A limit of stability in supercooled liquid clusters

Eduardo Mendez-Villuendas
Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5C9, Canada

Ivan Saika-Voivod
Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5C9, Canada and Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. Johns, Newfoundland A1B 3X7, Canada

Richard K. Bowles[a)]
Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5C9, Canada

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We examine the metastable liquid phase of a supercooled gold nanocluster by studying the free energy landscape using the largest solidlike embryo as an order parameter. Just below freezing, the free energy exhibits a local minimum at small embryo sizes and a maximum at a larger critical embryo size. At $T=660$ K the free energy becomes a monotonically decreasing function of the order parameter as the liquid phase becomes unstable, indicating that we have reached a limit of stability. In contrast to the mean-field theory predictions for a spinodal, the size of the critical embryo remains finite as the limit of stability is approached. We also calculate the rate of nucleation, independently from our free energy calculations, and observe a rapid increase in its temperature dependence when the free energy barrier is on the order of kT. We suggest that this supports the idea that freezing becomes a barrierless process at low temperatures. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2779875]

I. INTRODUCTION

When a liquid is cooled below its freezing temperature, we generally expect the system to crystallize. However, the nucleation process requires the formation of a small embryo of the new stable phase that introduces an energetically unfavorable liquid-solid interface and creates a free energy barrier between the liquid and solid phases. As long as the fluctuations in the liquid only result in the formation of embryos smaller than the critical size needed to overcome the barrier, the system will remain fluid. This is the metastable liquid.[1]

As the liquid is cooled further, the free energy barrier decreases, making nucleation more likely and shortening the lifetime of the metastable liquid. The question then arises: Is there a temperature below which the metastable liquid becomes unstable with respect to all fluctuations? Mean-field theories, such as the gradient theory developed by Cahn and Hilliard,[2] predict such a spinodal, for first order phase transitions such as the condensation of a gas or liquid-liquid phase separation in a mixture. They predict that the size of the critical nucleus diverges as the spinodal is approached as a result of the divergence in the mean-field isothermal compressibility of the fluid,[3] and that the nucleation lifetime should diverge, despite the fact that the free energy barrier is in the order of kT, as the dynamics become increasingly cooperative.[4] However, recent experiments of phase separating polymers[5] and simulations of the vapor-liquid transition in Lennard-Jones model[6] suggest that the size of the critical embryo remains finite as the spinodal is approached.

Whether a deeply supercooled single component liquid exhibits a spinodal singularity with respect to the crystal remains an open question.[1] Trudu *et al.*[7] studied freezing in a bulk Lennard-Jones fluid and found nucleation becomes a spatially diffuse and collective phenomenon when the system is deeply supercooled and suggested this was indicative of the presence of a mean-field spinodal. Recent nucleation experiments on water show nucleation times become extremely short when the liquid is highly compressed, thus defining a practical limit of stability to the liquid state.[8] These results provide strong but indirect evidence for the existence of a thermodynamic limit of stability for the supercooled liquid state.

Small liquid clusters represent an increasingly important class of system that challenges our understanding of the liquid state. In this paper, we address the question of whether or not liquid clusters have a limit of stability as they are cooled. We directly locate this limit of stability by calculating the free energy of the cluster using the largest-sized solid embryo as an order parameter. At temperatures just below freezing, the free energy exhibits a local minimum associated with the metastable liquid and a free energy barrier that separates this liquid from the solid phase. The height of the barrier decreases as the temperature is lowered and eventually disappears so that the free energy becomes a monotonically decreasing function of the order parameter and the liquid phase becomes unstable. This provides the first direct measurement of the limit of stability in a simple liquid system.

The remainder of the paper is structured as follows: Section II develops our free energy description of the metastable

[a)]Author to whom correspondence should be addressed. Electronic mail: richard.bowles@usask.ca

fluid and our simulation details are outlined in Sec. III. The results and discussion are contained in Sec. IV, followed by our conclusions in Sec. V.

