



Molecular Dynamics Simulation of Cylindrical Droplets

H. YAN^{1,*} and D.C. HUANG²

¹Department of Electronic Information and Physics, Changzhi University, Changzhi, P.R. China

²Department of Applied Physics, Nanjing University of Science and Technology, Nanjing 210094, P.R. China

*Corresponding author: Tel: +86 158 35586089, E-mail: yanh2010sx@yahoo.com.cn

(Received: 4 February 2011;

Accepted: 23 November 2011)

AJC-10701

Study of the surface properties is of great interest from the standpoint of both fundamental and practice. In this paper cylindrical droplets in nanoscale are investigated. A method to determine the surface tension is given by Gibbs theory of capillarity. The scheme is carried out by molecular dynamics simulation. The effect of temperature and cutoff distance are studied. It is found that surface tension decreases with increasing temperature and corresponding quantities sensitively depend on the interaction potential.

Key Words: Cylindrical droplet, Surface tension, Cutoff distance, Molecular dynamics simulation.

INTRODUCTION

Interfacial phenomena have been concerned for a long time. Study of the surface properties is of great interest from the standpoint of both fundamental and practice¹. Especially this interest is fueled by the development of nanotechnology. In this paper, we investigate the gas-liquid interface of cylindrical droplets. When droplets become so small in nanoscale, it is important to consider the thickness of the gas-liquid interface^{2,3}. Gibbs developed a theory of capillarity by the methods of thermodynamics⁴. For a two-phase coexistence system, a parallel set of mathematical surface, which perpendicular to the density gradient can be chosen by the dividing surface. Once the dividing surface is chosen, the original system is represented by a discontinuous model system *i.e.*, homogeneous liquid phase, homogeneous vapour phase and surface phase. The selection of dividing surface is not unique and the surface tension γ is different from the different dividing surface.

Based on the concept of Gibbs dividing surface, Nijmeijer *et al.*⁵ gave the generalized Laplace equation for cylindrical droplets.

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

where, p_{α} and p_{β} are the bulk pressures of liquid phase and vapour phase respectively, R is the radius of a dividing surface, $\gamma(R)$ is the surface tension of the corresponding dividing surface. The differential in square brackets denotes changes that follow from a notional change in the position of dividing surface, which does not cause any physical change for the system and affects only the description of the system.

For the particular dividing surface, if the expression is established.

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

Gibbs called it surface of tension with curvature radius R_s . The surface tension of the surface of tension is minimal. When the surface of tension is determined, the corresponding thermodynamic equations can be simplified. So the determination of surface of tension is very important and it is helpful to study the liquid-vapour system.

In this paper cylindrical droplets in nanoscale are the subject of investigation. The structural features of cylindrical droplets are analyzed. A method to determine the radius R_s of cylindrical droplets is given on Gibbs theory of capillarity. The surface tension corresponding R_s can be obtained by using Laplace equation^{6,7}.

EXPERIMENTAL

Theoretical basis and calculation scheme: Consider a single-component cylindrical droplet and its vapour. An illustration of this cylindrical system is shown in Fig. 1. It is convenient to choose cylindrical coordinates. The centre of the cylindrical droplet is the origin of the cylindrical coordinates. The axis of symmetry of the cylindrical system is Z-axis. The pressure tensor $P(r)$ can be written as:

$$P(r) = p_N(r)\vec{e}_r\vec{e}_r + p_T(r)\vec{e}_{\theta}\vec{e}_{\theta} + p_T(r)\vec{e}_z\vec{e}_z \quad (3)$$

where, r is the distance between the point and the axis of the cylindrical droplet, \vec{e}_r , \vec{e}_{θ} , \vec{e}_z are orthogonal unit vectors, $p_N(r)$

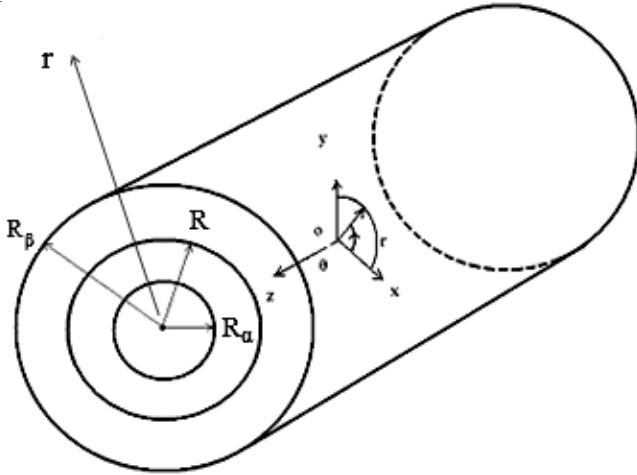


Fig. 1. An illustration of a cylindrical droplet and its vapour

is the normal component of the pressure tensor, $p_T(r)$ is the transverse component of the pressure tensor.

