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PHYSICAL CHEMISTRY OF NANOCLUSTERS AND NANOMATERIALS

On the Applicability of Young–Laplace Equation for Nanoscale Liquid Drops[1]

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Abstract—Debates continue on the applicability of the Young–Laplace equation for droplets, vapor bubbles and gas bubbles in nanoscale. It is more meaningful to find the error range of the Young–Laplace equation in nanoscale instead of making the judgement of its applicability. To do this, for seven liquid argon drops (containing 800, 1000, 1200, 1400, 1600, 1800, or 2000 particles, respectively) at $T = 78$ K we determined the radius of surface of tension R_s and the corresponding surface tension γ_s by molecular dynamics simulation based on the expressions of R_s and γ_s in terms of the pressure distribution for droplets. Compared with the two-phase pressure difference directly obtained by MD simulation, the results show that the absolute values of relative error of two-phase pressure difference given by the Young–Laplace equation are between 0.0008 and 0.027, and the surface tension of the argon droplet increases with increasing radius of surface of tension, which supports that the Tolman length of Lennard-Jones droplets is positive and that Lennard-Jones vapor bubbles is negative. Besides, the logic error in the deduction of the expressions of the radius and the surface tension of surface of tension, and in terms of the pressure distribution for liquid drops in a certain literature is corrected.

Keywords: liquid drop, surface tension, surface of tension, Young–Laplace equation, molecular dynamics simulation.

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1. INTRODUCTION

Interfacial phenomena involved in bubbles and droplets have attracted the attention of researchers for quite a long time due to their wide applications as well as due to their statistical uncertainties in engineering and science fields [1]. During a phase transition process that has heat and mass transfer, it must go through nanobubbles and nanodroplets for macroscopic droplets and vapor bubbles at early stages in the nucleation process. The research of droplets and vapor bubbles or bubbles in nanoscale is often needed owing to the development of nanotechnology.

The liquid–vapor transition layers of droplets and bubbles have a certain thickness and there exists nonuniformity for density distribution. The interfacial phenomena can be solved on the basis of Gibbs macroscopic thermodynamics theory of capillarity [1, 2]. For a two-phase coexistence system, a parallel set of mathematical surface in transition layer which are perpendicular to the density gradient can be chosen to be what Gibbs called the dividing surface. Once a dividing surface is chosen, the original continuous system is represented by a discontinuous model system. The dividing surface divides the model system into two homogeneous phases. The volumes of bulk liquid phase and vapor phase are corresponding to the volumes of the matter on both sides of the dividing surface of the original system. The value of any intensive quantity such as density, temperature and chemical potential is the same as that of the original system. The dividing surface is called interface phase or surface phase with the same chemical potential and temperature as in the bulk phase. When the dividing surface is round or planar, the extensive quantities of the surface phase are defined to be the ratio of the difference between the corresponding quantities of the original system and the model system to the area of the dividing surface. If the number density of a dividing surface is zero, it is called the equimolar surface, its radius is R_e. For a spherically symmetric system, surface tension γ is different for different dividing surface. The

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homogeneous phase that is on one side located in the center of curvature is marked by α, the other bulk phase is β. The pressure difference of p^α and p^β satisfies the generalized Young–Laplace equation [1]

$$p^\alpha - p^\beta = \frac{2\gamma(R)}{R} + \left[\frac{d\gamma(R)}{dR}\right]. \quad (1)$$

The symbol in square brackets denotes the derivative of $\gamma(R)$ to the radius of dividing surface R for the same original system. For the particular dividing surface, if

$$\left[\frac{d\gamma(R)}{dR}\right]_{R_s} = 0 \quad (2)$$

it is called surface of tension. Its radius is indicated by R_s. The corresponding surface tension is written as $\gamma_s = \gamma(R_s)$. Then Eq. (1) is translated to the traditional Young–Laplace equation

$$p^\alpha - p^\beta = \frac{2\gamma_s}{R_s} = \frac{2\gamma(R_s)}{R_s}. \quad (3)$$

There is no consensus on whether the macroscopic theory of capillarity is applicable for nanosystem.