II. A FREE ENERGY DESCRIPTION OF THE METASTABLE LIQUID

A rigorous molecular theory of a metastable system requires the introduction of constraints that prevent the system from accessing regions of phase space that will cause the system to evolve towards the more stable state. In the context of a supercooled liquid, we need to prevent the appearance of solidlike embryos above the critical size that would cause the liquid to freeze, which suggests we should choose the size of the largest solidlike embryo, $n_{\max}$, as an order parameter to describe the state of the cluster.[9] Furthermore, $n_{\max}$ seems to be a particularly appropriate order parameter in small nanoscale systems where the nucleation volume is sufficiently small that the appearance of a single postcritical embryo leads to the termination of the metastable state throughout the entire system. When $n_{\max}=0$, all the atoms in the cluster are liquidlike, but when $n_{\max}=N$, the total number of atoms in the cluster, the cluster is a single crystal. The probability of finding the cluster in a given state is

$$P(n_{\max}) = \frac{Q(n_{\max})}{\Sigma_{n_{\max}=0}^{V} Q(n_{\max})}, \tag{1}$$

where

$$Q(n_{\max}) = \frac{1}{N!\Lambda^{3N}} \int_V e^{-\beta U(\mathbf{r_N};n_{\max})} d\mathbf{r_N}, \tag{2}$$

is the canonical partition function for the system constrained to contain *at least one* largest embryo of size $n_{\max}$, $U(\mathbf{r_N};n_{\max})$ is the potential energy of the system under the constraint, Λ is the de Broglie wavelength, and $\beta=1/kT$, where k is Boltzmann's constant and T is the temperature. $P(n_{\max})$ can be calculated by simulation and the free energy obtained from

$$\Delta F(n_{\max}) = -kT \ln P(n_{\max}), \tag{3}$$

where $\Delta F(n_{\max})$ is the work required to take the entire system from a state where there is no solidlike embryo present, to a state where there is at least one largest embryo of size $n_{\max}$. Equation (3) closely resembles the intensive free energy introduced by ten Wolde and Frenkel[10,11] to calculate the conventional free energy barrier associated with nucleation,

$$\Delta F_c(n) = -kT \ln(P_n/N) \approx -kT \ln(N_n/N_0), \tag{4}$$

where P_n is the probability of observing an n-sized embryo, N_n is the equilibrium number of embryos, and N_0 is the equilibrium number of liquidlike atoms which is usually taken to be N. $\Delta F_c(n)$ is the work of forming an n-sized embryo within the metastable phase. In the limit that embryos are rare (i.e., under conditions of mild undercooling), $P(n_{\max})$ is approximately equal to the equilibrium number of embryos[12] and the two free energies become equivalent, but it should be stressed that the two free energies are fundamentally different and that we would expect them to behave differently in deeply supercooled systems.

Bhimalapuram *et al.*[6] have recently used Eq. (3) to identify the liquid-gas spinodal in the supersaturated Lennard-Jones gas as the point at which $\Delta F(n_{\max})$ is a monotonically decreasing function of $n_{\max}$. They find this occurs at a supersaturation consistent with previous estimates of the spinodal[13] and that the nucleation mechanism in the deeply metastable system changes from classical nucleation, characterized by fluctuating growth of a single large embryo, to a mechanism involving the coalescence of embryos. However, from the definition of $P(n_{\max})$, it should be apparent that the free energy is an extensive quantity, and it is likely that the location of the spinodal in a bulk system would shift depending on the number of particles in the simulation. In a small, finite-sized system, such as a liquid nanoparticle, the applicability of Eq. (3) is clearer.