Substituting eqn. (3) into the condition of mechanical equilibrium, *i.e.* $\nabla \cdot P = 0$, where ∇ is the symbol of divergence operation of tensor, we obtain:

$$\frac{\delta p_N}{\delta r} + \frac{p_N - p_T}{r} = 0 \quad (4)$$

The pressure is expressed by a step function on the basis of Gibbs theory. We introduce the following notation:

$$p_{\alpha\beta}(r, R) = \begin{cases} p_\alpha, & r < R \\ p_\beta, & r > R \end{cases} \quad (5)$$

where, R is an arbitrary dividing surface.

From eqns. (4) and (5), we have

$$R(p_\alpha - p_\beta) = \int_{R_\alpha}^{R_\beta} dr [p_{\alpha\beta}(r; R) - p_T(r)] \quad (6)$$

where, R_α and R_β are two arbitrary positive integration boundaries.

In \bar{e}_θ direction expand a part of liquid column (a section column with length L) from θ to $\theta + d\theta$. During the process the work done by pressure tensor is:

$$dW = \int_{R_\alpha}^{R_\beta} r p_T(r) L dr d\theta \quad (7)$$

In eqn. (5), a thermodynamics model is constructed. The real system is replaced by a model system. The work done dW' expressed in another way is:

$$dW' = \int_{R_\alpha}^R r p_\alpha L dr d\theta + \int_R^{R_\beta} r p_\beta L dr d\theta - \sigma L R d\theta \quad (8)$$

According to the equivalence the work done, $dW = dW'$ *i.e.*, we have:

$$\gamma(R) = \frac{1}{R} \int_{R_\alpha}^{R_\beta} r [p_{\alpha\beta}(r, R) - p_T(r)] dr \quad (9)$$

From eqns. (1), (6) and (9), we obtain:

$$\frac{d\gamma}{dR} = - \int_{R_\alpha}^{R_\beta} \left(\frac{r}{R^2} - \frac{1}{R} \right) dr [p_{\alpha\beta}(r; R) - p_T(r)] \quad (10)$$

So the surface of tension can be determined by the following expression:

$$\int_{R_\alpha}^{R_\beta} (r - R_s) dr [p_{\alpha\beta}(r; R_s) - p_T(r)] = 0 \quad (11)$$

Equation (11) can be transformed into:

$$\begin{aligned} & \frac{1}{2} (p_\alpha - p_\beta) R_s^2 - (p_\alpha R_\alpha - p_\beta R_\beta + P_1) R_s \\ & + \frac{1}{2} [p_\alpha (R_\alpha)^2 - p_\beta (R_\beta)^2 + 2P_2] = 0 \end{aligned} \quad (12)$$

where,

$$\begin{cases} P_1 = \int_{R_\alpha}^{R_\beta} p_T(r) dr = \int_{R_\alpha}^{R_\beta} \left(p_N + r \frac{dp_N}{dr} \right) dr \\ P_2 = \int_{R_\alpha}^{R_\beta} r p_T(r) dr = \int_{R_\alpha}^{R_\beta} \left(p_N + r^2 \frac{dp_N}{dr} \right) dr \end{cases} \quad (13)$$

The curvature radius of surface of tension is:

$$R_s = \frac{p_\alpha R_\alpha - p_\beta R_\beta + P_1 + \sqrt{(p_\alpha R_\alpha - p_\beta R_\beta + P_1)^2 - [p_\alpha (R_\alpha)^2 - p_\beta (R_\beta)^2 + 2P_2](p_\alpha - p_\beta)}}{p_\alpha - p_\beta} \quad (14)$$

