

Microscopic Expression of the Surface Tension of Nano-Scale Cylindrical Liquid and Applicability of the Laplace Equation

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There is no consensus on whether the macroscopic Laplace Equation of capillarity is applicable for nanoscale systems. The microscopic expression for the radius and surface tension of the surface of tension for cylindrical liquid were deduced on Gibbs theory of capillarity. The radii and tensions of the surfaces of tension and the differences between internal and outside pressure for several argon liquid cylinders consisting of different numbers of atoms with Lennard-Jones (LJ) potential under the temperature of 90 K were obtained by combination of molecular dynamics simulation and calculation. The results suggested that Laplace equation could be applicable in nanoscale with fairly good approximation.

Keywords: Nano-Scale Cylindrical Liquid, Gibbsian Surface of Tension, Molecular Dynamics Simulation, Surface Tension.

1. INTRODUCTION

With the rapid development of nanotechnology in recent years,^{1–3} the capillarity theory of nanoscale has become very important research branch of nanotechnology. It has a profound influence on preparation and research of nano-materials. The Laplace equation to predict additional pressure of curved interfaces and Young equation to determine macroscopic contact angle are the fundamental theories for capillarity phenomena. The question how to modify these equations in nanoscale has become very active.^{4,5}

Gibbs developed a rigorous theory of the capillary phenomena by the methods of thermodynamics.^{6,7} For a thermodynamic system comprising a liquid in equilibrium with its vapor, there exists a gradual transition layer. In Gibbs's thermodynamic theory of capillary phenomena, the transition layer is modeled as a geometrical surface of zero thickness called dividing surface. The dividing surface can be one of the equi-density surfaces in the transition layer, so it is not unique. Different dividing surface have different surface tension and different extensive quantities, for instance, the molecule number of the liquid–vapor interface. The dividing surface with radius R is called the surface of tension if the Laplace's equation is

valid at it. Later theoretical studies have been made further discussions by several authors.^{8–13} In 1992, Nijmeijer et al.¹⁴ generalized the theory to cylindrical liquid and derived the general Laplace Equation ($r = R$)

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

where p^α and p^β are the pressure of liquid phase and vapour phase respectively, γ is the surface tension of the dividing surface and $[dr/dR]$ is the derivative for the same physical state of the same system.

General Laplace equation is the basic equation of capillarity. There is no unique answer for whether the general Laplace equation is applicable in nanoscale. In order to clarify the applicability of the general Laplace equation, it is enough to study the special case, i.e., the Laplace's equation for the surface of tension

$$p^\alpha - p^\beta = \frac{2\gamma}{R_0} \quad (2)$$

R_0 is the radius of the surface of tension.

Many papers^{14–16} have taken Eqs. (1) or (2) as the starting point of theoretical analysis and molecular dynamics simulation without proving it. Some unsatisfied results were

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often attributed to statistical fluctuation of small number of molecules or computable error. In 2006, Nagayama et al.¹⁷ proposed that their results disagreed with the Laplace equation for nano-sized bubble. In 2008, Matsumoto and Tanaka⁴ confirmed that the Laplace equation was valid even for nano-scale bubbles. They obtained the radius of the surface of tension and the difference between inside pressure and outside pressure of a spherical bubble by MD simulation, and put them into Eq. (2) to get the surface tension. Their results showed that surface tension was independent of R_0 and very close to that of a planar interface. However strong doubts about their analysis still exists. For nano-scale bubbles, the Tolman's effect cannot be neglected, that is to say, surface tension is dependent of the radius. So Matsumoto's conclusion may be incorrect.

One of the causes of above difference may lie in the fact that the system size is so tiny and the density of the molecules in the bubble is so small that the statistical error is too large. Therefore in the present paper we take a cylindrical nano droplet as an object to be investigated.

The aim of this work is to derive a microscopic expression for the radius and surface tension of the surface of tension for cylindrical liquid on Gibbs theory of capillarity. The results are used to discuss the applicability of Laplace equation in nanoscale. In Section 2, we propose the theoretical analysis of surface tension. In Section 3, we describe the molecular dynamics simulation, results, and discussion. The conclusion is given in Section 4.

2. THEORETICAL ANALYSIS OF THE SURFACE TENSION (γ_0) OF CYLINDRICAL LIQUID

2.1. The Integral Form of Surface Tension of Arbitrary Dividing Surface

Consider the cylindrical liquid of a liquid phase α surrounded by a vapour phase β , separated by a dividing surface of radius R located in the thin transition layer of the physical system, and so R is not unique. R^α and R^β are the radius of two cylindrical surfaces located in interiors of liquid and vapor respectively, which is shown in Figure 1.