III. SIMULATION DETAILS

We have previously calculated $\Delta F_c(n)$ for a gold cluster with $N=456$ atoms, for temperatures above $T=690$ K,[14] focusing on the role of wetting phenomena and the location of the embryo at the nanoparticle surface. In the present paper, we calculate both $\Delta F(n_{\max})$ and $\Delta F_c(n)$ to lower temperatures for the same cluster in search of the limit of stability of the metastable liquid cluster using the same approach of combining umbrella Monte Carlo (MC) sampling simulation techniques with parallel tempering. The application of these techniques to nucleation are outlined in detail in Ref. 11. We use the semiempirical embedded-atom method (EAM) potential[15] to describe the atomic interactions and study the cluster in the *NVT* ensemble with a simulation cell of $V=1500$ Å^3 and periodic boundaries. At each temperature, we run eight parallel simulations or windows, each with a parabolic biasing potential $w(n_{\max})=0.0005(n_{\max}-n_0)^2$, which biases the system to sample states where the largest embryo, $n_{\max}$, in the cluster is around n_0. We choose $n_0=0,10,20,30,\ldots,70$ and use $T=750$, 730, 710, 690, 680, 670, 660, and 650 for tempering.

Our embryo criterion has been previously described in Ref. 14 and closely follows that developed by Auer and Frenkel[11] to study crystal nucleation in hard sphere colloids. In brief, we determine the local order around a single atom i using the Steinhardt bond order parameter,[16]

$$q_{6m}(i) = \sum_{j=1}^{n_b(i)} Y_{6m}(\hat{r}_{ij}), \tag{5}$$

where the sum is over all the neighboring atoms closer than 3.5 Å, $Y_{6m}(\theta,\phi)$ is the sixth order spherical harmonic, and $\hat{r}_{ij}$ is the unit vector pointing from particle i to a neighbor j. Furthermore, we characterize the correlation of the order between two neighbors by

$$c_{ij} = \sum_{m=-6}^{6} \hat{q}_{6m}(i) \cdot \hat{q}^*_{6m}(j), \tag{6}$$

where

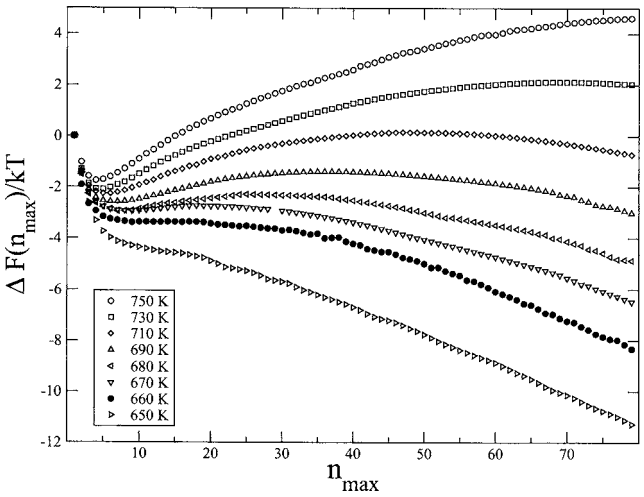

FIG. 1. $\Delta F(n_{\max})$ as a function of $n_{\max}$ for temperatures in the range $T=750-650$.

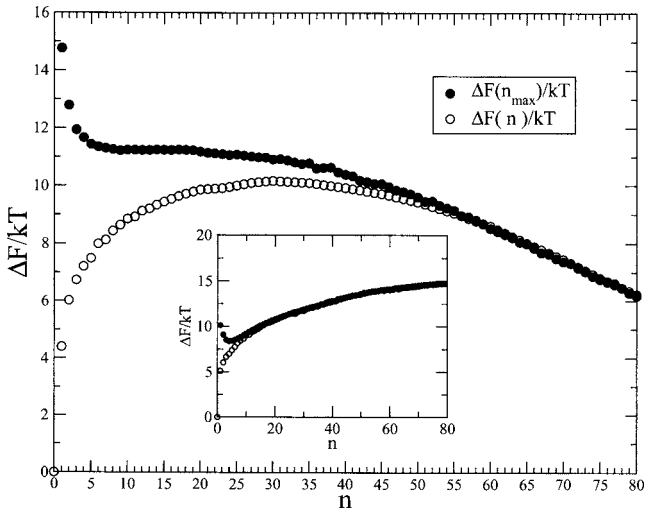

FIG. 2. Comparison of $\Delta F_c(n)$ and $\Delta F(n_{\max})$ at $T=660$ K where $\Delta F(n_{\max})$ has been shifted upward by $14.9kT$. Insert: The same comparison at $T=750$ K with $\Delta F(n_{\max})$ shifted upwards by $10.2kT$.

