Elucidating the mechanism of nucleation near the gas-liquid spinodal

Prabhakar Bhimalapuram,[1,2] Suman Chakrabarty,[1] and Biman Bagchi[1,*]
[1]*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, INDIA*
[2]*The James Franck Institute, University of Chicago, Chicago, IL 60637, USA*

(Dated: April 10, 2007)

We have constructed, using a variant of umbrella sampling technique, a multidimensional free energy surface of nucleation of the liquid phase from the parent vapor phase near the gas-liquid spinodal as a function of relevant nucleation coordinates. Extensive simulation studies have been performed for the supercooled Lennard-Jones gas and the 3-dimensional Ising model. In particular, we remove the Becker-Doring constraint of having *only one* growing cluster in the system. Close to the spinodal, the free energy, as a function of the size of the largest cluster, develops surprisingly *a minimum at a sub-critical* cluster size. It is *this minimum at intermediate size* that is found to be responsible for the barrier towards further growth of the nucleus at large supersaturation. An alternative free energy pathway involving the participation of many sub-critical clusters is found near the spinodal where the growth of the nucleus is promoted by a coalescence mechanism. Temperature quench trajectory analyses reveal that the growth of the stable phase becomes more collective and spatially diffuse, and the significance of a 'critical nucleus' is lost for deeper quenches.

PACS numbers: 68.55.Ac, 82.60.Nh, 07.05.Tp
Keywords: nucleation, growth, spinodal decomposition, classical nucleation theory, non-Boltzmann sampling

First order phase transitions usually occur via the formation of a droplet of the stable phase within the metastable parent bulk phase through an activated process called nucleation [1–5]. The classical nucleation theory (CNT) (of Becker-Doring-Zeldovich) provides a simple, yet elegant description for homogeneous nucleation. CNT assumes that a single droplet of the new stable phase grows in a sea of parent metastable bulk phase by *addition of single molecules* and this droplet has to grow beyond a certain 'critical size' (r_c) to compensate for the energy required to form the surface between the two phases. The free energy of formation of a droplet of radius r is given by:

$$\Delta G(r) = -\frac{4\pi}{3} r^3 \Delta G_V + 4\pi r^2 \gamma \qquad (1)$$

Where ΔG_V is the free energy difference per unit volume between the daughter and the parent phase and γ is the surface tension of the interface between them.

While several aspects of CNT have been analyzed critically [6–13] and different lacunae have been removed, yet the important problem of the mechanism of nucleation at large supercooling, especially that near the gas-liquid spinodal, remains unresolved and somewhat controversial. The well-known droplet model [14] suggests a kinetic origin of the spinodal. Mean field theoretic investigations of the spinodal nucleation close to the critical point predicts that the critical size should diverge with increasing quench depth and the process can have 'universal characteristics' [10, 15]. For the liquid to vapor transition the critical vapor nucleus has been found to be a large web-like non-spherical cavity for a wide range of superheating suggesting a strong deviation from the CNT [16]. A changeover to a coalescence mechanism of nucleation near the spinodal was also predicted in a three dimensional Ising model with long range interactions [11]. Bustillos *et al* have constructed the free energy surface for the three-dimensional Ising model as a function of the magnetization and the external field, and found that for states deep in the two-phase region (where the system was expected to be mechanically unstable) the nucleation barrier does become small but does not disappear, suggesting that *there is no spinodal* [17]. Very recently Parrinello and coworkers have studied the freezing of a Lennard-Jones (LJ) fluid as a function of the degree of supercooling to find that the nucleation acquires a spinodal character for deeper quenches and crystallization proceeds in a more continuous and collective fashion and becomes spatially more diffuse as the spinodal is approached [13]. In the present work we confirm this observation in the case of gas-liquid transition and substantiate our findings with extensive computation of relevant free energy surfaces and temperature quench trajectory analyses as follow.

