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Citation: Chin. Phys. B, 2021, 30 (1): 016801. DOI: 10.1088/1674-1056/abb65a

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Tolman length of simple droplet: Theoretical study and molecular dynamics simulation*

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(Received 1 July 2020; revised manuscript received 13 August 2020; accepted manuscript online 9 September 2020)

In 1949, Tolman found the relation between the surface tension and Tolman length, which determines the dimensional effect of the surface tension. Tolman length is the difference between the equimolar surface and the surface of tension. In recent years, the magnitude, expression, and sign of the Tolman length remain an open question. An incompressible and homogeneous liquid droplet model is proposed and the approximate expression and sign for Tolman length are derived in this paper. We obtain the relation between Tolman length and the radius of the surface of tension (R_s) and found that they increase with the R_s decreasing. The Tolman length of plane surface tends to zero. Taking argon for example, molecular dynamics simulation is carried out by using the Lennard–Jones (LJ) potential between atoms at a temperature of 90 K. Five simulated systems are used, with numbers of argon atoms being 10140, 10935, 11760, 13500, and 15360, respectively. By methods of theoretical study and molecular dynamics simulation, we find that the calculated value of Tolman length is more than zero, and it decreases as the size is increased among the whole size range. The value of surface tension increases with the radius of the surface of tension increasing, which is consistent with Tolman’s theory. These conclusions are significant for studying the size dependence of the surface tension.

Keywords: Tolman length, surface tension radius of surface of tension, radius of equimolecular surface, molecular dynamics simulation

PACS: 68.03.Cd, 68.35.Md, 68.08.Bc

DOI: 10.1088/1674-1056/abb65a

1. Introduction

A fundamental property of small liquid droplets is the dependence of surface tension on droplet radius, this is size effect. And it is important in chemical physics, for instance, wetting, nucleation, adhesives, condensation, gas absorption.^[1,2] Early in the 19th century, Gibbs concluded that surface tension would be subject to the curvature when the droplet size is very small. In 1949, Tolman extended the idea of Gibbs and showed that if the radius of the surface of tension of a droplet does not coincide with the equimolecular radius, the surface tension must vary with droplet size.^[3] Tolman derived a relation that has become known as the Gibbs–Tolman–Koenig–Buff differential equation

$$\frac{d\gamma_s}{\gamma_s} = \frac{2 \left[\delta/R_s + (\delta/R_s)^2 + (\delta/R_s)^3 \right]}{1 + 2 \left[\delta/R_s + (\delta/R_s)^2 + (\delta/R_s)^3 \right]} \frac{dR_s}{R_s}, \quad (1)$$

where γ_s is the surface tension, δ is the Tolman length, $\delta = R_e - R_s$ (see Fig. 1). R_s is the radius of the surface of tension

on which the Laplace’s equation ($\Delta p = 2\gamma_s/R_s$) is valid. The position of the surface of tension is given in the next section. Here, R_e is the radius of the equimolecular dividing surface on which Gibbs absorption is equal to zero ($\Gamma = 0$), or the number of molecules on which is zero.

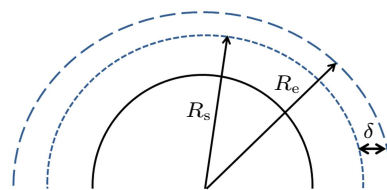


Fig. 1. Schematic diagram of Tolman length δ , equimolecular surface (dashed) and surface of tension (dotted).

Neglecting the terms δ^2/R_s^2 and $\delta^3/3R_s^3$ in comparison with unity, and treating δ as a constant, the integral of Eq. (1) can be readily evaluated to give the simple result

$$\gamma/\gamma_\infty = 1/(1 + 2\delta/R_s), \quad (2)$$

where γ_∞ is the surface tension of liquid for a flat surface.

*Project supported by the National Key Research and Development Program of China (Grant No. 2016YFB0700500), the Scientific Research and Innovation Team of Cangzhou Normal University, China (Grant No. cxtld1907), the Key Scientific Study Program of Hebei Provincial Higher Education Institution, China (Grant No. ZD2020410), the Cangzhou Natural Science Foundation, China (Grant No. 197000001), and the General Scientific Research Fund Project of Cangzhou Normal University, China (Grant No. xnjj11906).

