System size dependence of the free energy surface in cluster simulation of nucleation [55d]

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Introduction

Recently, we presented a simulation approach to map out the free energy landscape of nucleation.[1,2] One of the key ingredients of the approach was to choose a proper system volume V so that it satisfies the following two conditions due to Nishioka and Pound:[3] (1) V is large enough so that the system can be regarded as statistically independent of its surroundings. (2) V is small enough that the probability of finding more than one uncorrelated fluctuation at any instant in the system is negligible. Insofar as nucleation is a rare event that proceeds by forming a spatially-localized high-intensity fluctuation, we expect that these conditions are satisfied simultaneously by a wide range of V.

In the case of non-associative fluids, such as Lennard-Jones fluids above the triple point,the free energy determined by this method exhibits some non-trivial volume dependence. Nonetheless, if nucleation in such a system still proceeds through a spatially-localized fluctuation, the Nishioka-Pound conditions will be satisfied by a wide range of V. Since the simulation cell can be regarded as defining the field of vision involved in our observation of nucleation process, the exact choice of V should have no effect on the observed nucleation behavior. It is then natural to inquire exactly how V independent nucleation behavior arises from the apparently V dependent free energy surface. Since nucleation is a dynamical process, a part of the answer undoubtedly lies in the dynamical consideration. In what follows, however, we shall limit ourselves to the free energy consideration alone and show that, by means of an example, the free energetics relevant to the steady-state nucleation remains unchanged for a wide range of the system size.

Method

The basic idea of our cluster simulation method is to follow the stochastic evolution of the system by means of Monte Carlo simulation.[1,2] Because of the second condition imposed on V, the system can be regarded as containing at most a single cluster at any given instant, which is characterized by a set of properly chosen order parameters $\mathbf{x} = (x_1, \cdots, x_c)$. Using umbrella sampling technique,[4] we estimate the probability $p\Delta\mathbf{x}$ of finding the system within the volume element $\Delta\mathbf{x} = \Delta x_1 \cdots \Delta x_c$ in order parameter space taken around $\mathbf{x}$, from which the free energy W follows:

$$\beta W(\mathbf{x}; \Delta\mathbf{x}) = -\ln p(\mathbf{x})\Delta\mathbf{x}, \tag{1}$$

where $\beta = (k_B T)^{-1}$ is the reciprocal temperature. For $\Delta\mathbf{x}$ of a finite size, this approach yields W only for a discrete set of points. If a limit is taken in which $\Delta\mathbf{x}$ becomes infinitesimally

small, $p(\mathbf{x})$ approaches a value independent of $\Delta\mathbf{x}$. Then, it is convenient to introduce

$$\beta\phi(\mathbf{x}) = -\ln p(\mathbf{x}) \tag{2}$$

which may be regarded as a continuous function of $\mathbf{x}$. Using this quantity, and adopting a Kramers type picture,[5–7] we found the expression for the steady state nucleation rate I_{ss}:[8]

$$I_{ss} = |\kappa|(2\pi)^{c/2-1}e^{-\beta\Delta W_{ss}}, \tag{3}$$

where κ is a kinetic prefactor, evaluation of which is not attempted in this work. W_{ss} is defined as

$$\beta\Delta W_{ss} = \beta(W^* - W_A) + \ln V - \beta\delta w^< + \ln\sqrt{|\det H_\Delta|}, \tag{4}$$

where W^* is the value of W at the saddle point of the free energy surface and W_A is the local minimum of the free energy W in the region of order parameter space corresponding to the metastable phase and we defined

$$e^{-\beta\delta w^<} = \sum_{\mathbf{X}}{}^< e^{-\beta[W(\mathbf{X};\Delta\mathbf{X})-W_A]}, \tag{5}$$

where the sum is over all metastable region of the order parameter space. Finally, $H_{\alpha\beta} = \partial^2\beta\phi/\partial x_\alpha\partial x_\beta$ and $H_{\Delta\alpha\beta} = H_{\alpha\beta}\Delta x_\alpha\Delta x_\beta$.

In Eq. (4), $\ln V$ accounts for the entropic contribution to the free energy due to the translational degrees of freedom of the critical nucleus, $\delta w^<$ is the correction to the free energy of the metastable phase due to the fluctuation around the local minimum of the free energy, and $\ln\sqrt{|\det H_\Delta|}$ accounts for both the flux around the saddle point and the deviation of the steady-state distribution from the equilibrium one. We note that the entropic contribution to the free energy from the rotational degrees of freedom of the cluster, which is included in W^*, is independent of the system size and hence need not be considered explicitly in the present context.

