

Diffuse interface analysis of crystal nucleation in hard-sphere liquid

László Gránásy^{a)} and Tamás Pusztai

Research Institute for Solid State Physics and Optics, H-1525 Budapest, POB 49, Hungary

(Received 22 August 2002; accepted 17 September 2002)

We show that the increase of the interface free energy with deviation from equilibrium seen in recent Monte Carlo simulations [S. Auer and D. Frenkel, *Nature (London)* **413**, 711 (2001)] can be recovered if the molecular scale diffuseness of the crystal–liquid interface is considered. We compare two models, Gránásy’s phenomenological diffuse interface theory, and a density functional theory that relies on the type of Ginzburg–Landau expansion for fcc nucleation, that Shih *et al.* introduced for bcc crystal. It is shown that, in the range of Monte Carlo simulations, the nucleation rate of the stable fcc phase is by several orders of magnitude higher than for the metastable bcc phase, seen to nucleate first in other fcc systems. The nucleation barrier that the diffuse interface theories predict for small deviations from equilibrium is in far better agreement with the simulations than the classical droplet model. The behavior expected at high densities is model dependent. Gránásy’s phenomenological diffuse interface theory indicates a spinodal point close to glass transition, while a nonsingular behavior is predicted by the density functional theory with constant Ginzburg–Landau coefficients. Remarkably, a minimum of the nucleation barrier, similar to the one seen in polydisperse systems, occurs if the known density dependence of the Ginzburg–Landau coefficients is considered. © 2002 American Institute of Physics. [DOI: 10.1063/1.1519862]

Crystallization of nonequilibrium liquids starts with nucleation during which crystal-like fluctuations appear, whose formation is governed by the free-energy gain when transferring molecules from liquid to the crystal and the extra free energy γ needed to create the crystal–liquid interface. The fluctuations larger than a critical size have a good chance to reach macroscopic dimensions, while the smaller ones dissolve with a high probability. Since the critical size is normally in the nanometer range, direct observation of nucleation is very difficult. Recent experiments on colloidal suspensions, where the constituent particles are in the micrometer range (available for light scattering/microscopy) and their interaction closely mimics the hard-sphere (HS) behavior, revolutionize our understanding of crystal nucleation and growth.^{1,2} The nucleation rate, the features of critical fluctuations (nuclei), and their time evolution can be observed directly.² Further essential knowledge is gained from computer simulations that use the exact hard-sphere potential.^{3–5} In a recent paper, Auer and Frenkel⁴ show that, according to Monte Carlo (MC) simulations, nucleation in the hard-sphere system is suppressed by an increase of the interface free energy with deviation from equilibrium. So far no theoretical explanation has been put forward to account for this behavior.

In this paper we show that considering a diffuse crystal–liquid interface seen in computer simulations,⁶ the increase of the interface free energy with increasing driving force for crystallization can be recovered. We find, however, that the predictions in the high-density limit depend on the choice of model. In Gránásy’s diffuse interface theory, due to spinodal nucleation predicted at high densities, a maximum of the

interface free energy is expected above the range of volume fraction ($\phi \leq 0.5343$) MC simulations cover so far, whereas the density functional theory with constant Ginzburg–Landau coefficients predicts a monotonic behavior without spinodal. An increasingly steeper dependence of the interface free energy is found, however, that leads to a minimum in the height of the nucleation barrier, if the density dependence of the Ginzburg–Landau coefficients is taken into account.

We present two nonclassical approaches to model crystal nucleation in the HS system:

- (i) The phenomenological diffuse interface theory (DIT) relies on the assumptions that bulk properties exist at least at the center of critical fluctuations and that the distance of surfaces of zero excess enthalpy and entropy is independent of cluster size.⁷ The height of the nucleation barrier reads as

$$W^* = -\frac{4\pi}{3} \delta^3 \Delta g \psi, \quad (1)$$

where $\delta = \gamma v_S / \Delta H_f$, v_S is the molar volume of the solid, ΔH_f (>0) the molar heat of fusion, $\psi = 2(1+q)\xi^{-3} - (3+2q)\xi^{-2} + \xi^{-1}$, $q = (1-\xi)^{1/2}$, and $\xi = \Delta g / \Delta h$, while Δg and Δh (<0) are, respectively, the volumetric Gibbs free energy and enthalpy differences between the solid and liquid. This model has been tested extensively.^{8,9} It is in a considerably better agreement with vapor condensation experiments than the classical theory,⁸ and in the range of interest, it reproduced W^* predicted by density functional theory to a high accuracy.¹⁰ Besides the Cahn–Hilliard approach, the DIT is the only other approach that proved consistent with crystal nucleation experiments on a broad variety of substances including liquid metals, oxide glasses, and hydrocarbons.⁹ Provided that the