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According to the Taylor's expression, the first approximation of Eq. (2) is

$$\gamma_s = \gamma_\infty \left(1 - \frac{2\delta}{R_s} \right). \quad (3)$$

From Eq. (3), we can see that δ is an important parameter to obtain γ_s . Although the Tolman length has received increasing attention, there still exists controversy on the sign and magnitude of the Tolman length. Many researchers considered the magnitude of the Tolman length to be on the order of molecular dimension. However, the experimental determination of the Tolman length is very difficult and the experimental values have not yet been determined. Until now, the sign of the Tolman length is still controversial.^[4-9] There are some approaches to studying the Tolman length. One can note thermodynamical method,^[10] statistical method,^[11] molecular theory,^[12] density functional method,^[13,14] molecular dynamics simulation,^[5,15-17] *etc.* It is general to assume that $\delta > 0$ ^[18] for spherical droplets and $\delta < 0$ for bubbles in liquid.^[19] By molecular dynamics (MD) simulation Lei *et al.*^[5] showed that the Tolman length is positive, and much smaller in magnitude than previously reported. In particular, they found that the cut-length of interparticle interaction can significantly affect the magnitude of the Tolman length. Blokhuis and Kuipers^[10] obtained a relationship between the Tolman length and the isothermal compressibility, and pointed out that the discrepancy in sign or its dependence on the interaction potential is not yet understood. Yan and Zhu,^[19] Zhu and Wang,^[20] and Wang and Zhu^[21] discussed the expression of Tolman length through theory and MD study. More detailed descriptions about Tolman length are reported in Ref. [10]. Therefore, the computational, experimental, and theoretical studies of the Tolman length need to be further conducted. The results of these treatments are based on rather complex numerical calculations and on their respective hypothesis, so it would be helpful in determining the sign of Tolman length based on simple model and expressing $\delta(R_s)$ analytically in terms of physical properties of the system.

Our work is devoted to studying the Tolman length by theoretical analysis and molecular dynamics simulation. An incompressible droplet model is proposed and the approximate expression and sign for Tolman length is derived in this paper. We find the analytical relation between Tolman length and the radius of the surface of tension. Taking argon for example, molecular dynamics simulation is carried out by using the Lennard-Jones (LJ) potential between atoms at temperature 90 K. Five simulated systems are used, with a total of atoms 10140, 10935, 11760, 13500, and 15360 included respectively. By the theoretical study and molecular dynamics simulation, we find that the calculated values of Tolman length are greater than zero, and it decreases when the size increases in the whole size range.

The rest of the present paper is organized as follows. In Section 2, we give theoretical analysis of the Tolman length. In Section 3 we describe the molecular dynamics simulation, results, and discussion. In Section 4, we present some conclusions drawn from this study.

2. Theoretical analysis of Tolman length

2.1. On derivation of relation formula $\gamma_s/R_s = \gamma_\infty/R_e$

Some authors have used the relation formula $\gamma_s/R_s = \gamma_\infty/R_e$ as an assumption in thermodynamic treatment^[11,22] for Tolman length, and they provided explanation for agreement between derivation and experiment. In this section, the formula is derived by using an incompressible droplet model.

The following main physical parameters are included in Eqs. (4)–(15):

- γ_s the surface tension of liquid,
- γ_∞ the surface tension of liquid for a flat surface,
- R_s the radius of the surface of tension,
- R_e the radius of the equimolecular dividing surface,
- p_{in} the internal pressure,
- p_o the pressure outside,
- p_{inr} the repulsive pressure in the interior of the droplet,
- p_{ina} the attractive pressure in the interior of the droplet,
- ϕ_I the potential of particles in the interior,
- ϕ_S the potential of particles on the surface.

