Reply to "Comment on 'Simple improvements to classical bubble nucleation models'"

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We reply to the Comment by Schmelzer and Baidakov [Phys. Rev. E **94**, 026801 (2016)]. They suggest that a more modern approach than the classic description by Tolman is necessary to model the surface tension of curved interfaces. Therefore we now consider the higher-order Helfrich correction, rather than the simpler first-order Tolman correction. Using a recent parametrization of the Helfrich correction provided by Wilhelmsen *et al.* [J. Chem. Phys. **142**, 064706 (2015)], we test this description against measurements from our simulations, and find an agreement stronger than what the pure Tolman description offers. Our analyses suggest a necessary correction of order higher than the second for small bubbles with radius $\lesssim$1 nm. In addition, we respond to other minor criticism about our results.

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Our recent publications [1–3] report on large-scale molecular dynamics (MD) simulations of bubble nucleation and the corresponding improvements for theoretical bubble nucleation rate models which they motivate. Comments from Schmelzer and Baidakov are critical of some methodologies in our work [4]. In particular, they pointed out that the correction of the planar surface tension based on the Helfrich expansion [5] should be used rather than a simple first-order Tolman correction. We would like to thank them for the comments and take this opportunity to further clarify these points.

We agree with their statement that bubble nucleation can be described appropriately in terms of classical nucleation theory (CNT), if the size dependence of the surface tension is included adequately for nanosized bubbles. The model of surface tension based on the Helfrich expansion is interesting to consider, although it includes some additional parameters. Recently, Wilhelmsen *et al.* [6] obtained values for the parameters in the Helfrich expansion for various temperatures and cutoff radii in the case of a Lennard-Jones liquid using density functional theory (DFT) calculations. The validity of the Helfrich expansion for nanosized bubbles has not yet been fully clarified [6]. In this Reply, we test the Helfrich expansion model for various bubble sizes and temperatures, using results for surface tension from our MD simulations and from Baidakov and Babrov [7]. We also respond to minor comments given by Schmelzer and Baidakov.

First, we would like to comment on the preexponential factor in the nucleation rate. The surface tension of nanosized bubbles can be precisely estimated from the nucleation rates when given the correct preexponential factor. Kagan [8] formulated a suitable preexponential factor for the nucleation rate; however, he did not give the final explicit expression for the preexponential factor in general cases. For large negative pressures, bubble growth is regulated by the viscosity of the liquid. In this case, the approximate expression given by Kagan [8] is valid and widely used in the previous studies. Although a similar expression was also presented in Eq. (8) of Ref. [7], it contains a typographical error. In the expression, the molecular number density of the liquid should be replaced by that of the saturated vapor. Based on the method of Kagan [8], we have presented the final explicit expression for the preexponential factor [Eq. (49) in Ref. [3]]. We also pointed out the importance of the inertia effect on bubble growth at moderate negative pressures and derived another useful approximate expression including the inertia effect, which is more accurate than Kagan's. Our improved prefactor enabled us to evaluate the surface tension of nanosized bubbles precisely from the numerical (or experimental) data, as done in Ref. [3].

In Baidakov and Babrov [7], the Tolman equation is introduced as

$$\gamma = \frac{\gamma_0}{1 + 2\delta_\mathrm{T}/r}, \tag{1}$$

where γ is the surface tension, γ_0 is the planar surface tension, and r is the radius of the bubble. We have evaluated Tolman length δ_T, by comparing our simulation with Eq. (1) (see Figs. 3–5 in Ref. [3]):

Schmelzer and Baidakov pointed out that the sign of the second term in the denominator in the right-hand side of Eq. (1) should be negative in the case of a bubble. We agree with the use of a unified expression to avoid confusion, although in the literature, Eq. (1) is often used. In any case, our results suggest that the surface energy is smaller than the planar value at various temperatures ($\lesssim$ the triple point) for both bubbles as well as droplets [1,3,9,10]. Thus, if the custom that they suggested is followed, then the negative Tolman length indicates a smaller surface energy than the planar value for bubbles.