^{a)}Electronic mail: grana@power.szki.kfki.hu

interface free energy and the thermodynamic properties (Δg and Δh) are known, the nucleation barrier can be calculated without adjustable parameters.

- (ii) We develop a density functional approach based on a Ginzburg–Landau expanded free energy that Shih *et al.*¹¹ proposed for bcc structure. The excess free energy of the crystal is expanded in terms of the Fourier amplitudes of the crystal density. Retaining only the dominant (110) density waves (nearest-neighbor approximation in the reciprocal space), the excess free energy of the inhomogeneous system reads as $\Delta\omega = a_2 m^2 + a_3 m^3 + a_4 m^4$, where the structural order parameter $m = u/u_0 \in [0,1]$ is the (110) Fourier amplitude normalized with its value in the crystal. We generalize this for first-order phase transitions via prescribing $\Delta\omega(1) = \Delta g$ and $\partial\Delta\omega/\partial m|_1 = 0$, where Δg is the volumetric Gibbs free energy difference between the bulk liquid and crystal. Considering these, we obtain $\Delta\omega = a_2(m^2 - 2m^3 + m^4) + \Delta g(4m^3 - 3m^4)$. Relying on the square-gradient approximation the excess free energy of the inhomogeneous system reads as

$$W_{\text{DFT}} = \int d\mathbf{r}^3 \{ \Delta\omega[m(\mathbf{r})] + c(\nabla m)^2 \}. \quad (2)$$

Provided that the interface free energy and the 10%–90% thickness of the interface, d , are known in equilibrium, the remaining two parameters of the model (a_2 and c) can be fixed,¹² and the calculation be made without adjustable parameters. As pointed out by Shih *et al.*,¹¹ this approach implicitly incorporates other Fourier components to lower order, including the density change $\eta = (\phi - \phi_L)/(\phi_S - \phi_L)$, where ϕ and ϕ_L are the local volume fraction and the volume fraction of the initial liquid, respectively, while ϕ_S is the volume fraction of the solid that is in mechanical equilibrium with the initial liquid [$p_L(\phi_L) = p_S(\phi_S)$, $p_L(\phi)$, and $p_S(\phi)$ are the respective equations of state]. Furthermore, the square-gradient term for the density change is negligible in the free-energy expansion; therefore, $\eta \propto m^2$,¹¹ while the respective coefficient has to be chosen so that the bulk density change is recovered. The critical fluctuation (nucleus) represents a saddle point of the W_{DFT} functional. The respective $m(\mathbf{r})$ emerges as a nontrivial solution of the Euler–Lagrange equation $0 = \partial\Delta\omega/\partial m - 2c\nabla^2 m$ under boundary conditions $m \rightarrow m_0$ for $|\mathbf{r}| \rightarrow \infty$ and $\nabla m \rightarrow 0$ for $|\mathbf{r}| \rightarrow 0$, where $m_0 = 0$ is the order parameter of the supersaturated liquid. Assuming spherical symmetry (reasonable approximation considering the weak anisotropy of γ ¹³), the Euler–Lagrange equation reduces to an ordinary differential equation, which has been solved here by a variable fourth/fifth-order Runge–Kutta method. While the work of Alexander and McTague¹⁴ and recent analyses¹⁵ indicate that in simple liquids the bcc phase is a precursor to fcc solidification, as confirmed for the Lennard–Jones system,¹⁶ even the smallest hard-sphere crystallites

show negligible bcc fraction.³ Therefore, the main virtue of this model is that it delivers information on the nucleation of the metastable bcc phase.