Some literatures admit the Young–Laplace equation (3) is applicable for nano-system and start analysis and computer simulation by the use of Eq. (3) directly. When the result obtained is not satisfactory, they attribute it calculation error or statistic fluctuation because the molecular number is not sufficient [3, 4]. For example it is the general way to follow a thermodynamics route and mechanical route in literature in molecular dynamics study [3, 5]. According to the Tolman effect $\gamma(R_s)$ is dependent on R_s. There is [1, 6]

$$\frac{\gamma_s}{\gamma_\infty} = \frac{1}{1+2\delta_\infty/R_s} + \ldots = 1 - 2\delta_\infty/R_s + \ldots, \quad (4)$$

where γ_∞, δ_∞ are the surface tension and the Tolman length of planar interface. For droplets and vapor bubbles that have the same single component the value of δ_∞ is opposite. A formula for thermodynamics route [3] is

$$R_s = \frac{3\gamma_\infty - [9\gamma_\infty^2 - 4\gamma_\infty R_e(p^\alpha - p^\beta)]^{1/2}}{p^\alpha - p^\beta}. \quad (5)$$

For thermodynamics route, R_s and $p^\alpha - p^\beta$ can be obtained by MD simulation. Substituting R_s and $p^\alpha - p^\beta$ into Eq. (3), γ_s is obtained. Since the result is given by use of the Young–Laplace equation, it is sure to satisfy Young–Laplace equation. This can't determine whether the Young–Laplace equation is established in nanoscale.

For mechanical route [3], there is

$$\gamma_s^3 = -\frac{1}{8}(p^\alpha - p^\beta)^2 \int_0^\infty r^3 \frac{dp_N(r)}{dr} dr, \quad (6)$$

where p_N is normal component of pressure tensor, γ_s is the surface tension obtained by MD simulation. Substituting γ_s and $p^\alpha - p^\beta$ into Eq. (3), R_s is given. The result meets the Young–Laplace equation because of the direct use of the Young–Laplace equation. Whether the Young–Laplace equation is applicable in nanoscale can't be approved by this way either.

Are there some literatures that test the applicability of the Young–Laplace equation? In 2008 Matsumoto et al. [7] made a series of molecular simulations to evaluate the pressure difference of bubbles and the radius of bubbles and then the surface tension was obtained from the Young–Laplace equation. They found that the surface tension is independent of the bubble radius and agrees with the surface tension of a planar interface. So they claimed that the Young–Laplace equation is applicable in nanoscale. However, as Cui et al. [8] pointed that this logic was at fault, obviously. From Eq. (4), Tolman effect should be in existence for nano bubbles and so the surface tension is dependent on the curvature radius [1, 6]. The contradiction between Eq. (4) and Matsumoto's results from Young–Laplace equation may means that the Young–Laplace equation is not applicable for nano bubbles. Droplets and bubbles in nanoscale are both liquid-vapor equilibrium system, they should follow the same basic theory. The difference is molecular number little inside bubbles and much outside bubbles. For droplets it is on the contrary. So the Tolman length of droplets and vapor bubbles are opposite.

Some literatures negated the applicability of the Young–Laplace equation in nanoscale. In 2005 Tartakovsky [8] considered that the Young–Laplace equation is fail when a droplet is very tiny. He adopted a qualitative approach and had no quantitative description. He didn't consider the Tolman effect. The rigorous concept of Gibbs surface of tension didn't mentioned in the paper. So it can't negate the applicability of the Young–Laplace equation. In 2006 Nagayama [9] pointed out the Young–Laplace equation is false according to their calculation of nano vapor bubbles. But they didn't discuss the magnitude of error of this equation in nanoscale.