In the interior of the model, $p_{in} = p_{inr} + p_{ina}$ is the internal pressure, where p_{inr} is the repulsive pressure in the interior of the droplet formed by the intermolecular rigid repulsive force in two sides of area element. It is positive; p_{ina} is the attractive pressure in the interior of the droplet formed by the intermolecular attractive force in two sides of area element. It is negative. We choose an arbitrary area element, $u(r)$ is the potential of intermolecular force and l_0 is its range. So we have

$$p_{ina} = \frac{1}{2} \rho^2 \int u(r) dr, \quad (4)$$

where ρ is the molecular number density, $d\mathbf{r}$ is a volume element which may be written here as $d\mathbf{r} = 4\pi r^2 dr$. Since is negative or zero everywhere, then p_{ina} is negative.

At a point in the droplet, ϕ is the potential, we have a potential energy density of attractive force, $(1/2)\rho\phi$. One finds that

$$\frac{1}{2} \rho \phi = \frac{\rho^3}{2} \int u(r) dr, \quad (5)$$

$$\phi = \rho \int u(r) dr, \quad (6)$$

According to the method of dividing surface of Gibbs, the droplet radius is the radius of equimolecular surface. From Eq. (6), the potential of particles in the interior is ϕ_I

$$\phi_I = 4\pi\rho \int_0^d r^2 u(r) dr. \quad (7)$$

The potential of particles on the surface of the liquid is ϕ_S , if is the angle between the vector r and the radius of equimolecular surface R_r , we have

$$\begin{aligned} \phi_S &= 2\pi\rho \int_0^d dr r^2 u(r) \int_0^{\cos^{-1}(r/2R)} d\theta \sin\theta \\ &= 2\pi\rho \int_0^d r^2 \left(1 - \frac{r}{2R_e}\right) u(r) dr. \end{aligned} \quad (8)$$

Combining Eqs. (4) and (7), one has

$$\rho\phi_S - \rho\phi_I = -p_{\text{ina}} + \frac{2\gamma_\infty}{R_e}, \quad (9)$$

where

$$\gamma_\infty = -\frac{1}{2}\rho^2 \int_0^d r^3 u(r) dr \quad (10)$$

with γ_∞ being the surface tension of liquid for a flat surface. According to Bernoulli's equation

$$\rho\phi_S = \rho\phi_I + p_{\text{inr}}, \quad (11)$$

from Eqs. (9) and (11), we obtain

$$p_{\text{inr}} + p_{\text{ina}} = \frac{2\gamma_\infty}{R_e} = p_{\text{in}}. \quad (12)$$

According to the proposed model, we can see that the pressure outside p_o is zero. The difference pressure between p_{in} and p_o gives

$$\Delta p = p_{\text{in}} - p_o = p_{\text{in}}. \quad (13)$$

The Laplace's equation is

$$\Delta p = \frac{2\gamma_s}{R_s}. \quad (14)$$

Combining Eqs. (13) and (14), and using Eq. (12), $\Delta p = p_{\text{in}} - p_o = p_{\text{in}} = 2\gamma_\infty/R_e = 2\gamma_s/R_s$, we have

$$\frac{\gamma_s}{R_s} = \frac{\gamma_\infty}{R_e}. \quad (15)$$

2.2. Magnitudes of R_e and R_s

The thermodynamic description of droplet is macroscopic in nature. In order to establish a link with molecular properties, it would seem more natural to use a mechanical picture. This approach would allow one to relate the surface tension and surface of tension of a droplet to microscopic quantities, such as the pressure tensor. By considering the force and moment acting on a hypothetical strip cutting the surface of the droplet, Rowlinson and Widom,^[1] and Buff^[23] showed that it is possible to obtain a mechanical definition of the surface tension. The position of the surface of tension is given by

$$R_S = \frac{\int_0^\infty r^2 dr [p^{\alpha,\beta}(r;R_s) - p_T(r)]}{\int_0^\infty r dr [p^{\alpha,\beta}(r;R_s) - p_T(r)]}, \quad (16)$$

where p_T is the tangential pressure and $p^{\alpha,\beta}$ is a step function. In our droplet model, we have $p^\alpha(r;R_s) = p_{\text{in}} (R < R_s)$, $p^\beta(r;R_s) = p_o = 0 (R > R_s)$

$$R_S = \frac{\int_0^{R_s} r^2 p_{\text{in}} dr - \int_0^{R_e} r^2 p_T(r) dr}{\int_0^{R_s} r p_{\text{in}} dr - \int_0^{R_e} r p_T(r) dr}. \quad (17)$$