To address fcc solidification, we introduce an analogous single-order-parameter density functional theory, which relies on the nearest-neighbor approximation in reciprocal space. Since the (111) reciprocal lattice vectors cannot form an equilateral triangle, the coefficient of the m^3 term is zero¹¹ and only second- and fourth-order terms occur. To obtain a first-order phase transition, one needs to incorporate higher order terms allowed by fcc symmetry, of which the lowest order is the sixth-order term. Making the same assumptions as in deriving the theory for bcc structure, one finds that the local grand potential density has the form $\Delta\omega = a_2(m^2 - 2m^4 + m^6) + \Delta g(3m^4 - 2m^6)$. Apart from the explicit form of $\Delta\omega$, the formulation and solution of the problem is the same as for the bcc structure.

Application to hard spheres: For the fcc structure, the Gibbs free-energy difference between the solid and liquid (the driving force of crystallization) has been obtained by integrating the equations of state by Hall,¹⁷ starting from the volume fractions of the coexisting solid and liquid $\phi_{\text{fcc,coex}} = 0.546$ and $\phi_{\text{L,coex}} = 0.494$ at pressure $p = 12kT/\sigma^3$. The corresponding enthalpy density difference can be expressed as $\Delta h = p_L(\phi)[v_S(\phi_S) - v_L(\phi)]/v_S(\phi_S)$, where v_L is the molar volume of the liquid. For the bcc solid, we used the equation of state $p_{\text{bcc}}v/kT = 2.33731/(0.72047 - \phi)$, obtained by least-square fitting to the simulation data of Woodcock.¹⁸ The coexisting bcc and liquid volume fractions at equilibrium pressure $p = 14.5kT/\sigma^3$ are $\phi_{\text{bcc,coex}} = 0.551$ and $\phi_{\text{L,coex}} = 0.517$, respectively.

The free energy of the HS fcc crystal–liquid interface is known for several orientations from the molecular dynamics simulations of Davidchack and Laird:¹³ $\gamma_{\text{fcc}}\sigma^3/kT = 0.58 \pm 0.01$, 0.62 ± 0.01 , and 0.64 ± 0.01 for the (111), (100), and (110) interfaces, respectively (σ is the HS diameter). Considering that the nuclei tend to minimize their interfacial free-energy contribution, we perform isotropic calculations with $\gamma_{\text{fcc}}\sigma^3/kT = 0.58$. Mainly due to the smaller entropy of fusion, the free energy of the bcc crystal–liquid interface is smaller $\gamma_{\text{bcc}}\sigma^3/kT = 0.47$, as predicted by the density functional theory.¹⁹ Unfortunately, the density functional theory overestimates the bcc entropy of fusion ($0.98k$ versus the exact $0.9k$), and thus the interfacial free energy. Utilizing that $\gamma \propto \Delta S_f$,¹¹ we use here a corrected value, $\gamma_{\text{bcc}}\sigma^3/kT = 0.43$.

The order-parameter profiles at the equilibrium hard-sphere crystal–liquid interface have been studied by Davidchack and Laird using molecular dynamics simulations.⁶ In agreement with DFT,¹⁹ it is found that for the orientational order, diffusion, and coarse-grained density profiles the 10%–90% thickness is about 3.1 – 3.3σ .⁶ We adopt here $d_{\text{fcc}} = 3.2\sigma$. The bcc–liquid interface is considerably broader, $d_{\text{bcc}} = 5.3\sigma$.¹⁹

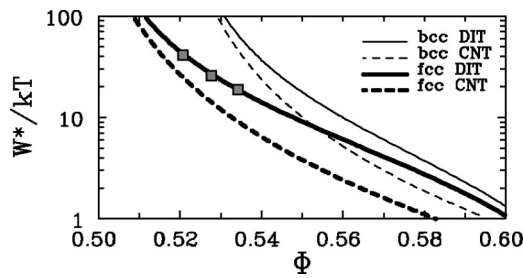


FIG. 1. Height of the nucleation barrier vs initial volume fraction of liquid for fcc and bcc phases as predicted by the diffuse interface theory (DIT) and the classical nucleation theory (CNT). For comparison, results from MC simulations (Ref. 4) are also shown (squares).