We suppose that it is more effective to express the applicability of the Young–Laplace equation in nanoscale by error estimation. For this aim, we must use the micro-expressions suitable for MD of the uniform phase pressures and those of the surface tension and radius of surface of tension. To compare thus obtained surface tension with those directly calculated from the Young–Laplace equation will be able to test the magnitude of error of the Young–Laplace equation. Shuwen Cui et al. did this for nano-scale cylindrical liquid and got the conclusion that Laplace equation is applicable in nanoscale with fairly good approximation [8]. The nanodroplets are the objects of our studies. In Section 2 below, we give the formulas suitable for MD calculations based on some basic micro-expressions appeared in [1] with an improved deduction. In the

Appendix the logic error in the deduction of [1] is analyzed. In Section 3 the simulation, results and discussions are given. The conclusion is given in Section 4.

2. THEORETICAL BASIS AND CALCULATION SCHEME

Consider a single-component droplet. We choose the section from the radius R^α to R^β of solid angle. It satisfies $R^\alpha < R_e < R^\beta$, $R^\beta - R_e \gg b$, and $R_e - R^\alpha \gg b$ where b is the thickness of interfacial layer. In spherical coordinates the pressure tensor can be written as

$$\overline{\overline{p}} = p_N(r)\mathbf{e}_r\mathbf{e}_r + p_T(r)\left[\mathbf{e}_\theta\mathbf{e}_\theta + \mathbf{e}_\varphi\mathbf{e}_\varphi\right], \quad (7)$$

where $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_\varphi$ are orthogonal unit vectors, $p_T(r)$ is the transverse component of the pressure tensor.

The isothermal differential thermodynamic equation of the droplet model is [1]

$$\begin{aligned}(dF)_T &= -p^\alpha dV^\alpha - p^\beta dV^\beta + \gamma dA \\ &+ A[d\sigma/dR]dR + \mu dN.\end{aligned} \quad (8)$$

Now keep the radius of the general dividing surface R constant. Consider the isothermal imaginary change of solid angle. Equation (8) becomes

$$\begin{aligned}(dF)_T &= -p^\alpha dV^\alpha - p^\beta dV^\beta + \gamma dA + \mu dN \\ &= -\int_{R^\alpha}^{R^\beta} r^2 p^{\alpha,\beta}(r,R)\sin\theta dr d\theta d\varphi \\ &+ \gamma\sin\theta R^2 d\theta d\varphi + \mu dN,\end{aligned} \quad (9)$$

where

$$p^{\alpha,\beta} = \begin{cases} p^\beta, & r > R \\ p^\alpha, & r < R. \end{cases} \quad (10)$$

The expression of $(dF)_T$ of the real system is

$$(dF)_T = -\int_{R^\alpha}^{R^\beta} r^2 P_T(r,R)\sin\theta dr d\theta d\varphi + \mu dN. \quad (11)$$

From Eqs. (9) and (11), we obtain the surface tension of general dividing surface

$$\gamma(R) = \int_{R^\alpha}^{R^\beta}\left(\frac{r}{R}\right)^2 dr\left[p^{\alpha,\beta}(r;R) - p_T(r)\right]. \quad (12)$$

This equation was obtained in [1] as Eq. (4.217) by other method. Our method is much simpler than the method in [1]. Equation (12) is suitable for surface of tension certainly.

According to the definition of surface of tension, Eq. (8) is simplified as

$$(dF)_T = -p^\alpha dV^\alpha - p^\beta dV^\beta + \gamma_s dA_s + \mu dN, \quad (13)$$

where A_s is the area of surface of tension. Now consider an imaginary isothermal process, put a thin column with thickness dh into the thin space with the same thickness between two hemispheres, then Eq. (13) becomes

$$\begin{aligned}(dF)_T &= -p^\alpha dV^\alpha - p^\beta dV^\beta + \gamma_s dA + \mu dN \\ &= -2\pi\int_{R^\alpha}^{R^\beta} rp^{\alpha,\beta}(r,R_s)drdh + 2\pi R_s\gamma_s dh + \mu dN,\end{aligned} \quad (14)$$

where dh is the extended thickness. For the real system, there is

$$(dF)_T = -2\pi\int_{R^\alpha}^{R^\beta} rP_N(r,R_s)drdh + \mu dN. \quad (15)$$

From Eqs. (14) and (15), we obtain the surface tension of R_s

$$\gamma(R_s) = \int_{R^\alpha}^{R^\beta}\left(\frac{r}{R_s}\right)\left[p^{\alpha,\beta}(r,R_s) - p_T(r)\right]dr. \quad (16)$$