Equation (17) can also be written as

$$p_{\text{in}} R_s^2/6 - R_s \int_0^{R_e} r p_T(r) dr + \int_0^{R_e} r^2 p_T(r) dr = 0. \quad (18)$$

In order to discuss the solution of R_s , $p_T(r)$ can be approximately written as

$$p_T(r) = p_N(r) - \gamma \bar{\delta}(r - R'_e), \quad (19)$$

where $\bar{\delta}$ is the function delta, $r = R'_e$ is the center point of pressure distribution, which is impossible out of the sphere droplet, so $R'_e < R_e$. In order to satisfy the condition of $\nabla \cdot \bar{p} = 0$ and $p^\alpha(r;R_s) = p_{\text{in}}$, $p^\beta(r;R_s) = p_o = 0$, $p_N(r)$ is

$$p_N(r) = \begin{cases} 0, & r > R'_e, \\ p_{\text{in}}, & r < R'_e. \end{cases} \quad (20)$$

By substituting Eqs. (19) and (20) into the mechanical equilibrium condition of pressure tensor $\nabla \cdot \bar{P} = 0$, it gives

$$\gamma = \frac{p_{\text{in}} R'_e}{2}. \quad (21)$$

Using Eqs. (18) and (19), equation (21) gives

$$R_s^3 - R_e^3 = 0. \quad (22)$$

The solution to Eq. (22) can be written as

$$R_s = R'_e < R_e. \quad (23)$$

So

$$\delta = R_e - R_s > 0. \quad (24)$$

The Tolman length is more than zero.

2.3. Analytical relation between $\delta(R_s)$ and R_s

In this subsection, we show the analytical relation between $\delta(R_s)$ and R_s . Using Eq. (15), we obtain

$$\delta = \left(\frac{\gamma_\infty}{\gamma_s} - 1\right) R_s. \quad (25)$$

We can obtain the following differential equation:

$$\frac{d\delta}{dR_s} = \frac{d[(\gamma_\infty/\gamma_s - 1)R_s]}{dR_s} = R_s \frac{d(\gamma_\infty/\gamma_s)}{dR_s} + \frac{\gamma_\infty}{\gamma_s} - 1. \quad (26)$$

Combining Eqs. (1) and (26), we have

$$\begin{aligned} \frac{d\delta}{dR_s} &= \frac{\delta}{R_s} - \left(\frac{\delta}{R_s} + 1\right) \\ &\times \frac{2 \left[\delta/R_s + (\delta/R_s)^2 + (1/3)(\delta/R_s)^3 \right]}{1 + 2 \left[\delta/R_s + (\delta/R_s)^2 + (1/3)(\delta/R_s)^3 \right]} \frac{dR_s}{R_s}. \end{aligned} \quad (27)$$

Let the term on the right-hand side of Eq. (27) be $f(\delta/R_s)$, specifically,

$$f\left(\frac{\delta}{R_s}\right) = \frac{\delta}{R_s} - \left(\frac{\delta}{R_s} + 1\right) \times \frac{2\left[\delta/R_s + (\delta/R_s)^2 + (1/3)(\delta/R_s)^3\right]}{1 + 2\left[\delta/R_s + (\delta/R_s)^2 + (1/3)(\delta/R_s)^3\right]}. \quad (28)$$

Equation (27) can be written as

$$\frac{d\delta}{dR_s} = f\left(\frac{\delta}{R_s}\right). \quad (29)$$

From $d(\delta/R_s) = (1/R_s)d\delta - (\delta/R_s^2)dR_s$, it can be given as

$$\frac{d\delta}{dR_s} = \frac{\delta}{R_s} + R_s \frac{d(\delta/R_s)}{dR_s}. \quad (30)$$