First, we compute the free energy as a function of two relevant order parameters for LJ fluid in a grand canonical (μVT) ensemble. Those are the total number of particles (N_{tot}) and the 'liquidness (analogous to the magnetization in the Ising model) of the system. The latter is given by the total number of 'liquid-like particles' (N_{liq}) identified by their local densities. Following the definition by Stillinger [18] and the successful modification by Frenkel and coworkers [9], we consider a particle to be liquid-like if it has more than five nearest neighbors within a cut-off distance ($R_c = 1.5\sigma$). Liquid-like particles that are connected by neighborhood (within the cut-off distance) form liquid-like clusters. We have used transition matrix Monte Carlo (TMMC) method [19], a very efficient non-Boltzmann sampling scheme, to obtain the 3-dimensional free energy surfaces at small and large

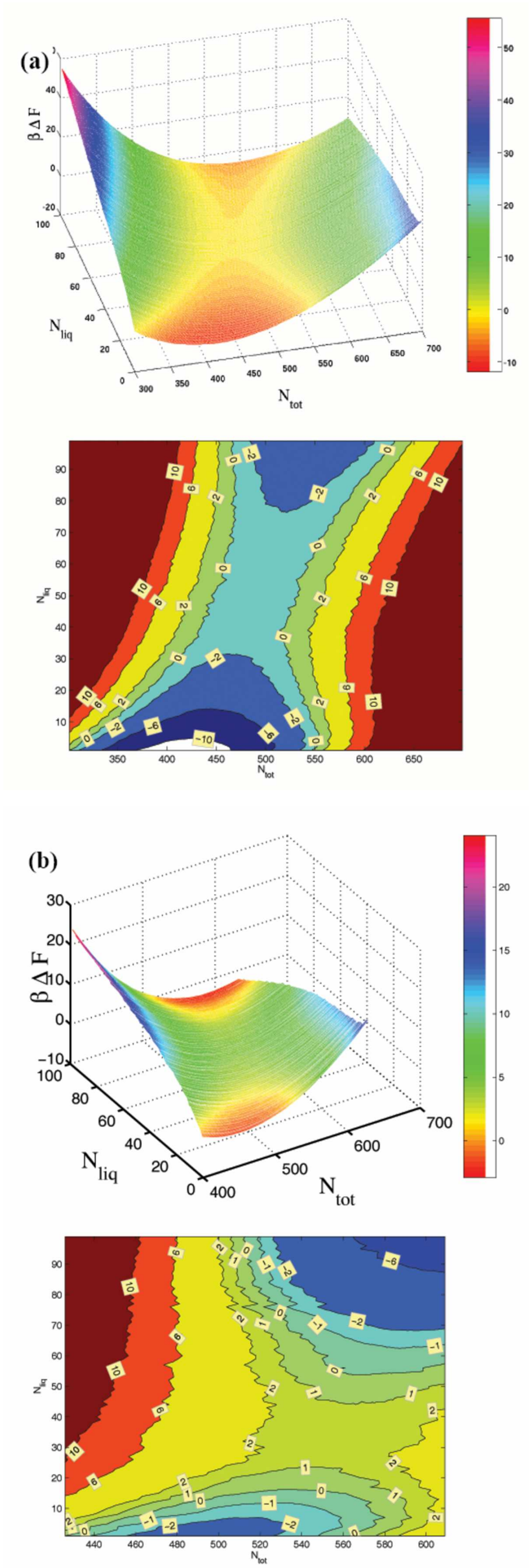

FIG. 1: The 3-dimensional free energy surfaces and corresponding 2-dimensional contour plots computed in grand canonical (μVT) ensemble at reduced temperature $T^* = 0.741$ and volume $V = (25\sigma)^3$. Activity is defined as $\xi = \exp(\mu/k_BT)/\lambda^3$, where λ is the de Broglie wave length and μ is the chemical potential. (a) $\xi = 0.018$, corresponds to $S \simeq 1.8$, (b) $\xi = 0.020$, corresponds to $S \simeq 2.4$.

