Response to "Comment on 'Theoretical prediction of crystallization kinetics of a supercooled Lennard-Jones fluid'" [J. Chem. Phys. 151, 017101 (2019)]

K. G. S. H. Gunawardana[1,a)] and Xueyu Song[2,b)] (iD)

AFFILIATIONS

[1] Department of Engineering Technology, Faculty of Technology, University of Ruhuna, Matara, Sri Lanka and Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA
[2] Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA

a) harshadewa@etec.ruh.ac.lk
b) xsong@iastate.edu

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The Classical Nucleation Theory (CNT) describes the Gibbs free energy cost to create a crystallite of N atoms out of a metastable phase as follows:

$$\Delta G = -N|\Delta\mu| + \gamma A. \qquad (1)$$

The first term gives the Gibbs free energy cost to create a crystallite of N atoms in its bulk phase. The term $\Delta\mu = \mu_c - \mu_l$ is the thermodynamic driving force, where μ_c and μ_l are the chemical potentials of bulk crystal and liquid phases. The second part is the contribution from the solid-liquid interface, where γ is the solid-liquid interfacial free energy and A is the area of the interface. The driving force is estimated with bulk properties of liquid and crystal phases. The interfacial free energy $\gamma = \gamma_0$ is often estimated from its planar interface value γ_0, the capillarity approximation. These independently estimated quantities lead to a nucleation profile, where the critical nucleus locates at the maximum of the profile and the resulting nucleation barrier can be used to estimate the nucleation rate. It has been a long standing goal of the classical nucleation theory to be able to predict accurate nucleation rate from these independently estimated thermodynamical properties.

Besides the question that the temperature dependent interfacial free energy should used, it has been known that the curvature dependent interfacial free energy may well be important for the nucleation barrier estimation as evidenced from many works cited in our paper.[1] If the nucleus can be approximated by a spherical one, then the curvature dependence of γ can be approximated as

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

where δ is the first order correction to the γ_0 due to curvature($1/R$), analogous to the "Tolman length"[2] widely used for liquid-vapor interfaces.

Our paper presented a thermodynamic methodology to calculate δ independently by utilizing the long lifetime critical nuclei under weakly supercooled conditions, in contrast to the usual seeding method,[3,4] but similar to the work of Statt et al. for the direct estimation of nucleation barrier.[5]

As pointed out by the author of the comment,[6] the finite size effect of simulations can lead to artifacts, but it can also be exploited to study many interesting phenomena, nucleation in particular; for example, see Ref. 5. The strategy in our paper[1] is to utilize the metastable coexisting line for the curved interfaces in a finite simulation system. For example, at $T = 0.62$, several spherical crystalline clusters of Lennard-Jones particles which coexist with its liquid in a simulation box in an NVT ensemble are shown in Fig. 1.

Such metastable coexistence for curved interfaces is not just a simulation observation; it is also well known experimentally. For example, the Gibbs-Thomson effect, in which the melting temperature of nanoparticles is lower than the bulk one, is well documented in the literature; see Ref. 7 and the extensive references therein.

With the above discussion in mind, let us address the issues raised in the comment. The gist of the first paragraph of the comment is that our critical nucleus is too large from his estimate and
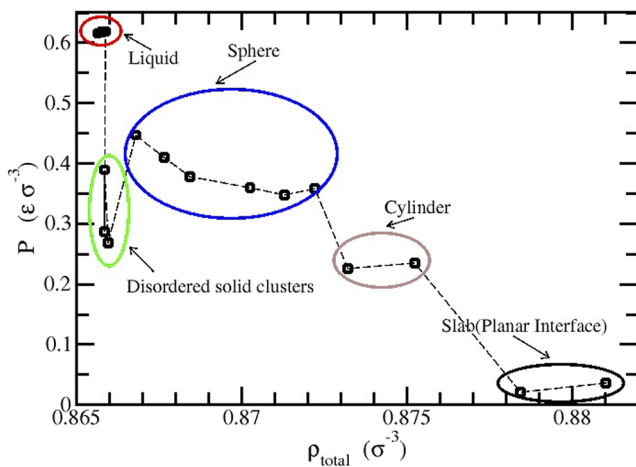
FIG. 1. Pressure density phase diagram at $T = 0.62$. The x axis is the total density of the simulation box. As the total density of the simulation box is reduced from $\rho_{total} = 0.95$ in the crystalline phase at $T = 0.62$, a coexisting planar slab with its liquid around $\rho_{total} = 0.88$ is first observed, which is the normal phase coexistence condition under thermodynamic limit. Further reducing the total density (by removing atoms from the liquid region), the transition of the planar slab to a cylindrical shape of crystal coexisting with its liquid is observed, then to a spherical shape cluster, and finally to a liquid below $\rho_{total} = 0.866$. A similar phase diagram is observed for other potentials; for example, see Ref. 5.