We choose the dividing surface $r = R$ and define the function $p^{\alpha,\beta}(r; R)$:

$$p^{\alpha,\beta} = \begin{cases} p^\alpha & r < R \\ p^\beta & r > R \end{cases} \quad (3)$$

Considering the θ change ($\theta \rightarrow \theta + d\theta$) in \vec{e}_θ direction, the change of work would be

$$dW = \int_{R^\alpha}^{R^\beta} r p_T(r) L dr d\theta$$

If the notional discrete system replaces the physical one, it would be

$$dW' = \int_{R^\alpha}^R r p^\alpha L dr d\theta + \int_R^{R^\beta} r p^\beta L dr d\theta + \gamma LR d\theta$$

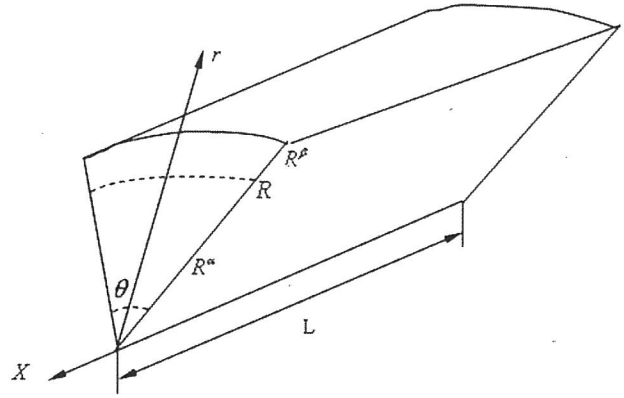


Fig. 1. Schematic figure of column coexisting liquid and vapor.

According to the equivalence between the new system and the physical one, it can be $dW = dW'$, The form of surface tension arbitrary dividing surface for cylindrical liquid is

$$\gamma(R) = \frac{1}{R} \int_{R^\alpha}^{R^\beta} r dr [p^{\alpha,\beta}(r; R) - p_T(r)] \quad (4)$$

2.2. The Condition About Surface of Tension

The pressure tensor in cylindrical components is given by

$$\vec{p} = p_N(r) \vec{e}_r \vec{e}_r + p_T(r) (\vec{e}_\theta \vec{e}_\theta + \vec{e}_x \vec{e}_x) \quad (5)$$

where \vec{e}_r , \vec{e}_θ and \vec{e}_z are orthogonal unit vectors and $p_N(r)$ and $p_T(r)$ are the normal and transverse components of the pressure tensor respectively. The mechanical equilibrium condition of pressure tensor $\nabla \cdot \vec{P} = 0$ gives

$$\begin{cases} \frac{\partial p_N}{\partial r} + \frac{p_N - p_T}{r} = 0 \\ \frac{\partial p_T}{\partial x} = 0 \end{cases} \quad (6)$$

where p_T is independent of x . Combination of Eqs. (3) and (6) gives

$$R(p^\alpha - p^\beta) = \int_{R^\alpha}^{R^\beta} dr [p^{\alpha,\beta}(r; R) - p_T(r)] \quad (7)$$

From Eqs. (4) and (7), Eq. (1) gives

$$\frac{d\gamma}{dR} = - \int_{R^\alpha}^{R^\beta} \left(\frac{r}{R^2} - \frac{1}{R} \right) dr [p^{\alpha,\beta}(r; R) - p_T(r)] \quad (8)$$

By combining the condition of Gibbsian $[d\gamma/dR]_{R=R_0} = 0$ with Eqs. (4) and (8), we can get the formulae for the radius and surface tension of the surface of tension

$$\int_{R^\alpha}^{R^\beta} (r - R_0) dr [p^{\alpha,\beta}(r; R_0) - p_T(r)] = 0 \quad (9)$$

$$\gamma_0 = \int_{R^\alpha}^{R^\beta} dr [p^{\alpha,\beta}(r; R_0) - p_T(r)] \quad (10)$$