Utilizing these, the DIT and the DFT predictions for the nucleation barriers W_{bcc}^* and W_{fcc}^* are free of adjustable parameters.

The nucleation barriers predicted for fcc and bcc structures by the DIT and DFT are shown as a function of volume fraction in Figs. 1 and 2. For comparison, the predictions of the classical nucleation theory (CNT) $W_{CNT}^* = (16\pi/3)\gamma^3\Delta g^{-2}$ and the exact results from Monte Carlo simulations⁴ are also presented. The W^* values predicted by the DIT and the DFT for the fcc structure are in remarkable agreement with the MC results. Unlike the Lennard-Jones system, where the bcc phase is a precursor of fcc solidification, in the HS system the high nucleation barrier predicted for the bcc phase prevents bcc solidification. (The rate of bcc nucleation is further reduced if the uncorrected $\gamma_{bcc}\sigma^3/kT = 0.47$ is used.) This finding is in full agreement with MC simulations and experiment. While the classical nucleation theory predicts similar relationship between the barrier heights for fcc and bcc nucleation, W_{fcc}^* is too low, while W_{bcc}^* is far too high when compared to the MC results. Since the nucleation rate is proportional to $\exp(-W^*/kT)$, these differences amount to several orders of magnitude. Note that the MC data for W^*/kT were obtained directly by “umbrella sampling;” therefore, possible uncertainties associated with the nucleation prefactor²⁰ do not plague them. The radial order parameter and density profiles corresponding to the volume fractions used in MC simulations (0.5207, 0.5277, and 0.5343) are shown for fcc and bcc structures in Fig. 3. While the fcc profiles are in reasonable agreement with the respective critical fluctuation from MC simulation (Fig. 3 of Ref. 3), the corresponding bcc nucleus is far too large.

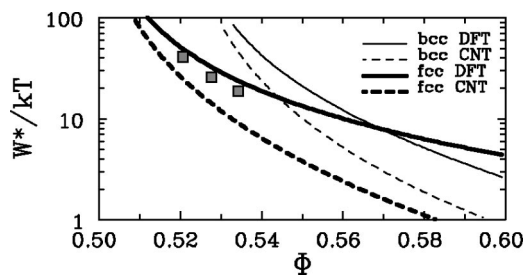


FIG. 2. Height of the nucleation barrier vs initial volume fraction of liquid for fcc and bcc phases as predicted by the density functional theory (DFT) and the classical nucleation theory (CNT). For comparison, results from MC simulations (Ref. 4) are also shown (squares).

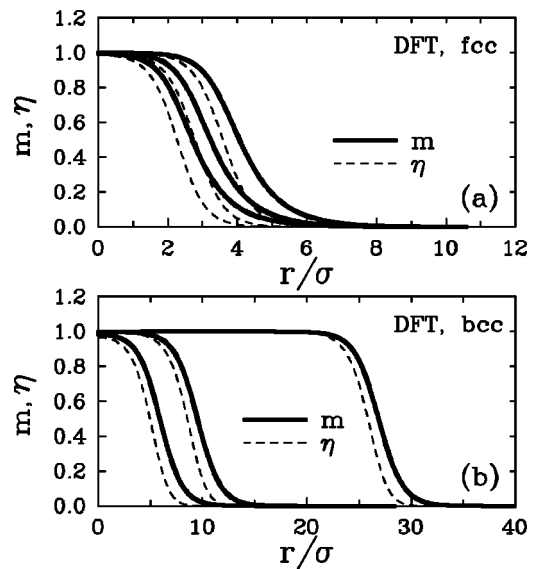


FIG. 3. Radial order parameter (m) and fractional density change η profiles for the critical fluctuations (nuclei) predicted by the density functional theory with constant Ginzburg–Landau coefficient at $\phi=0.5207$, 0.5277 , and 0.5343 . (a) fcc phase. (b) bcc phase.