thus our "$R(T)$, shown in Fig. 2(a) in our paper has no physical meaning . . . ." Clearly, the author did not realize that the metastable coexistence for curved interface has an extra degree of freedom and hence can exist with different temperatures and pressures from the bulk one. To be more concrete, the author estimates that our $T = 0.64$ critical nucleus cannot be as large as $\approx 17\,000$ particles, but his calculation is based on an incorrect liquid density. The cluster size shown in Fig. 1 of our paper is from supercooling of $T/T_m = 0.64/0.67$, rather than $T/T_m = 0.64/0.69$ as the author claimed. The mistake is due to his incorrectly used liquid density $\rho_l = 0.8722$, which is the total density of the simulation box, rather the true coexisting liquid density shown in Fig. 3 of our paper, $\rho_l = 0.8556$. If the correct coexisting density is used, then the coexisting liquid pressure is $P_l = 0.555$ from Fig. 3 of our paper, which will lead to the bulk melting temperature $T_m = 0.67$ if the result of Ref. 3 of the comment is used.

In the second paragraph of the comment, the author pointed out that some how our $P_s < P_l$ cannot be true for a critical nucleus, rather a finite size effect in Fig. 3 of our paper. On the contrary, an important point of our Fig. 3 is that the generalized Laplace equation is a mechanical equilibrium condition,[8] which could lead to $P_s < P_l$ due to the strain of liquid-solid interface in contrast to the liquid-vapor interface. As for the slight mismatch of the density and pressure numbers with his equation of state (EOS) in Ref. 3 of the comment, it could be the statistical error or slightly different temperature, which is beyond the purpose of this short reply.

On the other hand, we do agree with some of the comment's author's points on the calculation of the chemical potential difference, namely, the difficulty in accurately measuring the chemical potential of deeply supercooled liquid. This is the reason we adopted the classical density functional theory to calculate such quantities, but the characterization of the deeply supercooled liquid state turns out to be difficult. In our paper, we did repeat the nucleation rate simulations under the same conditions as the cited paper,[9] which is total density $\rho_t = 0.95$ at $T = 0.58$. From our simulations, once we quenched the system from $T = 1.2$ to $T = 0.58$, we did observe the formation of crystal, but the state at $\rho_t = 0.95$ and $T = 0.58$ is a mixture of liquid and crystalline clusters with large pressure and total energy fluctuations. This is why we adopted a mixture model for the chemical potential calculation. In retrospect, it may lead to reasonable result as shown in Fig. 4 of our paper (the y-axis is mislabeled in the paper, and it should be in terms of $\beta\epsilon$), but the mixture model may not be accurate enough for the chemical potential calculations. A better way to address these issues may be to work with mild supercooled liquid states for the nucleation profile and nucleation rate simulations, the simulation time constraint notwithstanding. We do not share the confidence of the comment's author that his EOS will lead to accurate chemical potential of the deeply supercooled state, which only can be obtained from large extrapolation of his simulation data. Therefore, his estimate of the nucleation barrier, which is very close to the simulated one, may well be fortuitous. To us, a systematic study at various supercooled states is needed to resolve this issue.

As for the comment of the last paragraph raised by the author regarding the inconsistently used dividing surfaces in our thermodynamic approach, we cannot comment on that at this point of time as Ref. 12 cited is not available to us, but we will stand by our derivation, which only uses the Gibbs dividing surface throughout. We expect that the readers will form their own opinion about this.

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