Combining Eq. (29) and Eq. (30), we have

$$R_s = C_1 \exp\left[\int \frac{d(\delta/R_s)}{f(\delta/R_s) - (\delta/R_s)}\right], \quad (31)$$

where C_1 is integral constant obtained by integrating Eq. (30), and

$$\int \frac{d(\delta/R_s)}{f(\delta/R_s) - (\delta/R_s)} = -\frac{1}{2} \ln\left(\frac{|\delta/R_s| \left[(\delta/R_s)^2 + 3(\delta/R_s) + 3\right]}{|1 + (\delta/R_s)|}\right) - C_2, \quad (32)$$

where C_2 is integral constant. By substituting Eq. (32) into Eq. (31), we obtain

$$R_s = C \sqrt{\frac{|1 + \delta/R_s|}{|\delta/R_s| \left[(\delta/R_s)^2 + 3(\delta/R_s) + 3\right]}}, \quad (33)$$

where $C = C_1 e^{-C_2}$. From Eqs. (24) and (33), we also have analytical relation between $\delta(R_s)$ and R_s below:

$$\begin{aligned} R_s^2 &= C^2 \frac{(1 + \delta/R_s)}{(\delta/R_s)[(\delta/R_s)^2 + 3(\delta/R_s) + 3]}, \\ R_s^2 [(\delta/R_s)^2 + 3(\delta/R_s) + 3] &= C^2 (1 + \delta/R_s), \\ \delta &= \sqrt[3]{\frac{R_s^3}{2} + \sqrt{\left(\frac{R_s^3}{2}\right)^2 - \left(\frac{C^2}{3}\right)^3}} \\ &\quad + \sqrt[3]{\frac{R_s^3}{2} - \sqrt{\left(\frac{R_s^3}{2}\right)^2 - \left(\frac{C^2}{3}\right)^3}} - R_s, \end{aligned} \quad (34)$$

where C is a coefficient depending on physical properties of the system under consideration. It may depend, in general, on thermodynamic conditions like temperature or pressure but is independent of droplet size. The behavior of the solution resembles those of DFT solutions (for example $\delta = 0.2R_e$ ^[22]). The task of relation of constant C to physical properties of the system remains to be done. We can determine the relationship between $\delta(R_s)$ and through a series of values of coefficient as shown in Fig. 2.

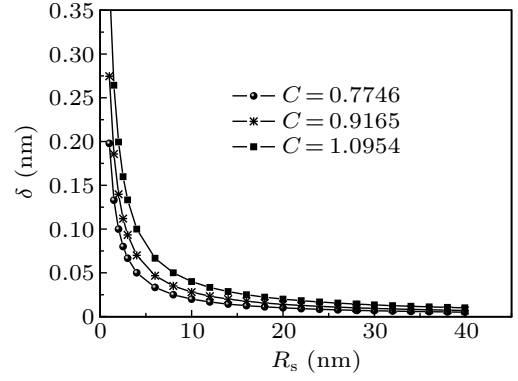


Fig. 2. Variations of $\delta(R_s)$ with R_s .

It is observed from Fig. 2 that the calculated values of Tolman length are more than zero. It is consistent with the general assumption,^[4] that is, $\delta > 0$ for spherical droplets. The Tolman length decreases when the size increases in the whole size range, which is consistent with the results of statistical thermodynamics,^[22,24] computer simulations results,^[25,26] the results from other methods for LJ fluids and the literature^[27] $\delta = 0.275$ nm (Aurum particle), $\delta = 0.5$ nm (cadmium sulfide particle). When $R_s > 10$ nm, the effect of droplet size on the Tolman length can be omitted, and the abrupt increase occurs at $R_s < 5$ nm. The asymptotic Tolman length (δ_∞) tends to zero in the limit of $R_s \rightarrow \infty$.