$$\hat{q}_{6m}(i) = \frac{q_{6m}}{\left[\Sigma_{m=-6}^{6}(|q_{6m}(i)|^2)\right]^{1/2}}, \tag{7}$$

and q^* is the complex conjugate. If two neighbors are correlated above a threshold value of $c_{ij} > 0.65$, we then consider them to be *bonded*. This threshold value is obtained by considering distributions of c_{ij} obtained from liquid configurations at $T=750$ and configurations of the solid taken at $T=700$, and selecting the value where these distributions intersect. An atom is finally considered to be solidlike if it is bonded to, and hence, correlated with, at least half its neighbors. Two neighboring, solidlike atoms are considered to be in the same embryo if they are connected through a bond.

The embryo criterion is computationally expensive to apply so we use trajectories that consist of ten normal MC moves per atom sampling the atomic interaction potential, followed by a test against $w(n_{\max})$. If the final move is rejected, the system is returned to the state at the beginning of the trajectory. We attempt tempering switches every five trajectories, alternating between switches in n_0 (T fixed) and T switches (n_0 fixed). These tempering switches have acceptance ratios of about 0.4 and 0.6, respectively. The free energies in each window differ by an unknown additive constant, so the full free energy curve is constructed by fitting the curves to a polynomial in $n_{\max}$ (Ref. 11), and a total of 1.74×10^6 trajectories are sampled in each window.

IV. RESULTS AND DISCUSSION

Figure 1 shows the free energy calculated using Eq. (3). At temperatures just below the freezing temperature for the cluster, $\Delta F(n_{\max})$ exhibits a minimum at small values of $n_{\max}$ before it increases to a maximum at a larger critical embryo size $n^*_{\max}$. Fluctuations in the cluster that keep the largest embryo below its critical size are locally stable and represent the configuration space available to the metastable liquid, while larger fluctuations cause the system to freeze. The critical size identifies the constraint required to keep the liquid in metastable equilibrium.

As the temperature is lowered, $n^*_{\max}$ decreases in size and the barrier becomes smaller. Eventually we reach a point, at $T=660$ K, where the barrier disappears and all fluctuations which increase the size of the largest cluster lower the free energy, suggesting we have reached the limit of stability for the fluid phase. Further decreases in T simply increase the thermodynamic driving force towards forming the solid as the free energy curves become steeper.

Figure 2 shows the two free energies calculated from Eqs. (3) and (4) where $\Delta F(n_{\max})$ has been shifted vertically to maximize the overlap between the two curves. At $T=750$ K (see insert), the two free energies are identical for embryo sizes larger than about 15 since there is generally just one large embryo in the system and both have the same critical embryo size. The minimum in $\Delta F(n_{\max})$ suggests that the cluster usually contains a largest embryo of $n_{\max}\approx5$. On the other hand, $\Delta F_c(n)$ always has a positive slope at small n, indicating that there must be a larger equilibrium number of embryos smaller than $n_{\max}$. At the limit of stability ($T=660$ K), the two curves are very different and only overlap at the largest embryo sizes.

If we define the height of the barrier, $\Delta F'(n^*_{\max})$, as the difference in free energy between the maximum and the small embryo minimum of $F(n_{\max})$, we can compare this with the usual nucleation barrier, $\Delta F_c(n^*)$. Figure 3(a) shows that as $\Delta F'(n^*_{\max})$ goes to zero at the limit of stability, $\Delta F_c(n^*)$ plateaus as a function of temperature at around $10kT$. At the same time, the size of the critical embryo for both free energies decreases as a function of temperature. At $T=660$, $\Delta F(n_{\max})$ exhibits a flat region, where the embryo sizes in the range $n_{\max}=5-25$ have approximately the same free energy, so we can expect considerable fluctuations in the embryo size. Nevertheless, $n^*_{\max}$ remains finite [Fig. 3(b)] as the limit of stability is approached from above. This is in direct contrast to the predictions of mean-field theories applicable to the vapor-liquid transition.[2,3] Our results are consistent with those of Pan *et al.*[5] and Bhimalapuram *et al.*[6]

