

Theoretical prediction of crystallization kinetics of a supercooled Lennard-Jones fluid

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The first order curvature correction to the crystal-liquid interfacial free energy is calculated using a theoretical model based on the interfacial excess thermodynamic properties. The correction parameter (δ), which is analogous to the Tolman length at a liquid-vapor interface, is found to be 0.48 ± 0.05 for a Lennard-Jones (LJ) fluid. We show that this curvature correction is crucial in predicting the nucleation barrier when the size of the crystal nucleus is small. The thermodynamic driving force ($\Delta\mu$) corresponding to available simulated nucleation conditions is also calculated by combining the simulated data with a classical density functional theory. In this paper, we show that the classical nucleation theory is capable of predicting the nucleation barrier with excellent agreement to the simulated results when the curvature correction to the interfacial free energy is accounted for. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5021944>

I. INTRODUCTION

The quest for new crystalline materials for technological applications has drawn immense attention of researchers for many years. One of the major hindrances of growing a material with desired physical properties is the inadequacy of the knowledge of atomic scale mechanisms of crystal nucleation and growth.

The mechanism of growing a stable crystalline cluster in a metastable phase is controlled by two competing factors: The interfacial free energy (γ) cost to create the interface and the thermodynamic driving force due to the metastability of the liquid phase.^{1–5} The latter is given by the difference of chemical potentials ($\Delta\mu = \mu_c - \mu_l$) of bulk crystal (μ_c) and liquid (μ_l) phases. In this context, a thermodynamic description of the formation of crystallites in a metastable phase is well formulated by the Classical Nucleation Theory (CNT).^{5–8} According to the CNT, the Gibbs free energy cost to create a crystallite of N atoms out of a metastable phase (supercooled liquid) is given by

$$\Delta G = \gamma A + N\Delta\mu, \quad (1)$$

where A is the area of the crystal-liquid interface.

However, many attempts of testing the CNT may lack an accurate estimation of the γ , especially its curvature dependence. For example, the often used γ approximation from a planar interface (γ_0) for spherical crystallites is indeed incapable of predicting the simulation and experimental results.^{9–11} Parameter fitting of the simulation data to the functional form of Eq. (1) also suggests significant deviation of γ from its

planar value.^{12–14} It has also been reported that the non-spherical shapes of the crystallites could be a source of the problem.¹⁵ Therefore, the role of curvature dependence of γ for a crystal-liquid interface in CNT is not resolved yet. The planar limit of the crystal-liquid interfacial free energy (γ_0) has been studied extensively for several model materials including the LJ fluid.^{16–19} However direct calculation of the curvature dependence of crystal-liquid interfacial free energy has not been reported in the literature to the best of our knowledge.

In this paper, a theoretical model is developed and tested to calculate the curvature dependence of γ at a crystal-liquid interface. The first order correction to the γ_0 due to the curvature ($1/R$, R is the radius of the crystallite) can be expressed as

$$\gamma(R, T) = \gamma_0(T) \left(1 + \frac{2\delta}{R} \right), \quad (2)$$

where δ is called the Tolman length²⁰ in analogous to the liquid-vapor interface. To the lowest order, we assume that the temperature dependence of δ is negligible. As the main result of this paper, an analytical expression for the constant δ is derived from an equilibrium thermodynamic approach. Then the value of δ is calculated using a spherical shape crystalline cluster which coexists with its liquid in atomistic simulations. We show that this curvature correction is crucial in predicting the nucleation barrier when the size of the crystallites is small. Furthermore, the driving force ($\Delta\mu$) corresponding to known simulation conditions¹² is calculated by combining the simulated data with a classical density functional theory.²¹ These independently calculated values of δ , $\Delta\mu$, and γ_0 are used to predict the nucleation barrier within the CNT. Our theoretically predicted nucleation barrier is in good agreement with the simulated nucleation barrier.¹²

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II. THEORY

The formulation of Laird *et al.*¹⁶ for a planar interface is extended to a spherical interface under the hydrostatic condition in the crystalline region; namely, the interfacial free energy of a spherical interface is derived in terms of excess quantities of the interface, which can be measured from molecular simulations.