supersaturation. In Fig. 1(a) and Fig. 1(b) we show the calculated free energy surfaces of formation of liquid-like clusters in a system of LJ spheres at two different supersaturation S (given by P/P_C, where P is the pressure of the system and P_C is the pressure at coexistence at the same temperature) equal to 1.8 and 2.4 at a reduced temperature $T^* = 0.741$. We estimate the spinodal limit to be between 2.5-2.6, where the nucleation barrier disappears at the same temperature. It is to be noted that our estimate of the spinodal from free energy calculations is in close agreement with that of Moody *et al* [20] (who estimate it to be 2.7 from the surface tension calculations). At intermediate supersaturation ($S \simeq 1.8$), still away from the spinodal, both the activation barrier and the number of liquid-like particles at the barrier are large (Fig. 1(a)). The latter is about 50 (we discuss later that the critical nucleus alone contains nearly all the liquid-like particles) and the activation energy is about 9.5 k_BT. On the other hand, near the spinodal ($S \simeq 2.4$), the free energy surface near the saddle is very flat (Fig. 1(b)). The number of liquid-like particles at the saddle is just about 35 and the free energy barrier from the minimum is less than 4 k_BT. Importantly, these liquid-like particles are dispersed among several intermediate sized clusters, as discussed below in more detail.

To check the basic assumption of the classical nucleation theory, we have computed the free energy surface after restricting the system to have only a single growing liquid-like cluster present in the sea of gas particles. Interestingly, with this constraint the barrier height becomes higher by more than 1 k_BT. While the critical cluster contains around 25 liquid-like particles, the minimum free energy pathway and the surface near the saddle are quite different in this case. Even in the cluster size distribution of liquid-like particles, computed at two different regions of the free energy surface, one near the saddle region and one at the metastable minimum, we observe that the system at the saddle has a relative abundance of intermediate size clusters as compared to the metastable gas phase. This difference becomes particularly important as spinodal is approached. In contrast, at low supersaturation, the critical cluster contains all of the liquid-like particles and the homogeneous nucleation assumption appears to be valid.

We have carried out extensive non-Boltzmann sampling in isothermal-isobaric (NPT) ensemble to compute the nucleation barrier for the LJ system. Following the usual practice we have chosen the size of the largest liquid-like cluster ($N_{largest}$) in the system to be the appropriate reaction coordinate [7, 9]. In Fig. 2(a) we show the calculated free energy surfaces for a wide range of supersaturation across the spinodal. We find that at relatively small supersaturation (S=1.53; not shown here) the classical picture prevails unambiguously and our results (including the critical size and the free energy barrier) agree quantitatively with previous studies [9]. But

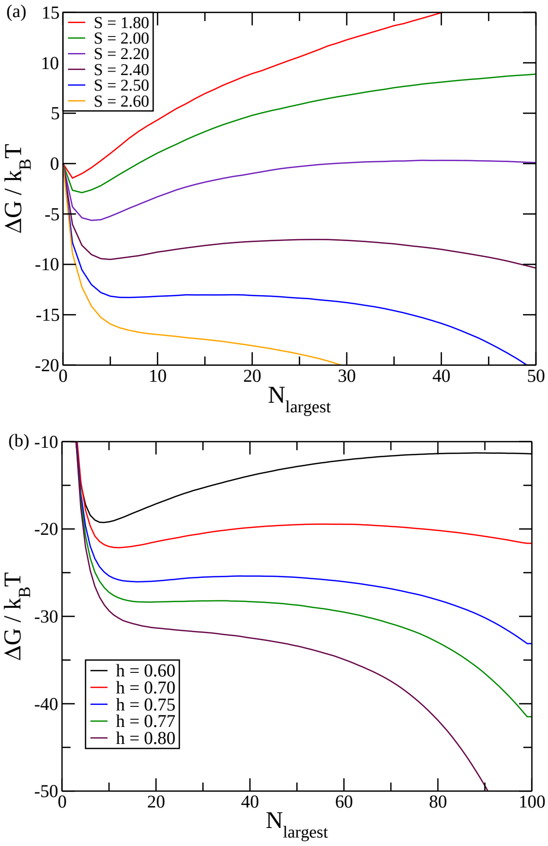

FIG. 2: (a) Free energy as a function of the size of the largest liquid-like cluster in the NPT ensemble ($T^* = 0.741$) for different S across the spinodal. (b) Free energy as a function of the size of the largest cluster of up-spins for 3-dimensional Ising model at $T = 0.6T_C$ for different magnetic fields (h) across the spinodal.