Up to now, we have argued with the simple formula of Eq. (1) in Refs. [1,3]; however, it is also important to compare with other models. Schmelzer and Baidakov recommend modeling the curvature dependence of the surface tension of

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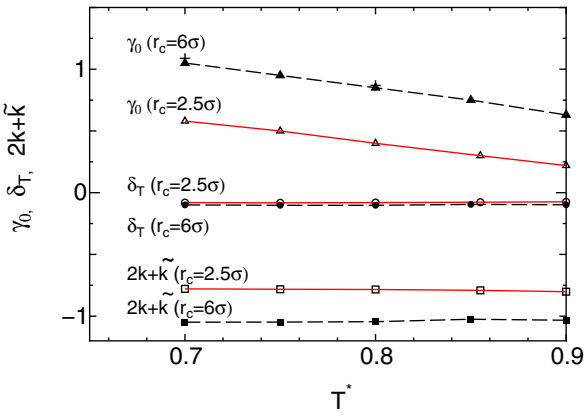

FIG. 1. Parameters in Eq. (3) as a function of the temperature $T^*(=k_BT/\epsilon)$ obtained by Wilhelmsen *et al.* [6], where T, k_B, and ϵ are the temperature, the Boltzmann constant, and the binding energy in the Lennard-Jones potential, respectively. The parameters obtained at $r_c = 2.5\sigma$ (6.0σ) are shown as open (filled) symbols. The surface energies γ_0 in Ref. [7] are also shown as cross marks.

bubbles and droplets by the relation

$$\gamma = \frac{\gamma_0}{1 + 2\delta_T c_s + l^2 c_s^2}, \tag{2}$$

where c_s is the bubble curvature ($c_s < 0$) or droplets ($c_s > 0$). We agree with the validity of Eq. (2), although there is an inconsistency in their Comment because $c_s > 0$ is used for bubbles, which is the same in Eq. (1), in Baidakov and Bobrov's paper (Ref. [7]).

The expression (2) follows from the interfacial free energy in the Helfrich form given by

$$\gamma = \gamma_0 \pm \frac{2\delta_T\gamma_0}{r} + \frac{2k + \tilde{k}}{r^2} + \cdots, \tag{3}$$

where k and $\tilde{k}$ are the bending rigidity and the rigidity constant associated with Gaussian curvature [5,6], respectively. In the double sign of Eq. (3), the upper one (i.e., +) corresponds to the bubble case, while the lower is the droplet case. From Eq. (3), the coefficient l^2 in Eq. (2) is given by $4\delta_T^2 - (2k + \tilde{k})/\gamma_0$ within the second-order accuracy. Note that the corrections higher than the second order should also be included in Eqs. (2) and (3) for very small bubbles. These expressions are reasonable, and should be compared with MD simulations as a separate model. Thus, we compare the surface energy obtained by MD simulations with Eqs. (2) and (3) (see below).

When comparing with MD simulations, we should be cautious regarding the cutoff radius in the MD simulations. The coefficients in the Helfrich expansion [and in Eq. (2)] are strongly sensitive to the cutoff radius. In our simulations [1,3], we adopt a cutoff radius of 2.5σ. Recently, Wilhelmsen *et al.* [6] obtained the coefficients δ_T, k, and $\tilde{k}$ in Eq. (3) for various values of the cutoff radius and temperature based on DFT, as shown in Fig. 1. With these parameter values, it is possible to compare the theoretical model of Eqs. (2) and (3) with the results from the MD simulations.