We assume that the shape of the crystal cluster is nearly spherical in which the two principal radii are equal. The thermodynamics of interfaces can be formulated by adapting a spherical Gibbs dividing surface from the center of the crystalline cluster that separates the crystalline and the liquid phases. The interfacial free energy per unit area (γ) can be given by^{8,16}

$$\gamma = e - T\eta - \mu\Gamma, \quad (3)$$

where e , η , and Γ are the interfacial excess energy per unit area, entropy per unit area, and number of particles per unit area, respectively. The temperature (T) and the chemical potential (μ) are the values under the coexistence condition of the interfacial system. The interfacial excess quantities are defined as follows:

$$eA = E - \rho_s^E V_s - \rho_l^E V_l, \quad (4)$$

$$\eta A = S - \rho_s^S V_s - \rho_l^S V_l, \quad (5)$$

$$\Gamma A = N - \rho_s V_s - \rho_l V_l, \quad (6)$$

where ρ_s^E (ρ_l^E), ρ_s^S (ρ_l^S), and ρ_s (ρ_l) are the energy, entropy, and number densities in the bulk solid (liquid) and V_s and V_l are the volume of the solid and liquid phases with respect to the Gibbs dividing surface with radius R which is defined by letting $\Gamma = 0$ or $N = N_s + N_l$ as $V = V_s + V_l$. E and S are the total energy and entropy of the system, respectively. A , V , and N are interfacial area, volume, and the total number of particles of the system, respectively. Thus the γ can be expressed as¹⁶

$$\gamma = e - T\eta. \quad (7)$$

Following Cahn,^{16,22} the interfacial thermodynamics can also be reformulated in a differential form equivalently for a spherical Gibbs dividing surface. The Gibbs free energy of the system containing a spherical crystalline cluster can be expressed as

$$G = E - TS + P_s V_s + P_l V_l, \quad (8)$$

where P_s (P_l) are the pressure of the solid (liquid) phase. The Gibbs free energy of the bulk phases without the interface can be written as

$$G_b = N\mu. \quad (9)$$

By subtracting Eq. (9) from Eq. (8), the interface free energy can be written as

$$\gamma A = G - G_b = E - TS + P_s V_s + P_l V_l - N\mu. \quad (10)$$

The total differential of the γA can be written as

$$d(\gamma A) = dE - TdS - SdT + P_s dV_s + P_l dV_l + V_s dP_s + V_l dP_l - \mu dN - Nd\mu. \quad (11)$$

For a crystalline cluster under hydrostatic conditions surrounded by its liquid, we can write

$$dE = TdS - P_s dV_s - P_l dV_l + \sum_{ij=1,2} (\sigma_{ij} - \delta_{ij}\sigma_{33}) V d\epsilon_{ij} + \mu dN, \quad (12)$$

where σ_{ij} and ϵ_{ij} are the ij components (mutually orthogonal) of the stress and the strain tensors in the plane of the interface. σ_{33} represents the component of the stress tensor perpendicular to the interface. This equation is a generalization of the Frolov and Mishin²³ and Laird *et al.*¹⁶ formulation for a planar interface. It should be noted that the fourth term in Eq. (12) represents the interfacial contribution to the mechanical work of the system, thus implicitly containing an integration over the interfacial region at constant volume as the strain tensor is traceless. Subtracting Eq. (12) from Eq. (11) yields

$$d(\gamma A) = -SdT + V_s dP_s + V_l dP_l + \sum_{ij=1,2} (\sigma_{ij} - \delta_{ij}\sigma_{33}) V d\epsilon_{ij} - Nd\mu. \quad (13)$$

