting with long-range potentials. In light of this it is important to note that very long-range potentials in Ising models are not needed to see these effects in three dimensions. A range of 2–3 lattice spacings sufficed.[9,10] In addition there is some indirect evidence that Lennard-Jones systems behave as if they had a moderately long-range potential. This includes the rather diffuse interface between the crystalline and fluid phases[7a,22] and the small size of the asymptotic region at the liquid-gas critical point[23] of systems which are modeled reasonably well by the Lennard-Jones potential. These properties are often exhibited by systems with moderately long-range potentials.

We wish to stress that we are *not* claiming that systems such as Lennard-Jones have spinodals. Our point is that the "spinodal" singularity affects the nature of the nucleation process in certain circumstances even when it is physically unreachable. In this regard we are claiming that metastable liquids are behaving in a manner analogous to Ising models where this same effect occurs.

Finally, these results suggest several simulations that might be done to test the ideas we have presented. Measurement of the static-structure factor of metastable liquids would give some indication of possible spinodal behavior. Systematic investigation of the time lag between the occurrence of a droplet with crystalline symmetry and the onset of a temperature increase, coupled with a finite-scaling analysis would also provide a useful test of the ideas presented in this Letter. These considerations also indicate that the form of the critical

droplet is sensitive to the depth at which nucleation occurs. This would imply that more attention should be paid to the precise quench depth and rate.

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[1]M. J. Mandell, J. P. McTague, and A. Rahman, J. Chem. Phys. **66**, 3070 (1977).

[2]J. N. Cape, J. L. Finney, and L. V. Woodcock, J. Chem. Phys. **75**, 2366 (1981).

[3]J. D. Honeycutt and H. C. Andersen, J. Phys. Chem. **90**, 1585 (1986).

[4]C. S. Hsu and A. Rahman, J. Chem. Phys. **71**, 4974 (1979); R. D. Mountain and A. C. Brown, J. Chem. Phys. **80**, 2730 (1984). In the above reference Hsu and Rahman have also obtained results which appear to be consistent with classical nucleation theory for extremely deep quenches. It is not clear that the method of quench they employed allowed the system to remain in a metastable state. In addition, such deep quenches would take the system far from the region of influence of the spinodal singularity.

[5]T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B **19**, 2775 (1979).

[6]A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **74**, 2559 (1981).

[7a]P. Harrowell and D. W. Oxtoby, J. Chem. Phys. **80**, 1639 (1984).

[7b]A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **84**, 1769 (1986).

[8]M. Grant and J. D. Gunton, Phys. Rev. B **32**, 7299 (1985).

[9a]D. W. Heermann, W. Klein, and D. Stauffer, Phys. Rev. Lett. **49**, 1262 (1982).

[9b]J. D. Gunton and M. C. Yalabik, Phys. Rev. B **18**, 6199 (1978).

[9c]M. Novotny, W. Klein, and P. Rikvold, Phys. Rev. B **33**, 7729 (1986).

[10]D. W. Heermann and W. Klein, Phys. Rev. Lett. **50**, 1062 (1983); D. W. Heermann and W. Klein, Phys. Rev. B **27**, 1732 (1983).

[11]J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **31**, 688 (1959).

[12]C. Unger and W. Klein, Phys. Rev. B **29**, 2698 (1984).

[13]C. Unger and W. Klein, Phys. Rev. B **31**, 6127 (1985).

[14]N. Grewe and W. Klein, J. Math. Phys. **18**, 1729 (1977), and **18**, 1735 (1977). A similar result was derived for hard spheres in the limit $d \rightarrow \infty$ in W. Klein and H. L. Frisch, J. Chem. Phys. **84**, 968 (1986).

[15]W. Klein and A. C. Brown, J. Chem. Phys. **74**, 968 (1981).

[16]J. D. Gunton and M. C. Yalabik, Phys. Rev. B **18**, 6199 (1978).

[17]S.-k. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Merlo Park, CA, 1976).

[18]J. S. Langer, Ann. Phys. **41**, 108 (1967).

[19]For a review and a more comprehensive list of references, see J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8.

[20]S. Alexander and J. P. McTague, Phys. Rev. Lett. **41**, 702 (1978).

[21]F. Leyvraz and W. Klein, to be published.

[22]D. W. Oxtoby and A. D. J. Haymet, J. Chem. Phys. **76**, 6262 (1982).

[23]R. Hocken and M. R. Moldover, Phys. Rev. Lett. **37**, 29 (1976).