2.3. The Solution of Surface Tension and the Radius of Surface of Tension

Integration of Eq. (9) yields

$$\frac{1}{2}(p^\alpha - p^\beta)R_0^2 - (p^\alpha R^\alpha - p^\beta R^\beta + P_1)R_0 + \frac{1}{2}[p^\alpha(R^\alpha)^2 - p^\beta(R^\beta)^2 + 2P_2] = 0 \quad (11)$$

where $P_1 = \int_{R^\alpha}^{R^\beta} p_T(r) dr$, $P_2 = \int_{R^\alpha}^{R^\beta} r p_T(r) dr$. The solution of Eq. (11) is

$$R_0 = (p^\alpha R^\alpha - p^\beta R^\beta + P_1 + ((p^\alpha R^\alpha - p^\beta R^\beta + P_1)^2 - [p^\alpha(R^\alpha)^2 - p^\beta(R^\beta)^2 + 2P_2](p^\alpha - p^\beta))^{1/2}) \cdot (p^\alpha - p^\beta)^{-1} \quad (12)$$

By substituting Eq. (12) into (10)

$$\gamma_0 = p^\beta(R^\beta - R_0) - p^\alpha(R^\alpha - R_0) - P_1 \quad (13)$$

3. MOLECULAR DYNAMICS SIMULATION, RESULTS, DISCUSSION

3.1. Molecular Dynamics Simulation

The intermolecular interactions between argon atoms are described by the Lennard-Jones potential

$$U_{ij}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (14)$$

where r , ε and σ are the interparticle distance, energy scale, and length scale, respectively. All quantities used in the simulation are dimensionless. According to the basic parameters of an argon atom, $m = 6.3382 \times 10^{-26}$ Kg, $\varepsilon = k_B 120$ K, $k_B = 1.38 \times 10^{-23}$ J/K, $\sigma = 0.3405$ nm, the dimensionless quantities are as follows:

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

$\rho^* = \rho\sigma^3/m$ for density, $f^* = f\sigma/\varepsilon$ for force, and $E^* = E/\varepsilon$ for energy.

The initial configuration is constructed on a finite cubic lattice located at the central part of the box, and the atomic separation is 1.2σ . The box size of simulation system is $x \times y \times z = 9.0 \times 39.0 \times 39.0$. The periodic boundary condition is used in x directions and mirror boundary condition is used in y and z directions. The simulated temperature is $T^* = 0.75$. The cut-off distance is $r_C = 3.0$.

The total simulated number of atoms (N) are 10140, 10935, 11760, 13500 and 15360 respectively. We take $N = 11760$ as an example to illustrate the results.

For simulated system $N = 11760$, the initial configuration is constructed by putting $15 \times 28 \times 28 = 11760$ particles on a finite cubic lattice located at the central part of the box.

For the cylindrical liquid systems and planar interface system, at the initial time all the particles are given velocities according to the Maxwell-Boltzmann distribution.

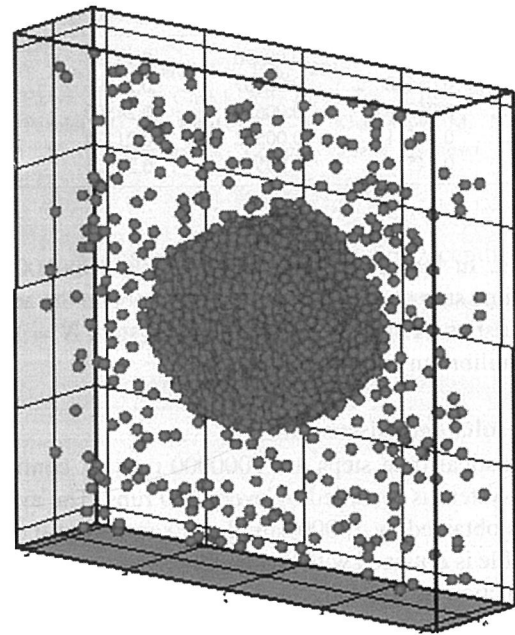


Fig. 2. A snapshot of simulated system $N = 11760$ after equilibrium.