Using the Gibbs-Duhem equation for the bulk solid and the liquid phases,

$$-S_s dT + V_s dP_s - N_s d\mu = 0, \quad (14)$$

$$-S_l dT + V_l dP_l - N_l d\mu = 0, \quad (15)$$

and the Gibbs dividing surface^{16,22} condition $N = N_s + N_l$, subtracting Eqs. (14) and (15) from Eq. (13) yields

$$d(\gamma A) = -\eta A dT + \sum_{ij=1,2} (\sigma_{ij} - \delta_{ij}\sigma_{33}) V d\epsilon_{ij}, \quad (16)$$

which is an equivalent differential form of Eq. (7).

For a spherical interface, we assume that the two tangential components of the strain tensor are equal $d\epsilon_{11} = d\epsilon_{22} = d\epsilon = dA/2A$, then

$$d(\gamma A) = -\eta A dT + (\sigma_{11} + \sigma_{22} - 2\sigma_{33}) V \frac{dA}{2A} \quad (17)$$

or

$$\frac{1}{A} d(\gamma A) = -\eta dT + \bar{\tau} \frac{dA}{A}, \quad (18)$$

where $\bar{\tau} = (\sigma_{11} + \sigma_{22} - 2\sigma_{33})V/(2A)$ is the interfacial stress, which is calculated as $\bar{\tau} = R \int_0^\infty \frac{2\tau(r)}{r} dr$ with mechanical equilibrium condition²⁴ and $\tau(r) = (\sigma_{11}(r) + \sigma_{22}(r) - 2\sigma_{33}(r))/2$ being the excess stress in the system. Due to the spherical symmetry of the growing crystalline cluster in liquid, the off-diagonal components of the stress tensor are assumed negligible. The calculation of the stress tensor of the simulated spherical cluster indeed confirms that the off-diagonal components are smaller than the diagonal terms by several orders of magnitudes.

As $\gamma = e - T\eta$, we have

$$\frac{1}{A} d(\gamma A/T) = -\frac{e}{T^2} dT + \frac{\bar{\tau}}{T} \frac{dA}{A}, \quad (19)$$

where e and $\bar{\tau}$ are the curvature dependent excess energy and interfacial stress, respectively. Along the coexistence path, Eq. (19) can be written as

$$\frac{1}{A} \frac{d(\gamma A/T)}{dT} = -\frac{e}{T^2} + \frac{\bar{\gamma}}{T} \frac{1}{A} \frac{dA}{dT}. \quad (20)$$

Using Eq. (2), the derivative of γ with respect to temperature can be expressed as

$$\frac{d\gamma}{dT} = \frac{d\gamma_0}{dT} \left(1 + \frac{2\delta}{R}\right) - \frac{2\gamma_0\delta}{R^2} \frac{dR}{dT}, \quad (21)$$

where we assume that the Tolman length δ does not depend on temperature. Combining Eqs. (21) and (20), we find

$$\delta = \frac{\frac{-e}{T^2} + \frac{\bar{\gamma}}{T} \frac{1}{A} \frac{dA}{dT} - \left(\frac{1}{T} \frac{d\gamma_0}{dT} + \frac{\gamma_0}{T} \frac{1}{A} \frac{dA}{dT} - \frac{\gamma_0}{T^2}\right)}{\frac{2}{R} \left(\frac{1}{T} \frac{d\gamma_0}{dT} + \frac{\gamma_0}{T} \frac{1}{A} \frac{dA}{dT} - \frac{\gamma_0}{T^2}\right) - \frac{2\gamma_0}{R^2 T} \frac{dR}{dT}}, \quad (22)$$

where $\frac{dR}{dT}$ is the change of the spherical radius with temperature. As the differential dA/A accounts for a small change of the strain in the interfacial region, the derivative dA/dT can be estimated from the density change of the bulk solid along the coexistence path of the system. Since the surface area of a spherical cluster containing N_s atom can be written as $A = 4\pi(3N_s/4\pi\rho_s(T))^{2/3}$, we find

$$\frac{1}{A} \frac{dA}{dT} = \frac{-2}{3\rho_s} \frac{d\rho_s}{dT}. \quad (23)$$

Equation (22) is the major result of the paper, which expresses the Tolman length δ in terms of interfacial excess quantities which can be measured from simulations.