Here the derivation of Eq. (16) is superior to that of the same equation (4.205) in [1] logically. Equations (16) and (12) are suitable for the surface of tension. Equating them gives the equation that determines R_s

$$\int_{R^\alpha}^{R^\beta} r(r - R_s)\left[p^{\alpha,\beta}(r,R_s) - p_T(r)\right]dr = 0. \quad (17)$$

This is the transformation of Eq. (4.207) in page 110 of [1], but our derivation has corrected the logic flaw. A detailed comment is given in Appendix. By rearrangement of Eq. (17), we obtain

$$\begin{aligned}&R_s^3\left(\frac{p^\beta}{6} - \frac{p^\alpha}{6}\right) + R_s\left(\frac{p^\alpha R^{\alpha^2}}{2} - \frac{p^\beta R^{\beta^2}}{2} + \int_{R^\alpha}^{R^\beta} rp_T(r)\,dr\right) \\ &+ \left(\frac{p^\beta R^{\beta^3}}{3} - \frac{p^\alpha R^{\alpha^3}}{3} - \int_{R^\alpha}^{R^\beta} r^2 p_T(r)\,dr\right) = 0.\end{aligned} \quad (18)$$

For convenience, we introduce the following notation

$$D_1 = \int_{R^\alpha}^{R^\beta} rp_T(r)\,dr, \quad D_2 = \int_{R^\alpha}^{R^\beta} r^2 p_T(r)dr. \quad (19)$$

Then Eq. (18) becomes

$$\begin{aligned}&R_s^3\left(\frac{p^\beta - p^\alpha}{6}\right) + R_s\left(\frac{p^\alpha R^{\alpha^2} - p^\beta R^{\beta^2}}{2} + D_1\right) \\ &+ \left(\frac{p^\beta R^{\beta^3} - p^\alpha R^{\alpha^3}}{3} - D_2\right) = 0,\end{aligned} \quad (20)$$

where p^{α}, p^{β}, and D_i $(i = 1,2)$ can be obtained by MD simulations. Eq. (20) becomes a cubic equation in one variable R_s. The solution procedure is stylized. For simplified calculation of MD, according to the equilibrium equation [3],

$$\frac{\partial p_N}{\partial r} + \frac{2(p_N - p_T)}{r} = 0, \tag{21}$$

we have

$$p_T(r) = \frac{r}{2}\frac{\partial p_N(r)}{\partial r} + p_N(r). \tag{22}$$

Equation (19) can be written in the following form

$$D_1 = \frac{1}{2}(R^{\beta^2} p^{\beta} - R^{\alpha^2} p^{\alpha}), \tag{23}$$

$$D_2 = \frac{1}{2}(R^{\beta^3} p^{\beta} - R^{\alpha^2} p^{\alpha}) - \frac{1}{2}\int_{R^{\alpha}}^{R^{\beta}} r^2 p_N(r) dr. \tag{24}$$

Similarly Eq. (12) is transformed into

$$\gamma_s = \frac{R_s}{3}\left(p^{\alpha} - p^{\beta}\right) + \frac{1}{3R_s^2}\left(R^{\beta^3} p^{\beta} - R^{\alpha^3} p^{\alpha}\right) - \frac{D_2}{R_s^2}. \tag{25}$$

By MD simulations we obtain $p_N(r)$; then p^{α}, p^{β}, and D_i $(i = 1,2)$ can be obtained. Substituting them into Eq. (20), we have R_s. Then the surface tension γ_s is obtained from Eq. (25). This calculation idea avoids the determination of surface tension by substituting p^{α}, p^{β}, and R_s into the Young–Laplace equation.