The rate at which clusters freeze can be determined by considering an ensemble of temperature quenched, molecular dynamics (MD) simulations.[17] The liquid cluster is initially equilibrated at $T=900$ K, well above the freezing tempera-

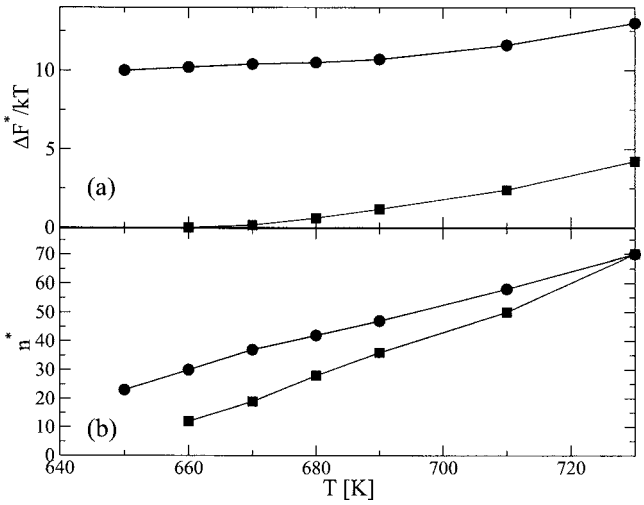

FIG. 3. (a) The height of the free energy barrier, $\Delta F'(n^*_{\max})$, (squares) compared to $\Delta F_c(n^*)$ (circles). See Ref. 14 for details. (b) The size of the critical embryo obtained using the two methods. Symbols are the same as (a).

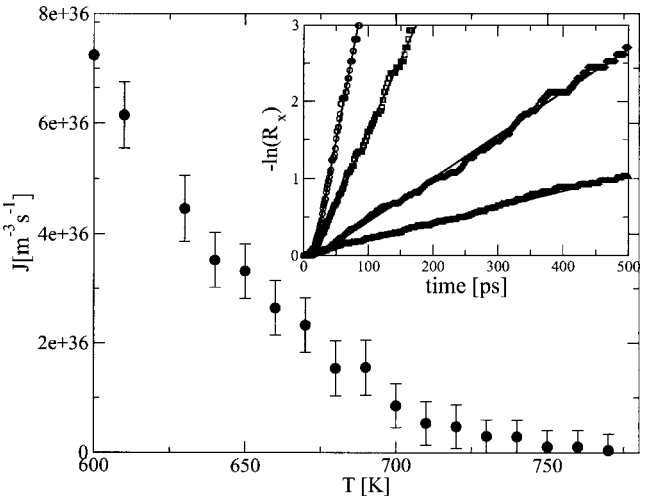

FIG. 4. The nucleation rate as a function of temperature. Insert: $-\ln[R(t)]$ as a function of time for $T=610$ K (circles), $T=660$ K (squares), $T=700$ K (diamonds), and $T=730$ K (triangles). The solid lines represent linear best fits to the data.

ture, before the temperature is instantaneously quenched below freezing by rescaling the particle velocities. The MD trajectory is then followed as the cluster freezes. Assuming this process is described by a first order rate law, the nucleation rate J can be obtained from the relation