III. SIMULATION METHODOLOGY AND RESULTS

Nearly spherical crystalline clusters can be realized with NVT conditions in classical molecular dynamics (MD) simulations.²⁵ Thermodynamic equilibrium of a spherical crystalline cluster with its liquid was achieved via the finite size effect.²⁶ The LJ pair potential due to Broughton and Gilmer is used to describe the atomic interactions²⁷ and all the measurements in this paper are in LJ units. The typos in some parameters of the above LJ potential are corrected as described in Ref. 16. This potential has been used in previous studies to study the interfacial properties of planar interfaces¹⁶ and nucleation barrier.¹² In Fig. 1, a snapshot of the spherical crystalline nucleus which coexists with its liquid at total density 0.8722 and $T = 0.64$ is shown. The crystalline atoms are determined by analyzing the common neighbors within the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package;^{28,29} namely, atoms belonging to the crystalline region have a fcc or hcp structure. All the atoms inside the outermost boundary of the crystalline region are considered to belong to the crystalline phase. The geometric center of the cluster is calculated from these identified atoms, and it is considered as the origin of the spherical coordinate system during the rest of the calculation. Once the origin of the coordinate systems is identified, the above separation of crystalline and liquid phases is not required for further analysis.

Figure 3(c) shows the radial distribution of the atomic number density from the center of the crystalline cluster at $T = 0.64$. The bulk properties of the crystal and the liquid phases were calculated using a small spherical region inside the crystalline cluster and a thin shell in the outermost liquid

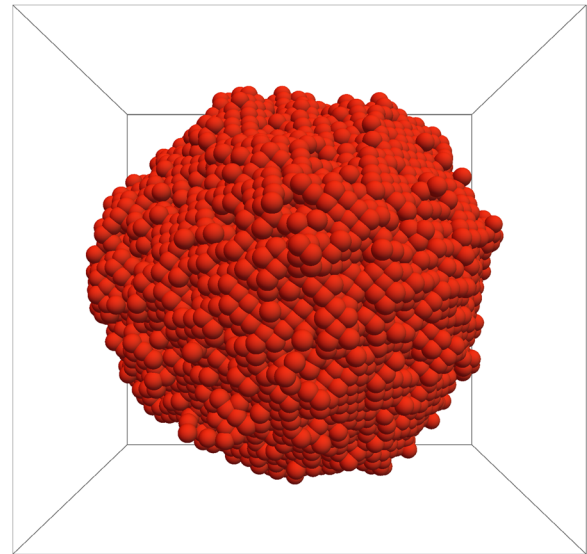


FIG. 1. A spherical crystalline cluster coexists with its liquid at $T = 0.64$. The length of the cubic simulation box is 48.4433σ , and the total number of particles is 99 159. The crystalline cluster has approximately 17 000 particles.

region. The calculated atomic number density of the crystalline (liquid) phase at temperatures $T = 0.62, 0.63$, and 0.64 are $0.9536(0.8479)$, $0.9562(0.8525)$, and $0.9577(0.8556)$, respectively. The spherical nucleus melts when the temperature is increased beyond $T = 0.64$. In this narrow temperature range, a linear fit is used to describe the atomic density as a function of temperature. They are $\rho_s(T) = 0.83260 + 0.19553 \times T$ and $\rho_l(T) = 0.62178 + 0.36524 \times T$ for crystal and liquid phases, respectively. The radius of the spherical crystalline cluster (R) is calculated using the lever rule with above densities, which is consistent with the Gibbs dividing surface definition. Figure 2(a) depicts the variation of R against temperature. The calculated value of R at $T = 0.64$ is 16.43σ .