3. Molecular dynamics simulation, results, and discussion

In molecular dynamics simulations, the intermolecular interactions between argon atoms are described by the Lennard-Jones potential

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \quad (35)$$

where r , ϵ , and σ are the interparticle distance, energy scale, and length scale, respectively. All quantities used in the simulation are dimensionless and are expressed by adding superscript *. According to the basic parameters of an argon atom, $m = 6.3382 \times 10^{-26}$ kg, $\epsilon = k_B 120$ K, $k_B = 1.38 \times 10^{-23}$ J/K, $\sigma = 0.3405$ nm, and the dimensionless quantities are as follows: $r^* = r/\sigma$ for length, $T^* = k_B T/\epsilon$ for temperature, $t^* = t\sqrt{(\epsilon/m\sigma^2)}$ for time, $\rho^* = \rho\sigma^3/m$ for density, $f^* = f\sigma/\epsilon$ for force, and $E^* = E/\epsilon$ for energy.^[28]

The initial configuration is constructed on a finite cubic lattice located in the central part of the box, and the argon atomic separation is 1.2σ . The box size of simulation system is $x \times y \times z = 6.13$ nm \times 26.56 nm \times 26.56 nm. The periodic boundary condition is used in the x direction and mirror boundary condition is used in the y and z directions. The simulated temperature is $T^* = 0.75$. The cut-off distance is $r_C = 3.0$.

Five simulated systems are used, with numbers of argon atoms being 10140, 10935, 11760, 13500, and 15360 respectively. Some details of molecular dynamics simulation can be referred to our article.^[28] For the simulated systems, at the initial time all the particles are given velocities according to the Maxwell–Boltzmann distribution. The velocity–Verlet algorithm is used in molecular dynamics. The time step $\delta t = 5$ fs is used before equilibrium. When the equilibrium is reached, then we perform on the statistical treatment of the physical quantities of the system. When calculating the mean value of a physical quantity, we change the time step into $\delta t = 2$ fs. In order to find whether the step number N that is needed for a physical quantity, say, $g(t)$ reaches its steady value, we use an accumulative average method for the statistics

$$\overline{g(i \cdot \delta t)}^N = \frac{1}{N} \sum_{i=1}^N g(i \cdot \delta t), \quad (36)$$

where the number $\overline{g(i \cdot \delta t)}^N$ is the accumulative mean value. This step number is needed for the accumulative mean value to reach the steady value with acceptable small variation. In fact 10^6 runs with a time step of $\delta t = 2$ fs are used to obtain the acceptable statistics in our simulations.

The density profile of $N = 11760$ system is shown in Fig. 3. The statistical time steps are 10^6 runs. A configuration of system is recorded by every 100 runs. The average result is obtained by 10^4 samples. The example of the density profile is obtained with this method.

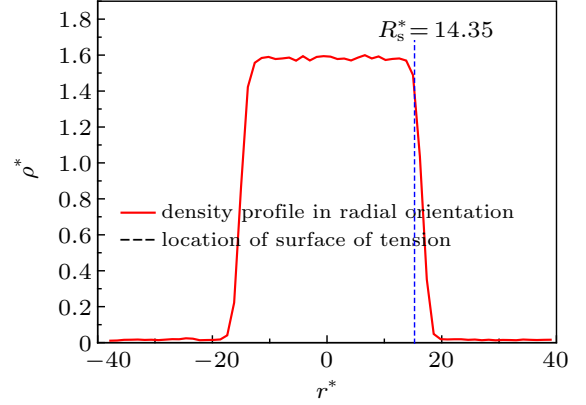


Fig. 3. Density profile of $N = 11760$ system.

The details of the calculation of γ_s and R_s are given in Ref. [29]. Here we only give the brief calculation. The numerical functions γ_s and R_s are calculated from the following equations:

$$\gamma_s = p^\beta (R^\beta - R_s) - p^\alpha (R^\alpha - R_s) - P_1, \quad (37)$$

$$R_s = \frac{p^\alpha R^\alpha - p^\beta R^\beta + P_1 + \sqrt{(p^\alpha R^\alpha - p^\beta R^\beta + P_1)^2 - [p^\alpha (R^\alpha)^2 - p^\beta (R^\beta)^2 + 2P_2](p^\alpha - p^\beta)}}{p^\alpha - p^\beta}, \quad (38)$$

where p^α is the pressure of liquid, p^β the pressure of vapor, $P_1 = \int_{R^\alpha}^{R^\beta} p_T(r) dr$, and $P_2 = \int_{R^\alpha}^{R^\beta} r p_T(r) dr$.

The values of p^α , p^β , P_2 , γ_s , and R_s of molecular dynamics simulation are listed in Table 1.