The velocity-Verlet algorithm¹⁸ is used in MD. The canonical ensemble (NVT ensemble) of temperature 90 K and the time step $\delta t = 5$ fs are used before equilibrium. On calculating the mean value of a physical quantity, we change the time step into $\delta t = 2$ fs. In order to find the number N that is needed for a physical quantity, say, $g(t)$ to reach its steady value, we use an accumulative average method for the statistics

$$\overline{g(i \cdot \delta t)^N} = \frac{1}{N} \sum_{i=1}^N g(i \cdot \delta t) \quad (15)$$

accumulative average $\overline{g(i \cdot \delta t)^N}$ was used, where the number $\overline{g(i \cdot \delta t)^N}$ must be large enough for the accumulative mean value to reach a constant with acceptable small

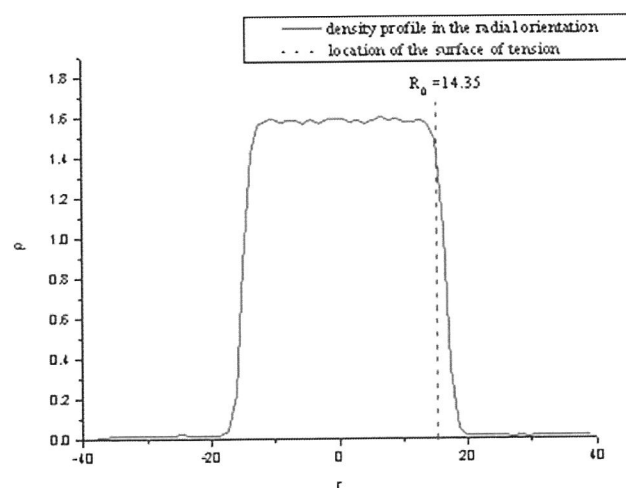


Fig. 3. The density profile in r direction.

Table I. Simulated results and surface tensions of five systems.

10140	0.04494	0.00590	0.15337	0.05988	12.99	0.570	0.520	0.050	8.7%
10935	0.05618	0.00607	0.26995	0.22471	13.42	0.647	0.672	0.025	3.9%
11760	0.05383	0.00621	0.24500	-0.00432	14.35	0.669	0.678	0.009	1.3%
13500	0.04611	0.00582	0.21134	-1.74382	16.90	0.694	0.680	0.014	2.0%
15360	0.04574	0.00574	0.20921	-1.97303	17.26	0.700	0.690	0.010	1.4%

variation. In fact in our simulations up to 1000000 runs with a time step of $\delta t = 2$ fs were used to obtain the acceptable statistics. A snapshot of simulated system $N = 11760$ after equilibrium shown in Figure 2.

3.2. Results and Discussion

The statistical time steps are 1000000 runs. A configuration of system is recorded by every 100 runs. The average result is obtained by 10000 samples. Examples of the density profile is obtained with this method. The density profile in r direction of simulated system $N = 11760$ is shown in Figure 3.

The results of Molecular dynamics simulation is shown in Table I. The numerical function R_0 and γ_0 are calculated by Eqs. (12), (13) and MD simulation.

For cylindrical liquid, we can also use Laplace Equation to calculate surface tension. In order to distinguish γ_0 , we denote γ as surface tension of Laplace Equation. The Laplace Equation is

$$p^\alpha - p^\beta = \frac{\gamma}{R_0} \quad (16)$$

which gives

$$\gamma = (p^\alpha - p^\beta)R_0 \quad (17)$$

In Table I, N is the total number of atoms, the difference of γ and γ_0 is $|\Delta\gamma| = |\gamma - \gamma_0|$. From Table I, we can see that γ_0 is close to γ and the values of relative difference $|\Delta\gamma|/\gamma_0$ decrease with total number of atoms N increasing. The error is attributed to the calculation. The second cause may lie in the fact that there exists some difference of Laplace's equation in nanoscale.

Owing to γ_0 is close to γ , these results suggest that Laplace equation could be applicable in nanoscale. Besides, the values of γ_0 in Table I increase with the radius of the surface of tension (R_0) increasing, which is consistent with Tolman's theory.^{14, 16, 19-23}

4. CONCLUSIONS

The microscopic expression for the radius and surface tension of the surface of tension for cylindrical liquid were deduced on Gibbs theory of capillarity. The molecular dynamics simulations were carried out on several argon liquid cylinders containing different numbers of atoms with Lennard-Jones (LJ) potential under the temperature of 90 K. The radii and tensions of the surfaces of tension and the differences between internal and outside pressure

for these argon liquid cylinder were obtained by combination of simulation and calculation. The results suggested that Laplace equation could be applicable in nanoscale with fairly good approximation.

In addition, the paper deals with some properties for nano-liquid by molecular dynamics simulation (modeling) approach. Other descriptions and approach for nano-matters are given for example in the Refs. [24–26]. In most cases dynamics approach is necessary for nanomaterials.

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