The energy densities in crystalline and liquid phases are given by ρ_s^E and ρ_l^E , respectively. These energy densities were calculated in the regions specified above. The fluctuations of

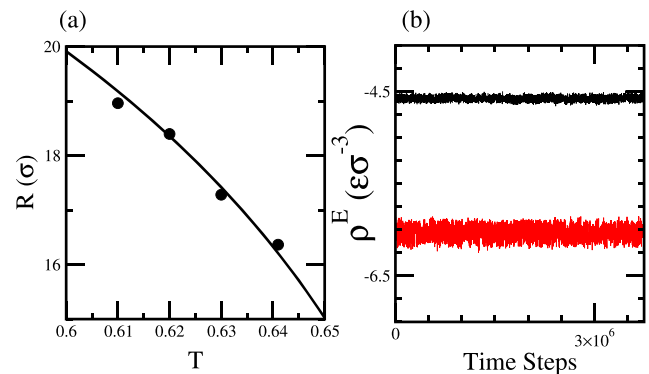


FIG. 2. (a) Temperature dependence of the radius (R) of the crystalline sphere. The R is calculated using the lever rule. The solid line is obtained by a fitting to the data points. At $T = 0.64$, we have $R = 16.43$ and $dR/dT = -110.7$. (b) Fluctuations of total energy density as a function of the simulation time. The top curve is for the liquid region, and the bottom curve is for the crystalline region.

ρ_s^E and ρ_l^E against the simulation time are plotted in Fig. 2(b). These fluctuations are steady over the time of the simulation, which is a good indication of the phase stability of the crystalline cluster. The interfacial excess energy per unit surface area e is calculated using Eq. (4), where $V_s = 4/3\pi R^3$, $V_l = V - V_s$, and $A = 4\pi R^2$. V is the volume of the simulation box, thus V_s and V_l are equivalent to be calculated according to the lever rule. The calculated interfacial excess energy is $e = 0.092 \pm 0.005 \epsilon \sigma^{-2}$ at $T = 0.64$.

The stress distribution in the system is calculated as described below. First, the six inequivalent components of the pressure tensor (p_{xx} , p_{yy} , p_{zz} , p_{xy} , p_{yz} , and p_{zx}) for each atom are calculated in the Cartesian coordinate system. Then the full pressure tensor of each atom is constructed and transformed into a spherical coordinate system. The resultant components of the pressure tensor in the spherical coordinate system are given by p_{rr} , $p_{\theta\theta}$, $p_{\phi\phi}$, $p_{r\theta}$, $p_{\theta\phi}$, and $p_{\phi r}$. The center of mass of the crystalline sphere is considered as the origin of both coordinate systems. It is found that the magnitude of the off-diagonal terms of the pressure tensor is negligible compared to the diagonal terms due to the spherical symmetry of the cluster. Thus, the pressure tensor can be expressed as

$$P(r) = P_r(r)\mathbf{e}_r\mathbf{e}_r + P_t(r)(\mathbf{e}_\theta\mathbf{e}_\theta + \mathbf{e}_\phi\mathbf{e}_\phi), \quad (24)$$

where $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_\phi$ are the unit vectors and P_r and P_t are the radial and the transverse components of the pressure tensor, respectively. The components of the pressure tensor on a spherical surface are found to be isotropic in the vicinity of the interface, i.e., $P_\theta = P_\phi = P_t$. The radial profiles of the components $P_r(r)$ and $P_t(r)$ are obtained by integrating out the angular degrees of freedom over thin spherical shells extending outwards from the origin. Figure 3(a) shows the