Table 1. Values of p^α , p^β , P_2 , γ_s , and R_s of molecular dynamics simulation.

N	p^α (MPa)	p^β (MPa)	P_1 (N/m)	P_2/σ (N/m)	R_s (nm)	γ_s (N/m)
10140	1.8851	0.2475	0.002191	0.0008552	4.42	0.00814
10935	2.3566	0.2546	0.003855	0.0032095	4.57	0.00924
11760	2.2580	0.2605	0.003499	-0.0000617	4.88	0.00956
13500	1.9342	0.2441	0.003018	-0.0249073	5.75	0.00991
15360	1.9186	0.2407	0.002988	-0.0281812	5.88	0.01000

The values of ρ_l , ρ_v , R_s , R_e , and δ of molecular dynamics simulation are listed in Table 2.

Table 2. Values of ρ_l , ρ_v , R_s , R_e , and δ of molecular dynamics simulation.

N	ρ_l (kg/m ³)	ρ_v (kg/m ³)	R_s (nm)	R_e (nm)	δ (nm)
10140	1239	12.04	4.42	4.99	0.57
10935	1278	11.72	4.57	5.13	0.56
11760	1287	10.11	4.88	5.34	0.46
13500	1292	4.97	5.75	5.81	0.06
15360	1419	4.01	5.88	5.92	0.04

The dimensional dependence of the surface tension is associated with the Tolman length. The values of R_s and R_e are very close to each other, and they increase with N increas-

ing. We can see that our result of molecular dynamics simulations for a Lennard–Jones system show that the Tolman length is more than zero.^[25,26] Our result of Tolman length being positive for an argon droplet is also consistent with that of Thompson’s.^[30]

In addition, we also make a qualitative comparison of the above theoretical study. The values of the Tolman length calculated from the theoretical study and molecular dynamics simulations are shown in Fig. 4.

Comparing with the above theoretical curve, we can see that the value of the Tolman length from molecular dynamics simulation is in agreement with those from theoretical study

at large R_s . The Tolman length from simulation deviates from the theoretical curve at small R_s . But in both cases it seems clear that the Tolman length decreases with R_s increasing, and $\delta > 0$. Small systems exhibit a significant oscillation in surface tension which is due to size effect. The finite-size effect can be the origin of this discrepancy. A precise quantitative estimate of this effect by numerical simulation would need very long computation time in order to obtain acceptable statistical errors and has not been realized in the present paper. Besides, the values of γ_s in Table 2 increase with the radius of surface of tension (R_s) increasing, which is consistent with Tolman's theory.

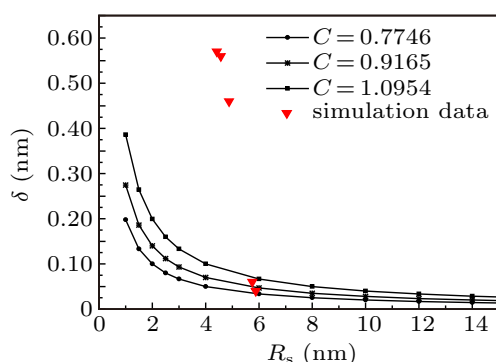


Fig. 4. Values of the Tolman length calculated using theoretical study and molecular dynamics simulation.

4. Conclusions

For decades the behavior of Tolman length has remained one of the most controversial issues in nanoscopic mechanics. For the Tolman length of incompressible and homogeneous liquid sphere, we obtain the relation between $\delta(R_s)$ and R_s , and found that they increase with R_s increasing. The Tolman length of plane surface (δ_∞) tends to zero in the limit of $R_s \rightarrow \infty$. Five simulated systems are used in molecular dynamics simulation, with numbers of argon atoms being 10140, 10935, 11760, 13500, and 15360 respectively. By the theoretical study and molecular dynamics simulation, we find that the calculated values of the Tolman length are more than zero, and they decrease as the size increases in the whole size range.

The values of surface tension increase with the radius of the surface tension increasing, which is consistent with the result from the Tolman's theory. These conclusions are significant for studying the size dependence of the surface tension.

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