The surface tension corresponding R_s is:

$$\gamma_s = R_s (p_\alpha - p_\beta) \quad (15)$$

Computer simulation study: Cylindrical droplets formed by argon atoms are our subjects investigated. The Lennard-Jones potential between particles takes the form:

$$U(d) = 4\epsilon \left\{ \left(\frac{\sigma}{d} \right)^{12} - \left(\frac{\sigma}{d} \right)^6 \right\} \quad (16)$$

where, d , ϵ and σ are the inter-particle distance, energy scale and atomic diameter respectively. The parameters of inter-atomic action are chosen as $\sigma = 0.3405$ nm, $k_B = 1.38 \times 10^{-23}$ J/K, $m = 6.63382 \times 10^{-26}$ Kg. All the quantities are dimensionless and are expressed by symbol *. On the basic parameters of argon atom, the quantities are nondimensionalized as follows:

length: $L^* = L/\sigma$; temperature: $T^* = k_B T/\epsilon$; time: $t^* = t\sqrt{\epsilon/m\sigma^2}$

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

Two systems in different conditions are simulated. The numbers of molecules N are 6000 and 8640 respectively.

The effect of temperature is studied on the system of $N = 6000$. The cutoff distance is 3.0σ . The temperature T^* we select is 0.65, 0.75 and 0.85.

The effect of cutoff distance is studied on the system of $N = 8640$. The temperature is 0.85. The cutoff distance is 2.0σ , 3.0σ and 4.5σ .

The cubic box size of simulation system is $x^* \times y^* \times z^* = 60.0 \times 60.0 \times 18.0$. The initial configuration is constructed by putting particles on a finite cubic lattice located at the central part of the box. The mirror boundary condition is used in X-direction and Y-direction. The periodic boundary condition is used in Z-direction. At the initial time the particles were given velocities according to the Maxwell-Boltzmann distribution. The Velocity Verlet algorithm is used in molecular dynamics simulation⁸. The cell index method is adopted to calculate the force acted on atoms (Fig. 2).

In order to reach equilibrium, we did up to 100,000 runs with a time step of $\delta t = 5$ fs. The method of temperature regulation is velocity scaling. After equilibrium, NVE ensemble is needed to give the statistics of different physical quantity. In present simulations long runs up to 1000,000 time

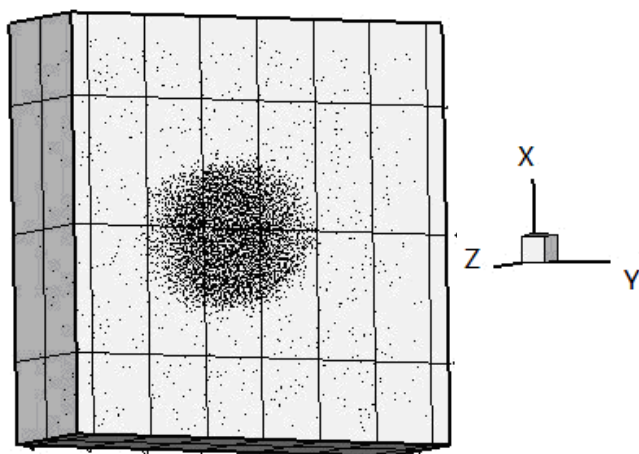


Fig. 2. A snapshot of cylindrical droplet after equilibrium

steps with $\delta t = 2fs$ are needed to obtain acceptable statistics. On calculating the mean value of any physical quantity $g(t)$,

we use accumulative average $\overline{g(i.\delta t)} = \frac{1}{M} \sum_{i=1}^M g(i.\delta t)$. The

number M must be large enough for the accumulative mean value to reach a constant with acceptable small variation.

RESULTS AND DISCUSSION

The density profile of the system of $N = 6000$ at temperature 0.65 in the radial orientation is shown in Fig. 3. The big fluctuation of ρ near the center of the liquid attributes to the poor statistics because of the low volume³.