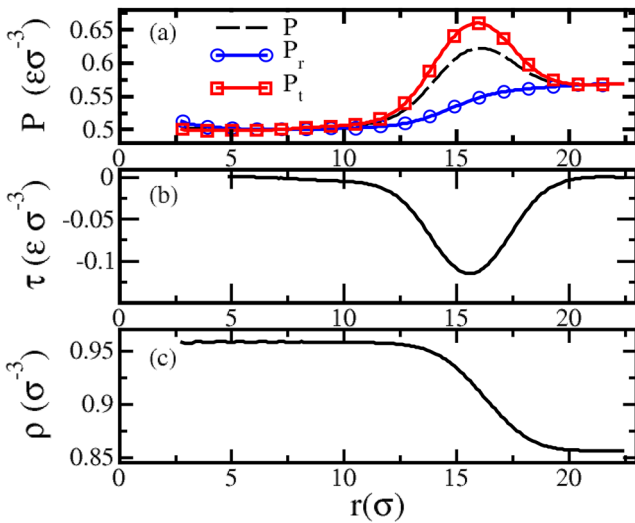


FIG. 3. (a) Variation of the pressure from the center of the crystalline cluster in the liquid region. The solid line with open circles is the $P_r(r)$. The dashed line shows the variation of the total pressure. (b) Variation of excess stress $\tau(r)$ from the center of the crystalline cluster. It is found that the mechanical equilibrium condition is indeed fulfilled, namely $P_s - P_l = \int_0^\infty \frac{2\tau(r)}{r} dr$, which is the generalization of the Laplace equation for liquid-vapor interfaces.²⁴ (c) Variation of the number density (ρ) from the center of the crystalline cluster.

calculated radial distributions $P_r(r)$, $P_t(r)$, and $P(r)$ as described above.

From Fig. 3(a), it is clear that the pressure inside the crystalline nucleus is lower than that of the liquid outside. This is a result of the negative interfacial excess stress at the solid-liquid interface in contrast to that of the liquid-vapor. The excess stress in the interfacial region can be calculated using the stress tensor as follows:

$$\tau(r) = \sum_i (p_{rr}^i - p_{\theta\theta}^i/2 - p_{\phi\phi}^i/2), \quad (25)$$

where i is the crystal atom index in a thin shell with a radius r . The profile of $\tau(r)$ along the radial direction is plotted in Fig. 3(b). The negligibly small excess stress inside the crystalline cluster confirms that the crystalline cluster is at a hydrostatic state. It is also observed that a non-zero negative excess stress is accumulated in the vicinity of the crystal-liquid interface. The total excess stress due to the interface can be calculated by taking the summation of Eq. (25) over all the atoms in the system. The net excess stress calculated at $T = 0.64$ is $\bar{\tau} = -0.483 \pm 0.003 \epsilon \sigma^{-3}$.

From the above analysis, we could assume that the stress distribution of the spherical crystalline cluster is spherically symmetric and hydrostatic. The magnitude of the excess stress is considerably lower than that of orientationally averaged stress of the planar interface.¹⁶ This could be a result of the re-adjustment of the crystal structure near the spherical interface to minimize the energy as well as the stress.

The temperature dependence of the interfacial free energy for the planar interface $\gamma_0(T)$ was obtained from Laird *et al.*¹⁶ by averaging the interfacial free energy data along (100), (110), and (111) directions. A fit to the data can be described by $\gamma_0(T) = 0.1081 + 0.3499T + 0.0880T^2$. From this fitting, the estimated values of γ_0 and $d\gamma_0/dT$ at $T = 0.64$ are 0.3680 ($\epsilon\sigma^{-2}$) and 0.4626 ($\sigma^{-2}k_B$), respectively.

Using the above calculated values and the temperature dependence of ρ_s , we can calculate the Tolman length (δ) using Eq. (22). The calculated Tolman length is $\delta = 0.48 \pm 0.05$. This value will make considerable deviation of γ along a spherical interface from its planar value when the size of the crystal cluster is small. In the following part of the paper, we show that this correction is crucial in predicting the nucleation barrier.