We check errors of the Young–Laplace equation (3),

$$\Delta(p^{\alpha} - p^{\beta}) = (p^{\alpha} - p^{\beta}) - \frac{2\gamma_s}{R_s}. \tag{26}$$

Substituting p^{α}, p^{β} obtained by MD simulation and R_s given from Eq. (20) and γ_s provided by Eq. (25) into Eq. (26), we have the error of $\Delta(p^{\alpha} - p^{\beta})$ of the Young–Laplace equation (3).

3. COMPUTER SIMULATION AND RESULTS AND DISCUSSION

The droplets formed by argon atoms are our subjects investigated. According to the scheme of Section 2, we study systems with numbers of particles (liquid + vapor) 800, 1000, 1200, 1400, 1600, 1800, 2000. The relation between the surface tension and curvature radius is analyzed. The applicability of the Young-Laplace equation is tested.

The Lennard-Jones potential (LJ) between argon atoms takes the form

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{27}$$

where r, ε, and σ are the inter-particle distance, energy scale and atomic diameter respectively. The parameters are chosen as $\varepsilon/k_B = 120$ K, $k_B = 1.38\times10^{-23}$ J/K, $\sigma = 0.3405$ nm, $m = 6.63382\times10^{-26}$ kg. All quantities are dimensionless and are expressed by symbol*. On the basic parameters of argon atom, the quantities are nondimensionalized as follows:

length: $r^* = r/\sigma$ temperature: $T^* = k_B T/\varepsilon$ time: $t^* = t\sqrt{(\varepsilon/m\sigma^2)}$;

density: $\rho^* = \rho\sigma^3/m$ force: $f^* = f\sigma/\varepsilon$ energy: $E^* = E/\varepsilon$;

pressure: $p^* = p\sigma^3/\varepsilon$.

The cubic box size of simulation system is $x^*\times y^*\times z^* = 30.0\times30.0\times30.0$. The simulations have been carried out at $T^* = 0.65$. The cutoff distance is $r_c^* = 3.0$.

The initial configuration was constructed by putting particles on a finite cubic lattice located at the central part of the box. The mirror boundary condition is used in all directions. At the initial time the particles were given velocities according to the Maxwell–Boltzmann distribution. The Velocity–Verlet algorithm is used in MD [10]. NVT ensemble was used before equilibration at temperature 78 K. The cell index method is adopted in calculation of force acted on atoms. The time step is $\delta t = 5$ fs before equilibrium. The temperature control method is velocity scaling scheme. The approaching equilibrium degree was monitored by total energy fluctuation of system. After equilibrium we used accumulative average method on the determinations of mechanical quantity, physical quantity, etc. The time step is changed to be $\delta t = 2$ fs. On

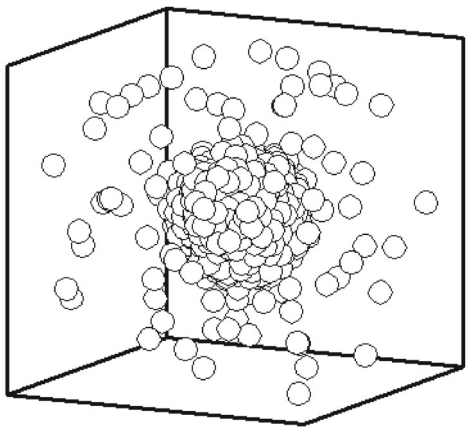

Fig. 1. A snapshot of $N = 1000$ system in equilibrium.