Figure 2 shows a comparison of the surface tension between the MD simulations [3,7] and theoretical models with Eqs. (1) and (3) as a function of the critical bubble radius, r. Figure 2(a)

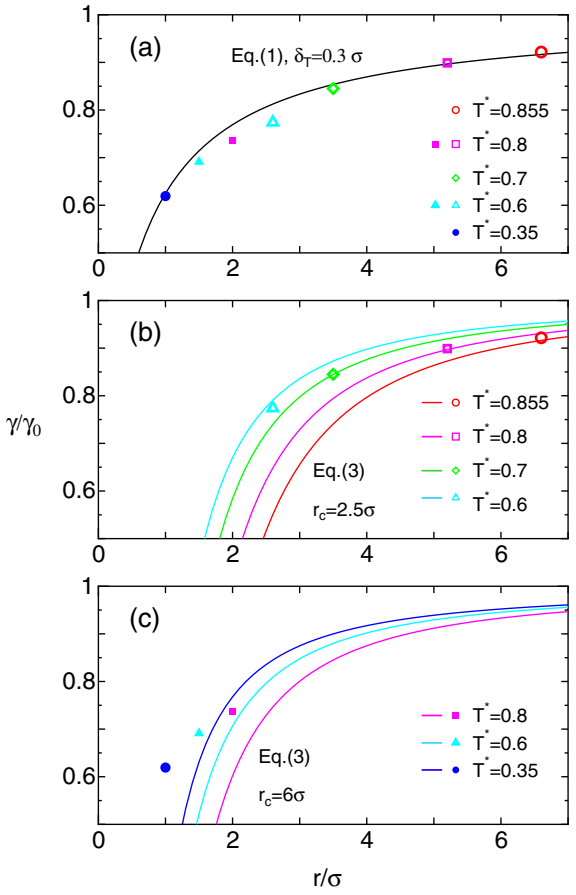

FIG. 2. Comparison of surface tension between the MD simulations [3,7] and theoretical models using Eqs. (1) and (3), as a function of the critical bubble radius, r. (a) Surface energy ratio γ/γ_0, obtained by our MD simulation (open symbols) and from Ref. [7] (filled symbols) with various temperatures. The Tolman equation, Eq. (1), with $\delta_T = 0.3\sigma$ is shown by the solid curve. (b) Our MD simulations at $T^* = k_BT/\epsilon = 0.6$, 0.7, 0.8, and 0.855 (open symbols) and the theoretical model with Eq. (3) (solid curves). (c) Results by Baidakov and Bobrov [7] (filled symbols) and with Eq. (3) (solid curves).

shows the results for various temperatures obtained from MD simulations [3,7] compared with the simple model of Eq. (1) with $\delta_T = 0.3\sigma$ proposed by Tanaka *et al.* [3]. This simple model can well reproduce the surface tension obtained from MD simulations [3,7] for a wide range of critical bubble radii, although the theoretical validity of this model is uncertain.

In Figs. 2(b) and 2(c), the model of Eq. (3) is compared with MD simulations [3,7], respectively. In Fig. 2(b), we used the parameter values with the cutoff radius 2.5σ obtained by Wilhelmsen *et al.* [6] for δ_T, $2k + \tilde{k}$, and γ_0. Wilhelmsen *et al.* did not calculate these for $T^* < 0.7$. The parameters δ_T and $2k + \tilde{k}$ are almost independent of temperature (see Fig. 1); therefore, we assumed that the values of δ_T and $2k + \tilde{k}$ at $T^* < 0.7$ are the same as those at $T^* = 0.7$. The values of γ_0 at $T^* = 0.6$ are obtained from a linear extrapolation of the values at $T^* = 0.7$ and 0.8. We find that the model of Eq. (3) also well reproduces all the results of our MD simulations [3] with relatively large critical bubble radii. Equation (2) was also tested and it was determined that the original Helfrich

expansion of Eq. (3) gives better agreement with the MD results than Eq. (2).