IV. DRIVING FORCE CALCULATION

To predict the nucleation barrier and to compare with the simulated data, we need to calculate $\Delta\mu$ which corresponds to the known simulation conditions. Accurate estimates of $\Delta\mu$ are difficult as accurate values of the thermodynamic properties of the growing crystalline phase and the supercooled liquid phases are hard to access using simulations due to their highly metastability. To overcome this problem, we combine classical Density Functional Perturbation Theory (cDFPT) with atomistic simulation data of the supercooled liquid to calculate the $\Delta\mu$ since cDFPT is known to yield accurate thermodynamics properties of bulk crystalline.²¹

First, the Helmholtz free energy per atom as a function of atomic number density at temperature $T = 0.58$ for both liquid and face center cubic (fcc) crystalline phases is calculated from the cDFPT. Polynomial fits to the calculated Helmholtz free energy of crystalline (F_{cryst}) and liquid (F_l) phases are given by $F_{cryst}(x) = 680.10 - 2581.94x + 3662.65x^2 - 2323.45x^3 + 556.13x^4$ and $F_l(x) = 721.75 - 2993.53x + 4986.7x^2 - 4203.67x^3 + 1790.49x^4 - 307.69x^5$, respectively, where $x = 1/\rho$. The pressure can be calculated as $P = -\partial F/\partial x$ and hence the chemical potential of each phases can be obtained from $\mu = F + P/\rho$.

To obtain the $\Delta\mu$ corresponding to the supercooling condition used in the simulation paper,¹² we need to know the exact densities of the supercooled liquid and the growing crystalline phases. To this end, simulations described in Ref. 12 are repeated with 4000 LJ particles at number density $\rho = 0.95$, under constant volume (V) and temperature (T). First the systems are heated to $T = 1.2$, the system melted, and the simulation run about 1×10^5 time steps. Then the system is supercooled to $T = 0.58$ and simulation was run continuously. The averaged pressure of the supercooled system is 2.466 ± 0.028 in LJ units. An abrupt drop of the pressure was observed around 7.5×10^6 time steps, and the whole system is transformed into a crystalline phase.

The supercooled liquid can be well approximated by a mixture of crystalline clusters and liquid regions.³⁰ The pressure of the crystalline clusters (p_1) may slightly differ from that of the liquid (p_2) due to the curvature at the interface. We assume that the total volume fraction of the liquid regions is the same as that of the crystalline clusters. Thus the measured average pressure will be $\bar{p} = (p_1 + p_2)/2$, and the pressure fluctuation of the supercooled system can be approximated by $\Delta p = (p_1 - p_2)/2$. This estimate can incorporate the major uncertainty due to the fluctuations of the pressure of the supercooled liquid. Using this approximation, the pressure of the liquid and the crystalline phases in the supercooled liquid can be estimated to be 2.44 and 2.49, respectively. At these pressures, the densities of the liquid and the crystalline cluster are extracted from the cDFPT data. The estimated densities of the liquid and the crystalline phases in the supercooled liquid are $\rho_l = 0.920$ and $\rho_s = 1.000$, respectively. At these liquid and crystal densities, the difference of the chemical potentials ($\Delta\mu$) is calculated from the cDFPT chemical potentials, which yield the driving force corresponding to the simulation conditions, $\Delta\mu = -0.320$.

V. PREDICTING NUCLEATION BARRIER

Using the CNT Eq. (1), the nucleation barrier (ΔG) can be expressed as a function of the number of atoms in the crystalline cluster as follows:

$$\Delta G(n) = n\Delta\mu + 4\pi\left(\frac{3n}{4\pi\rho_s}\right)^{2/3}\gamma_0\left(1 + 2\delta\left(\frac{3n}{4\pi\rho_s}\right)^{-1/3}\right). \quad (26)$$

γ_0 at $T = 0.58$ was estimated by extrapolating the temperature dependence of γ_0 of Ref. 16, and it is found that $\gamma_0 = 0.340$. The atomic density of the crystal clusters in the supercooled liquid is $\rho_s = 1.000$ from the above calculation. Using the

values of $\delta = 0.48$ and $\Delta\mu = -0.320$ calculated in this paper, $\Delta G(n)$ is plotted as a function of n as shown by the black solid line in Fig. 4. The shaded region shows the uncertainty of the nucleation barrier due to the uncertainty in $\delta = 0.48 \pm 0.05$.