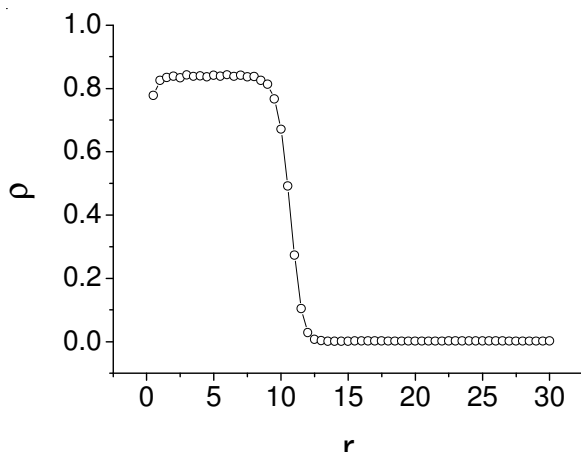


Fig. 3. Density profile in direction

The results of corresponding quantities of different systems are shown in Tables 1 and 2. The surface tension is calculated according to eqn. (14). The surface tension is given according to $\gamma_s = (p_\alpha - p_\beta)R_s$.

From Table-1, we know that the R_s decreases with increasing temperature. The tendency of γ_s decreasing with increasing temperature attributes not only to the temperature change itself but also to the decrease of R_s ⁹⁻¹¹.

The results (Table-2) indicate that γ_s sensitively depends on the interaction potential and it increases with the increasing

TABLE-1
SIMULATED RESULTS AND SURFACE TENSIONS
AT DIFFERENT TEMPERATURES

T	p_α	p_β	P_1	P_2	R_s	γ_s
0.65	0.0703	0.0097	0.2678	1.4117	9.117	0.552
0.75	0.0665	0.0144	0.4239	3.9855	9.035	0.471
0.85	0.0613	0.0194	0.5807	6.6348	8.968	0.376

TABLE-2
SIMULATED RESULTS AND SURFACE TENSIONS
AT DIFFERENT CUTOFF DISTANCES

r_{cut}	p_α	p_β	P_1	P_2	R_s	γ_s
2.0σ	0.0482	0.0231	0.9328	10.7905	15.36	0.385
3.0σ	0.0572	0.0193	0.4270	3.7604	12.13	0.463
4.5σ	0.0671	0.0063	0.0776	-2.4143	11.28	0.686

cutoff distance. R_s decreases with the increasing cutoff distance. When the cutoff distance is large, it is easy to form a droplet and the curvature radius is small in simulation.

Conclusion

In this paper cylindrical droplets in nanoscale are investigated. The structural features of cylindrical droplets are analyzed. A method to determine the radius R_s of cylindrical droplets is given on Gibbs theory of capillarity. The surface tension corresponding R_s can be obtained by using Laplace equation. Two systems in different conditions are carried out our scheme. The effect of temperature is studied on the system of $N = 6000$. We find that the R_s decreases with increasing temperature. The tendency of γ_s decreasing with increasing temperature attributes not only to the temperature change itself but also to the decrease of R_s . The effect of cutoff distance is studied on the system of $N = 8640$. It indicates that γ_s sensitively depends on the interaction potential and increases with the increasing cutoff distance. R_s decreases with the increasing cutoff distance.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China under Grant No. 10847146.

REFERENCES

1. J.S. Rowlinson and B. Widom, *Molecular Theory of Capillarity*, Clarendon Press, Oxford (1982).
2. R.C. Tolman, *J. Chem. Phys.*, **17**, 333 (1949).
3. S.M. Thompson, K.E. Gubbins, J.P.R.B. Walton, R.A.R. Chantry and J.S. Rowlinson, *J. Chem. Phys.*, **81**, 530 (1984).
4. J.W. Gibbs, *Collected Works*, Longmans Green and Company Press, New York, pp. 219-237 (1928).
5. M.J.P. Nijmeijer, C. Bruin, A.B. van Woerkom and A.F. Bakker, *J. Chem. Phys.*, **96**, 565 (1992).
6. S.H. Park, J.G. Weng and C.L. Tien, *Int. J. Heat Mass Transf.*, **44**, 1849 (2001).
7. M. Matsumoto and K. Tanaka, *Fluid Dynam. Res.*, **40**, 546 (2008).
8. M.P. Allen and D.J. Tildesley, *Computer Simulations of Liquids*, Clarendon, Press, Oxford (1992).
9. R.Z. Zhu and H. Yan, *Chin. Phys. B*, **20**, 016801 (2011).
10. M.J. Haye and C. Bruin, *J. Chem. Phys.*, **100**, 556 (1994).
11. A.E. van Giessen and E.M. Blokhuis, *J. Chem. Phys.*, **116**, 302 (2002).