It is thus demonstrated that for fcc nucleation, the models which incorporate a diffuse crystal–liquid interface are able to quantitatively predict the height of the nucleation barrier at small supersaturation. Considering the crudeness of the single-order-parameter model, the agreement with MC simulations is rather satisfactory. We mention that a different extension of the Ginzburg–Landau model by Iwamatsu and Horii²¹ breaks down at medium supersaturations when adopted for fcc structure: A spinodal-like behavior is predicted for $\phi_{\text{spinodal, fcc}} \approx 0.565$. While no simulation data are available for this range, experiments on colloidal suspensions clearly rule out the presence of a spinodal point at this volume fraction. The nonclassical predictions are in conflict at high supersaturations: The DIT displays a spinodal-like behavior at $\phi_{\text{spinodal, fcc}} \approx 0.629$ and $\phi_{\text{spinodal, bcc}} = 0.631$, which falls between the volume fractions for glass transition ($\phi_g \approx 0.58$)²² and dense random packing ($\phi_{\text{DRP}} \approx 0.644$). In contrast, the DFT predicts a monotonically increasing interfacial free energy (Fig. 4) for all physically achievable densities. For polydisperse HS systems Auer and Frenkel observed⁴ a

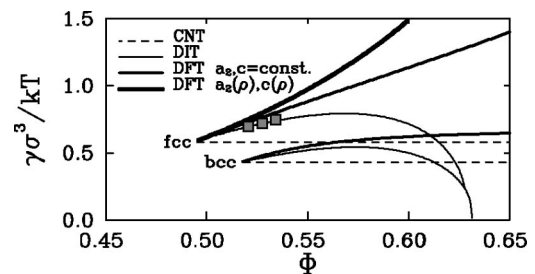


FIG. 4. Interface free energy of fcc and bcc critical fluctuations vs volume fraction predicted by the diffuse interface and density functional theories (with constant and density dependent Ginzburg–Landau coefficients). For comparison, the results from MC simulations (Ref. 4) (squares) and the equilibrium values used in the classical nucleation theory (dashed) are also shown.

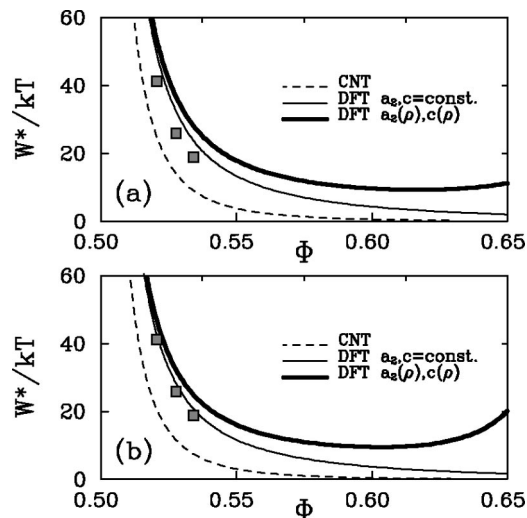


FIG. 5. The effect of density dependence of Ginzburg–Landau parameters on the height of the nucleation barrier for fcc phase: (a) Percus–Yevick approximation and the equations of state by Hall (Ref. 17); (b) with state-of-the-art structural properties and equations of state (Ref. 23). For comparison, the results from MC simulations (Ref. 4) (squares) and the predictions of the classical nucleation theory (dashed) are also shown.

minimum in the nucleation barrier, and raised the possibility that such behavior might be observed in the monodisperse case as well. It is interesting to note that such a behavior can be recovered, if the density dependence of the Ginzburg–Landau parameters is taken into account (Fig. 5): As pointed out by Shih *et al.*,¹¹ $a_2 \propto S^{-1}(K_{111})$ and $c \propto C''(K_{111})$, where S and C'' are the liquid structure factor and the second derivative of the liquid direct correlation function with respect to the wave number taken at the first neighbor distance in reciprocal space. First, we take them from the Percus–Yevick approximation. The predicted $W_{\text{fcc}}^*(\phi)$ shows a minimum [Fig. 5(a)], which becomes more pronounced and the numerical agreement with MC simulation improves, if more accurate equation of states and structural properties²³ are used [Fig. 5(b)].

The authors thank Professor D. W. Oxtoby for the enlightening discussions. This work was supported by the ESA Prodex Contract No. 14613/00/NL/SFe, by the Hungarian Academy of Sciences under Contract No. OTKA-T-037323, and forms part of the ESA MAP Project No. AO-99-101.