The solid symbols are from simulation results.¹² Figure 4 shows an excellent agreement of our theoretically predicted free energy (ΔG) profile with the simulated data, which are known to lead to an accurate nucleation rate,¹² with the assumption that the curvature correction δ at the metastable liquid-crystal coexistence is the same as the curvature correction for the nucleation free energy profile. The red arrow in Fig. 4 indicates the location of the theoretically predicted nucleation barrier, where $\Delta G = 16\epsilon$ and the critical nucleus size is $n^* = 68$ atoms. This prediction matches well with the simulated data under the given supercooling condition. The dashed line represents the CNT prediction without the curvature correction ($\delta = 0$) to the interfacial free energy. It underestimates the barrier height and also the critical size of the crystallites as pointed out in the literature. Therefore, the curvature correction to the interfacial free energy is a crucial part of consideration in the classical nucleation theory.

The notion of curvature correction to the interfacial free energy and even the higher order terms has been the subject of discussions.^{12,13,20,31–34} However, in previous attempts, the corrections are extracted from parameter fitting to the simulated data. Our approach presented in this work is a first attempt to calculate δ and $\Delta\mu$ directly from equilibrium thermodynamics methods to obtain the nucleation barrier.

An interesting issue could be raised on the uniqueness of the δ with respect to the choice of dividing surface. For the liquid-vapor case, a “surface of tension” dividing surface which is defined via the Laplace equation and a Gibbs dividing surface lead to a consistent definition of the Tolman length.²⁴ On the other hand, for a liquid-solid interface, the Laplace equation is related to the interfacial stress, not the interfacial free energy, thus a “surface of tension” dividing surface is not well defined. In our approach, the Tolman length is defined using the Gibbs dividing surface and the functional form of

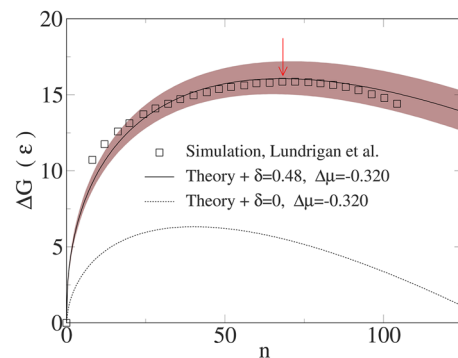


FIG. 4. Nucleation barrier (ΔG) as a function of the number of atoms in the crystalline cluster (n). The solid symbols are the simulation data.¹² The black solid line is the prediction from our theoretical approach. The red arrow represents the predicted peak of the nucleation barrier from the theoretical curve. The dashed line represents the CNT prediction using only the planar value for the interfacial free energy ($\delta = 0$). The shaded region is the uncertainty corresponding to the error in $\delta = 0.48 \pm 0.05$.

Eq. (2) from the liquid-vapor case. As for the uniqueness of this δ definition, it certainly is an interesting question worth pursuing.

VI. CONCLUSIONS

An analytical expression to calculate the first order curvature correction to the crystal-liquid interfacial free energy for a spherical interface (δ) is derived using equilibrium thermodynamics. δ is calculated directly using a spherical crystal cluster which coexists with its liquid using atomistic simulations. The correction parameter (δ) analogous to the Tolman length at liquid-vapor interfaces is found to be 0.48 ± 0.05 . The driving force $\Delta\mu$ corresponding to the same supercooled condition is calculated by combining the cDFPT calculated free energy with simulated data. With these major developments, we predict the nucleation barrier using the classical nucleation theory which shows an excellent agreement with the simulated data.

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