The results of surface tension and calculation error and the relative error etc of seven droplets

N	$p^{\alpha*}$	$p^{\beta*}$	D_1^*	D_2^*	R_s^*	γ_s^*	$\Delta(p^\alpha - p^\beta)^*$	$\frac{\Delta(p^\alpha - p^\beta)^*}{(p^{\alpha*} - p^{\beta*})}$
800	0.2452	0.0017	−1.295	−6.034	4.284	0.523	−0.0007	−0.0029
1000	0.2415	0.0016	−1.221	−7.099	4.801	0.573	0.0012	0.0050
1200	0.2389	0.0016	−1.118	−7.702	5.165	0.612	0.0003	0.0013
1400	0.2387	0.0016	−1.000	−8.044	5.532	0.661	−0.0063	−0.0270
1600	0.2386	0.0016	−0.983	−9.956	5.901	0.700	−0.0002	−0.0008
1800	0.2281	0.0016	−0.961	−11.041	6.301	0.716	−0.0008	−0.0035
2000	0.2240	0.0015	−0.871	−11.933	6.656	0.735	0.0016	0.0072

calculating the mean value of a certain physical quantity $g(t)$, the formula for accumulative average method is

$$\overline{g(i\delta t)}^N = \frac{1}{N}\sum_{i=1}^{N} g(i\delta t). \quad (28)$$

This method can help to judge whether the mean value is obtained. Figure 1 is a snapshot of a droplet and its vapor in equilibrium.

According to the scheme in Section 2, the equilibrium distribution of $p_N(r)$ should be obtained. We have

$$p_N(r) = p_K(r) + p_U(r), \quad (29)$$

where $p_K(r)$, $p_U(r)$ are kinetic and configurational terms respectively.

And there is

$$p_K(r) = k_B T \rho(r), \quad (30)$$

where k_B and $\rho(r)$ are Boltzmann constant and the number density of molecules, respectively. $\rho(r)$ and $p_U(r)$ can be calculated by MD simulations. For the determination of $p_U(r)$ Schofield and Henderson concluded that there are countless kinds of pressure tensor suitable for macroscopic fluid mechanics equation [11]. But Wajnryb [12] have shown that only the Irving–Kirkwood pressure tensor can satisfy the necessary symmetry needed. The Irving–Kirkwood pressure tensor is now extensively accepted for the calculation of $p_U(r)$ [5]. For our spherical symmetry system the Irving–Kirkwood pressure tensor is calculated by the method given in [1].

There is

$$p_U(r) = S^{-1}\sum_k f_k, \quad (31)$$

where $S = 4\pi r^2$ is the area of a spherical dividing surface of radius r with its center being mass center of the droplet, and the sum over k is over the normal components f_k of all the pair forces acting across the surface. In our simulations, thirty-six equidistant spherical surfaces are selected for the seven systems.

Figure 2 is the density profile $\rho^*(r)$ of $N = 800$ and 2000. We recorded configuration every one hundred time steps, and calculated approximate 10000 pictures for a mean value of density distribution. Figure 3 gives a detailed computing information for $N = 1400$ system about $\rho^*(r)$, $p_K^*(r)$, $p_U^*(r)$, and $p_N^*(r)$.

The results of $p^{\alpha*}$, $p^{\beta*}$, D_i^* $(i = 1, 2)$, R_s^*, γ_s^*, $\Delta(p^\alpha - p^\beta)^*$ and the relative error $\Delta(p^\alpha - p^\beta)^*/(p^{\alpha*} - p^{\beta*})$ are shown in table for seven systems. The last column in the table indicates that the absolute values of relative error are between 0.0008 and 0.027. The relative errors of different systems are different. This is because the difference of surface structure is comparatively large for different number systems. This is similar to the conclusion that exists in reference [9].

With the increasing of R_s^*, the corresponding surface tension γ_s^* increases. This is shown in table. This tendency is consistent with the Tolman theory that the Tolman length is positive for LJ droplets and Tolman length is negative for LJ vapor bubbles [6, 13]. It is identical to Fig. 8 in [5].

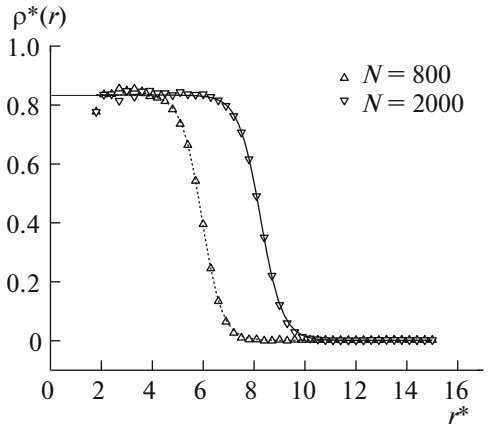

Fig. 2. The density profile $\rho^*(r)$ of $N = 800$ and 2000 system.