In Fig. 2(c), we used the values of γ_0 obtained by Baidakov and Bobrov [7]. For δ_T and $2k + \tilde{k}$, the parameter values with 6σ in Ref. [6] are used because $r_c = 6.7\sigma$ is adopted in the MD simulation by Baidakov and Bobrov [7]. For $T^* \leqslant 0.7$, δ_T and $2k + \tilde{k}$ are assumed to be constant. Figure 2(c) shows relatively large deviations between Eq. (3) and the MD results from Ref. [7]. Baidakov and Bobrov [7] have already reported similar deviations of their MD simulations from the results of DFT calculations. They suggested that the parameter values of l should be smaller than those obtained from previous DFT calculations [11].

It should be noted that Baidakov and Bobrov [7] used an overestimated preexponential factor, as stated above, which causes an overestimation of the surface tension. Therefore, the deviations in Fig. 2(c) would be reduced by the use of an accurate preexponential factor. These deviations between the MD results and the DFT calculations could also be due to small critical bubble radii. The Helfrich expansion assumes that the bubble radius is not very small. Wilhelmsen *et al.* [6] pointed out that the expression of Eq. (3) is valid only when $\gamma \gtrsim 0.8$ at $T^* = 0.9$ (see Fig. 5 in Ref. [6]). Thus, the deviations in Fig. 2(c) may indicate that higher order terms than the second order should also be included in the Helfrich expansion for small bubbles with radius <1 nm, although the higher order terms also require the estimation of additional parameters. Furthermore, another problem with the work required for the critical bubble formation was recently pointed out in Refs. [12,13]. These unclear points regarding the surface tension and formation work should be investigated in detail in future studies using DFT calculations and MD simulations.

In Refs. [1,3], we gave an approximate expression of the work for critical cluster formation as

$$\Delta G = \frac{16\pi\gamma^3}{3(P_{\mathrm{eq}} - P_{\mathrm{l}})^2\delta^2}, \tag{4}$$

where P_{eq} and P_{l} are the equilibrium vapor pressure at saturation and the liquid pressure, respectively, and δ is a correction factor referred to as the Poynting correction. The model with $\delta = 1$ (or $\delta < 1$) was labeled CNT (or PCNT) in Refs. [1,3]. Schmelzer and Baidakov [4] pointed out that the name CNT should be used for the exact expression rather than the above approximate one. In the most previous studies with MD simulations, however, the model with $\delta = 1$ is adopted as CNT since δ is close to unity in most cases [14–16]. Only a small deviation of δ from unity causes a huge difference in the evaluation of the nucleation rate because of its strong exponential dependence on ΔG. The deviation in the nucleation rate can be several orders of magnitude at temperatures below the triple point and moderate negative pressures, as shown in Fig. 4 of [3]. In such cases, the Poynting correction is crucial. We demonstrated the importance of the Poynting correction by comparing the PCNT with the CNT.

In the last paragraph of [4], they gave three additional comments. In comment (i), they emphasized that the results of their MD simulations are reproduced well with the appropriate expression for the curvature dependence of the surface tension based on the Helfrich expansion. However, their adopted value of l^2 is smaller than that obtained from the DFT calculations by [6]. If the value obtained from the DFT calculations is used for l^2, there are relatively large deviations between their MD results and Eq. (3), as shown in Fig. 2(c).

In comment (ii), they criticized our expression for the growth rate of bubbles. Indeed, the growth rate is the key factor in the prefactor of the nucleation rate. But what we need is the growth rate only around the critical size r_c. Around r_c, the growth rate is approximately proportional to $r - r_c$, as pointed out by [8]. Under this valid approximation for the growth rate, we also include the inertia effect, which is neglected in most previous studies.

In comment (iii), they disagreed with our statement that time-lag effects do not allow one to perform an accurate determination of the steady-state nucleation rates. As stated in Ref. [1], we can constrain the mean first passage times (MFPT) with a large number of simulations. However, due to the initial lag time and the early transient nucleation phase, the relation between MFPT and the steady-state nucleation rate is more complex and still under debate [1,9]. In a recent study, Makshin and Galimzyanov showed that estimates for the steady-state nucleation rate based on MFPT disagree by several orders of magnitude [17]. Therefore, we consider that the time-lag effect is still open to debate.

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