$$\ln[R(t)] = -JV_c(t-t_0), \tag{8}$$

where $R(t)$ is the fraction of un-nucleated clusters at time t, V_c is the volume of the cluster, and t_0 is the nucleation lag time, which is the time required to reach a steady state of clusters containing an embryo of a size large enough that we consider the cluster to have nucleated. In the present study, we consider a cluster to have nucleated when $n_{\max}$ is greater than 85 for the last time during the simulation, which runs for 500 ps. The nucleation size is defined as 85 because it is larger than the critical embryo size at all temperatures studied. Since we only follow the largest embryo, our rate calculation only explicitly accounts for single nucleation events. In this respect, the MD simulations are consistent with use of $n_{\max}$ as an order parameter in the free energy calculations. We do see multiple small embryos appearing in a single cluster during a nucleation run, but we generally only see one large embryo of size $n=85$. However, if embryo coalescence becomes an important factor when the free energy landscape is flat, this may impact our nucleation rates. A total of 300 quenched simulations are used at each temperature and the insert to Fig. 4 shows that a single exponential gives a reasonable description of the rate process for the temperatures studied. The volume of the cluster is determined using a "rolling sphere" algorithm[18] which defines the surface of a cluster using a hard sphere probe. In our case, the radius of the probe sphere and the gold atoms was taken to be 1.5 Å. At $T=750$ K, $V_c=7\times10^3\pm250$ Å^3, which is 12% smaller than would be predicted based on the volume per molecule of bulk liquid EAM gold.[19]

The intercept of the linear fits of $\ln R(t)$ give lag times in the range of 14–27 ps with an average over all temperatures of $t_0=19.4$ ps. The scatter in the data is too large to identify any temperature dependence in t_0. The short lag time suggests that Eq. (8) should be sufficient to determine our nucleation rates. However, at the lowest temperatures, we are entering a regime where a more rigorous analysis[20] could be used to determine how time-dependent features at early nucleation times impact our rate calculation. Figure 4 shows that the nucleation rate increases as the cluster is quenched to lower temperatures. For temperatures above 700 K, our rates are approximately the same as those obtained by Chushak and Bartell,[17] who used the same technique, but a larger cluster volume and a different nucleation criterion. Around $T=700$ K we see an unexpected increase in the rate with the slope $\partial J/\partial T$ becoming more negative. Classical nucleation theory expresses the rate of nucleation as

$$J = K\exp[-\Delta F_c(n^*)/kT], \tag{9}$$

where the kinetic prefactor[11] is given by $K=24\rho_n ZDn^{*2/3}/\lambda$, D is the diffusion coefficient, ρ_n is the number density of particles, λ is the typical distance a particle must diffuse in order to join the embryo, and $Z=(|\Delta\mu|/6\pi kTn^*)^{1/2}$ is the Zeldovich factor. $\Delta\mu$ is the difference in chemical potential between the nucleating stable and metastable phases. The temperature dependent parameters in the rate should vary continuously as a function of temperature and cannot account for the rapid increase in rate, while Fig. 3(a) suggests that the temperature dependence of $\Delta F_c(n^*)/kT$ would cause the rate to slow, rather than accelerate. However, at $T=700$ K, the barrier defined by $\Delta F(n^*_{\max})/kT$ is on the order of kT, which suggests that the observed deviation in the temperature dependence of the rate might be associated with a crossover from a barrier dominated nucleation process to a barrierless one. Consequently, both our direct barrier calculations and the independent MD rate calculations point to the strong possibility of a limit of stability for the fluid phase.

V. CONCLUSION

The main goal of the present work is to investigate the possibility that the supercooled liquid phase of a nanocluster

exhibits a limit of stability. In particular, we obtain a free energy landscape using the size of the largest embryo in the system as an order parameter to describe the state the system and provide a reaction coordinate leading from the liquid to the solid state. The local free energy minimum that appears at moderately supercooled temperatures, centered around small $n_{\max}$, characterizes the fluctuations available to the metastable liquid. However, the free energy becomes a monotonically decreasing function of $n_{\max}$ at lower temperatures, so that it is always thermodynamically more favorable to increase the size of the largest solid embryo, indicating that the liquid phase has become unstable. This conclusion is supported by our MD calculations of the rate. While our study has focused on a gold nanocluster, where nucleation occurs on the surface, it seems reasonable to speculate that this limit of stability for the fluid phase is quite general in these small liquid systems and it raises the interesting question as to weather such a limit of stability is also present in bulk systems.

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