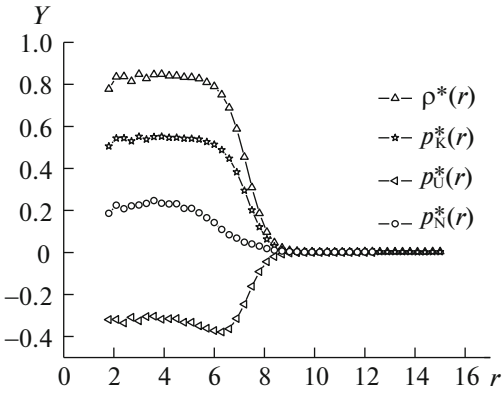

Fig. 3. The computing information of $N = 1400$ system.

4. CONCLUSIONS

For droplets and bubbles in nanoscale, debates continue on the applicability of the Young–Laplace equation. It is more meaningful to calculate the error of the Young–Laplace equation in nanoscale instead of discussing the applicability of the equation. In order to check the error of the Young–Laplace equation, we determine R_s and γ_s of droplets in nanoscale by MD simulations. Pressure difference between liquid and vapor phase ($p^\alpha - p^\beta$) is given by substituting R_s and γ_s into Young–Laplace equation. The results of ($p^\alpha - p^\beta$) obtained by MD simulations are also given. Compare them we have the error of ($p^\alpha - p^\beta$) of the Young–Laplace equation. Seven liquid argon drops (the number of particles are 800, 1000, 1200, 1400, 1600, 1800, 2000) are taken to carry out our scheme at $T = 78$ K. The results show that the absolute values of relative error of two-phase pressure difference are between 0.0008 and 0.027. It indicates that the surface tension of argon droplet increases with increasing radius of surface of tension, which supports the Tolman length of LJ droplets is positive and LJ vapor bubbles is negative.

APPENDIX

The flaw of the formula derivation in reference [1] on Eq. (17)

In reference [1] on page 110, there is a formula

$$R_s = \frac{\int_{R^\alpha}^{R^\beta} r^2[p^{\alpha,\beta}(r,R_s) - p_T(r)]dr}{\int_{R^\alpha}^{R^\beta} r[p^{\alpha,\beta}(r,R_s) - p_T(r)]dr}. \quad \text{(A.1)}$$

Eq. (A.1) is corresponding to Eq. (17) of this article. The derivation of reference [1] is shown as follows:

Consider a flat radial strip, stretching from radius R^α to R^β. The force acting on one side of this strip and the moment of the force about the centre should be equivalent with the values of corresponding model system with surface of tension being dividing surface (the radius is R_s). So we have

$$\int_{R^\alpha}^{R^\beta} r^n p^\alpha dr + \int_{R^\alpha}^{R^\beta} r^n p^\beta dr - R_s^n = \int_{R^\alpha}^{R^\beta} r^n p^{\alpha,\beta} p_T(r)dr, \quad (n = 1, 2), \quad \text{(A.2)}$$

which gives Eq. (A.1).

At first sight for the real system, both the force acting on one side of this strip and the moment of the force about the centre should be equivalent with the values of corresponding model system with any dividing surface (the radius is R). If so, Eq. (A.1) is applicable for any dividing surface. Therefore, it is necessary to prove that both of (A.2) are valid only for the surface of tension and for any other dividing surface, at least one of the two expressions is false. There is no such proof in reference [1], which is a logic error. The present paper gives a strict deduction for (A.2) from the fact that surface of tension and any other surface has different differential equation of thermodynamics. Our derivation of Eq. (17) corrects the flaw.

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