Results

We calculated W for a truncated and shifted Lennard-Jones fluid with cut-off radius 3 in reduced units. Following the previous study,[2] we employ two order parameters. One is the number of the particles N in the system and the other is the potential energy per particle $u_n \equiv \beta U_N/N$. The distribution over the latter was binned using the width of $\Delta u = 0.01$ for each bin. Cubic systems of various sizes were subjected to grand canonical Monte Carlo simulation at temperature $T = 0.741$ and fugacity $z = 0.01$. Periodic boundary conditions were employed. Thus, the system volume not only determines the field of vision for our observation of nucleation but also places a limit on the wavelength of fluctuation accessible to the system. This can influence actual nucleation behavior observed in simulation if the system size is too small, thereby making additional contribution to the expected V dependence of W.

Table 1: Changes in N, U_N, and W upon critical nucleus formation along with the corrections for the reversible work of critical nucleus formation.

L	ΔN	ΔU_N	$\beta(W^* - W_A)$	$\beta(W^* - W_A) + \ln V$	$\beta \Delta W_{ss}$
z=0.014					
6	38	−80.80	16.89	22.26	18.96
8	65	−152.5	19.09	25.33	23.76
10	76	−204.3	18.68	25.58	24.81
12	74	−203.8	18.34	25.80	25.07
16	77	−209.4	17.73	26.05	25.34
z =0.016					
6	33	−62.30	12.02	17.39	14.46
8	51	−104.2	11.38	17.62	16.82
10	50	−116.3	10.65	17.55	17.13
12	51	−117.1	10.22	17.67	17.33
16	56	−126.7	9.312	17.63	17.45
z =0.018					
6	29	−48.36	8.528	13.90	11.43
8	36	−69.84	6.300	12.54	12.51
10	37	−76.45	5.709	12.62	12.66
12	36	−76.74	5.106	12.56	12.70
16	39	−80.38	3.899	12.22	12.57
z =0.02					
6	25	−35.91	5.866	11.24	9.345
8	27	−46.65	3.146	9.384	9.744
10	29	−50.78	2.334	9.242	9.738
12	30	−52.64	1.519	8.974	9.659

Table 1 reports the difference in N, U_N, and W between the saddle point (W^*) and the bottom of the free energy well (W_A) corresponding to the metastable state. Results for $L = 16$ at $z = 0.02$ are not included in Table 1 because the free energy surface fails to exhibit a well-defined saddle point, implying that the droplet forms spontaneously in the system. Clearly, this choice of the system size is in violation of the second of the Nishioka-Pound conditions. The translational entropy of the cluster is responsible for the extra stability of the cluster. The agreement in the estimated values of ΔN or ΔU_N using various system sizes is somewhat modest. This is partly because of the large error involved in locating the saddle point and the bottom of the free energy well, where W changes only slightly even for a large change in N or U_N. In addition, there is a systematic error for smaller systems because of the limit they place on the wavelength of fluctuation accessible to the system. From the Table 1, we see that the value of $W^* - W_A$ depends rather strongly on the system

size. Moreover, with the exception of $L = 6$, the translational entropy of the cluster is seen to account for most of the V dependence.

For $L \geq 10$, simulation yields an estimate of $\beta\Delta W_{ss}$ practically independent of the system size, which not only testifies to the robustness of the simulation methodology but also provides us with some flexibility in choosing V. At $z = 0.014$, the value of $\beta\Delta W_{ss}$ for $L = 8$ shows a somewhat large deviation from the results for $L \geq 10$, indicating that the system might be still too small to embrace all the relevant fluctuations at the fugacity value in question. Interestingly, even the smallest system volume we used ($L = 6$) yields a quite accurate estimate of $\beta\Delta W_{ss}$ once the fugacity becomes large enough, and hence the critical nucleus becomes sufficiently small.

Conclusion

To summarize, we mapped out the free energy surface W of vapor phase nucleation for a truncated and shifted Lennard-Jones fluid. At the temperature we studied, the shape of the free energy surface depends strongly on the system size V. Nonetheless, free energetics of steady-state nucleation is shown to be independent of V. The correction terms we introduced afford direct physical interpretations.

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