as the supersaturation is increased, both the size of the critical cluster and the barrier height become progressively smaller and surprisingly *a minimum appears at sub- critical cluster size* ($N_{largest} \sim 5$)! At S=2.4, this minimum is very pronounced and essentially responsible for the existence of the nucleation barrier. As the supersaturation is increased towards the spinodal, the free energy barrier becomes lower and the minimum at intermediate cluster size becomes deeper and shifts to larger size. Finally it reaches an inflection point at the spinodal beyond which the expected barrier-less continuous growth takes over. To the best of our knowledge, this is the first calculation of the free energy surfaces across the spinodal for the transition from the vapor phase to liquid phase with respect to this particular reaction coordinate. The *unexpected appearance* of the free energy minimum *at a small liquid-like cluster size* indicates the relative abundance and importance of such clusters in the system near the spinodal. Thus, as the degree of supercooling or supersaturation is increased, the growth of the stable phase is not through a single critical nucleus any more and becomes spatially diffuse. The system attains a spinodal character and responds more collectively and the importance of a critical nucleus is diminished. This view, as discussed later, is also justified through non-equilibrium quench simulations.

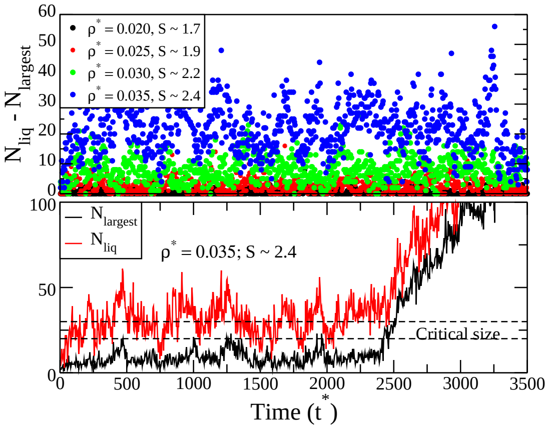

FIG. 3: (top) Evolution of the difference between the total number of liquid-like particles (N_{liq}) and the size of the largest liquid-like cluster ($N_{largest}$) subsequent to a temperature quench (from $T^* = 1.0$ to $T^* = 0.741$). As the same quench is performed at higher densities (nearer to the spinodal curve), the separation between N_{liq} and $N_{largest}$ grows markedly. (bottom) Time evolution of both N_{liq} and $N_{largest}$ is shown for $S \simeq 2.4$.

The above picture remains essentially the same in the 3-dimensional Ising model (Fig. 2(b)), where the minimum at the intermediate size and the maximum come closer and the free energy surface becomes increasingly flat as the spinodal is approached. This confirms that our observations are rather general. But we must note that the mechanism of nucleation can differ in these two model systems since in Ising model the growth proceeds by single spin flips and the clusters cannot physically move as compared to the liquid-like clusters.

Based on the present results, we envisage the following picture of spinodal decomposition. The free energy minimum develops at a cluster size where the contribution of the surface tension starts to become important, in the growth of the cluster, *for the first time* (surface effects can not dominate for very small clusters). As the supersaturation is increased further towards the spinodal, this minimum shifts to higher cluster size, making the volume term (r^3) larger than the surface term (r^2) in Eq. 1, leading to the disappearance of the nucleation barrier.