- ¹D. J. W. Aastuen, N. A. Clark, L. K. Cotter, and B. J. Ackerson, *Phys. Rev. Lett.* **57**, 1733 (1986); K. Schatzel and B. J. Ackerson, *Phys. Rev. E* **48**, 3766 (1993); D. Rosenbaum, P. C. Zamora, and C. F. Zukoski, *Phys. Rev. Lett.* **76**, 150 (1996); J. L. Harland and W. van Meegen, *Phys. Rev. E* **55**, 3054 (1997); P. Bartlett and P. B. Warren, *Phys. Rev. Lett.* **82**, 1979 (1999); Review: T. Palberg, *J. Phys.: Condens. Matter* **11**, R323 (1999).
- ²U. Gasser, E. R. Weeks, A. Schofield, P. N. Pusey, and D. A. Weitz, *Science* **292**, 258 (2001).
- ³S. Auer and D. Frenkel, *Nature (London)* **409**, 1020 (2001).
- ⁴S. Auer and D. Frenkel, *Nature (London)* **413**, 711 (2001).
- ⁵D. W. Oxtoby, *Nature (London)* **413**, 694 (2001).
- ⁶R. L. Davidchack and B. B. Laird, *J. Chem. Phys.* **108**, 9452 (1998).
- ⁷L. Gránásy, *J. Non-Cryst. Solids* **162**, 201 (1993); *J. Phys. Chem.* **100**, 10768 (1996).
- ⁸L. Gránásy, *Europhys. Lett.* **24**, 121 (1993); *J. Comput. Phys.* **104**, 5188 (1996).
- ⁹L. Gránásy and F. Igloi, *J. Chem. Phys.* **107**, 3634 (1997); L. Gránásy and P. F. James, *Proc. R. Soc. London, Ser. A* **454**, 1745 (1998).
- ¹⁰V. Talanquer and D. W. Oxtoby, *J. Phys. Chem.* **99**, 2865 (1995).
- ¹¹W. H. Shih, Z. Q. Wang, X. C. Zeng, and D. Stroud, *Phys. Rev. A* **35**, 2611 (1987).
- ¹²For bcc: $a_2 = (3/2^{1/2})\gamma/\delta$ and $c = 6\gamma\delta/2^{1/2}$, where $\delta = d/[2^{5/2}\text{atanh}(0.8)]$; for fcc: $a_2 = (2/3^{1/2})\gamma/\delta$ and $c = 6\gamma\delta/3^{1/2}$, where $\delta = d/\{3^{1/2}[1.5 \ln(9) - 0.5 \ln(1.9/1.1)]\}$.
- ¹³R. L. Davidchack and B. B. Laird, *Phys. Rev. Lett.* **85**, 4751 (2000).
- ¹⁴S. Alexander and J. McTague, *Phys. Rev. Lett.* **41**, 702 (1978).
- ¹⁵B. Groh and B. Mulder, *Phys. Rev. E* **59**, 5613 (1999); W. Klein, *ibid.* **64**, 056110 (2001).
- ¹⁶P. R. ten Wolde, M. J. Ruiz-Montero, and D. Frenkel, *Phys. Rev. Lett.* **75**, 2714 (1995); Y. C. Shen and D. W. Oxtoby, *ibid.* **77**, 3585 (1996).
- ¹⁷K. R. Hall, *J. Chem. Phys.* **57**, 2252 (1972).
- ¹⁸L. V. Woodcock, *Faraday Discuss.* **106**, 325 (1997).
- ¹⁹D. W. Marr and A. P. Gast, *J. Chem. Phys.* **99**, 2024 (1993).
- ²⁰L. S. Bartell, *Annu. Rev. Phys. Chem.* **49**, 43 (1998).
- ²¹M. Iwamatsu and K. Horii, *J. Phys. Soc. Jpn.* **65**, 2311 (1996); **66**, 1210 (1997).
- ²²P. N. Pusey and W. van Meegen, *Phys. Rev. Lett.* **59**, 2083 (1987).
- ²³S. B. Yuste and A. Santos, *Phys. Rev. A* **43**, 5418 (1991); S. Bravo Yuste, M. López de Haro, and A. Santos, *Phys. Rev. E* **53**, 4820 (1996).