The abundance of the small sized liquid-like clusters suggests the possibility of their coalescence as a mechanism of the formation of the liquid phase. Therefore, we have carried out many non-equilibrium molecular dynamics simulations that consisted of a temperature quench at a constant volume/density. The volume was chosen such that subsequent to the quench, the system is taken from a stable gas phase to a metastable state near/at/beyond

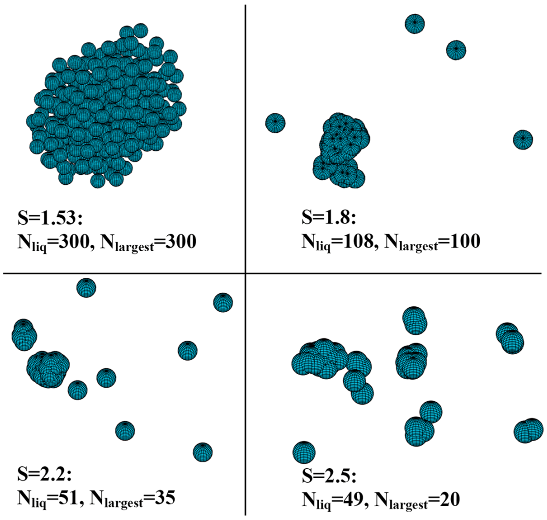

FIG. 4: Snapshots of the system at four different supersaturation (S): They show all the liquid-like particles of the system at the top of the barrier. For higher supersaturation, we find multiple large clusters are forming around the critical cluster and growth of the liquid phase becomes spread over the whole system rather than the single 'critical cluster'.

the spinodal curve. In Fig. 3, we show the time evolution of the difference between the size of the largest cluster and the total number of liquid-like particles after the quench. There are several remarkable features in these growth trajectories near the spinodal. Firstly, the separation between the largest cluster size and the total number of liquid-like particles grows enormously as the supersaturation is increased. That signifies formation of liquid-like particles throughout the system apart from the largest 'critical nucleus'. Secondly, at $S \simeq 2.4$, the time evolution of $N_{largest}$ shows severe fluctuations due to the coalescence and break-ups involving the largest cluster. For even higher supersaturation these jumps are more pronounced and the largest cluster can break-up even beyond the critical size. For a clear visual picture we include relevant snapshots of the system at different S in Fig. 4. For each case the largest cluster in the system is the critical cluster. This essentially supports the view of the emergence of a spatially diffuse, collective mechanism for the growth of the stable phase for very high supersaturation.

Previous analyses of the clusters near the critical point of Ising model suggest that the clusters become ramified near the spinodal [20]. In contrast, we find the clusters to be relatively compact for LJ fluid even at S=2.4, with average coordination numbers close to 8 and not ramified. Theoretical studies on spinodal nucleation near the gas-liquid critical point predicted the existence of a diverging length scale [10, 15]. The present study at lower temperatures finds no evidence of any such diverging length. However, we do find the emergence of a large number of liquid-like, sub-critical clusters due to the flatness of the free energy surface which is also a hallmark of all critical phenomena. We believe that it is the appearance of these intermediate sized liquid-like particles which may render spinodal decomposition a critical phenomena-like character, even at large supercooling.

Finally, in accord with the studies of Parrinello and coworkers [13] we reiterate that while CNT remains valid for low to moderate supersaturation, it breaks down at large supersaturation/supercooling. The stable phase starts forming in a spatially diffuse, collective and more continuous fashion. In the case of molecules with orientational degrees of freedom and/or hydrogen bonding ability, the onset of mechanical instability in the crystallization of a deeply supercooled liquid via the collective mechanism discovered here, may be hard to realize. This could be true particularly for water where the existence of several small ice-like clusters does not necessarily lead to immediate crystallization because of the frustration effects. However, while the present study does seem to suggest that it is the disappearance of the free energy barrier for the growth of liquid-like clusters that signals the onset of spinodal decomposition, the role of surface tension (if any) has remained unclear. Moreover, while the present study assumes a priori knowledge of the relevant reaction coordinates, recent theoretical developments, e.g. Transition Path Sampling [21] and the finite temperature string method [22], may help improve the choice of the reaction coordinates used in this study.

It is a pleasure to thank to thank Prof. Srikanth Sastry for many helpful discussions and suggestions. This work was supported in parts by grants from DST and CSIR, India. S.C. acknowledges CSIR, India for providing research fellowship.

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[*] Electronic address: `bbagchi@sscu.iisc.ernet.in`

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