Microsyst Technol (2005) 11: 1146–1153
DOI 10.1007/s00542-005-0516-6

TECHNICAL PAPER

S. Ogata · K. Fukuzawa · Y. Mitsuya · Y. Ohshima

# Molecular dynamics simulation of ultra-thin liquid bridging between surfaces having two-dimensional roughness

Received: 17 October 2003 / Accepted: 9 December 2003 / Published online: 24 May 2005
© Springer-Verlag 2005

**Abstract** By using the molecular dynamics, formation of molecularly thin liquid bridge between solid surfaces having molecular-scale roughness was simulated. Upon comparing the projected profiles of liquid bridges between solid surfaces with different roughness, it was found that the layered molecular arrangement inside the liquid bridge was disturbed by the molecular-scale roughness on the surfaces and the projected profiles were able to be approximated by arcs.

## 1 Introduction

Due to the Laplace pressure in a liquid bridge formed between two molecularly smooth surfaces, strong adhesion force (known as liquid bridge force) is generated and acts to oppose the relative motion between the two surfaces. Since this kind of phenomenon is widely observed in micro machine, nano and bio operation, head/disk interface and so forth, elucidation of the controlling mechanism has become a significant concern. In the macro-scale where physical properties can be described by continuum theory, Laplace pressure is given as a function of surface tension of liquid and curvature obtained by approximating the surface of liquid bridge with an arc. While in a molecularly narrow gap, the properties of a liquid system are different from the bulk because the interactions between molecules become predominant. It is thus expected that the surface shape of a liquid bridge can no longer be approximated by an arc and the magnitude of Laplace pressure will change accordingly. On the other hand, it is reported that a liquid bridge was formed even for film of several nanometers in thickness and the properties were well described by the conventional continuum theory on Laplace pressure (Homola 1991). However, since it is difficult to directly observe the actual shape of a liquid bridge in nanoscale, it is necessary to use an alternative method to investigate its properties.

So far, analytical results on non-arc-shaped liquid bridge formed in a nanoscale gap were obtained by assuming the liquid as a continuum and taking its surface energy into consideration (Gao et al. 1998). Additionally, molecular dynamics method, which is widely applied in many fields recently, has been tried and simulation of liquid bridge formation between a smooth surface and a molecularly rough surface represented by a one-dimensional sinusoidal wave was reported (Chen et al. 2001). However, the validity of the simulation was not confirmed in the report. In this research, considering a more realistic system, simulation of liquid bridge formation in a three-dimensional gap is implemented by expressing the two solid surfaces with two-dimensional sinusoidal waves, and the projected profile of the liquid bridge observed from the gap direction was calculated. The results show that in the case of perfectly smooth surfaces the projected profile significantly deviates from an arc and periodical roughness appears on the surface of the liquid bridge due to the layered arrangement of the molecules, while in the case of molecularly rough surfaces, the layered molecular structure is disturbed and the projected profile approaches arc shape.

S. Ogata (✉) · K. Fukuzawa · Y. Mitsuya
Department of Micro System Engineering,
Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku Nagoya 464-8603, Japan
E-mail: s_ogata@nuem.nagoya-u.ac.jp

Y. Ohshima
Early Childhood Education Department, Aichi Konan College,
172, Ohmatsubara, Takaya-cho Konan 483-8086, Japan

## 2 Simulation methodology

As a model molecule, monatomic molecule having intermolecular interaction is used. The interaction between two molecules is generally expressed by Lennard-Jones potential as,

$$\phi_{ij} = 4\varepsilon_{mn}\left\{\left(\frac{\sigma_{mn}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{mn}}{r_{ij}}\right)^{6}\right\}, \quad (1)$$

where $r_{ij}$ indicates the distance between the two molecules, ε represents the magnitude of the intermolecular interaction, σ denotes the diameter of the molecule, and subscripts *m, n* stand for the phases of the two interactive molecules, for example, in the cases of liquid–liquid, solid–solid, and liquid–solid, the subscripts are $mn = ll$, ss, ls, respectively.

By applying the law of Lorentz-Berthelot, parameters $\varepsilon_{ls}$ and $\sigma_{ls}$, which represent respectively the magnitude of liquid–solid interaction and the average diameter of liquid and solid molecules are obtained,

$$\varepsilon_{ls} = \sqrt{\varepsilon_{ll}\varepsilon_{ss}}, \quad (2)$$

$$\sigma_{ls} = \frac{\sigma_{ll} + \sigma_{ss}}{2}. \quad (3)$$

According to Eq. 2, in order to vary the magnitude of liquid–solid interaction, it is necessary to change the value of either $\varepsilon_{ss}$ or $\epsilon_{ll}$. In this work, the value of $\varepsilon_{ss}$ is changed to $\alpha^2\varepsilon_{ss}$ by multiplying a factor $\alpha^2$, where α is referred to as solid–solid interaction ratio. In the case of a large α, the liquid–solid interaction is strong and the solid surface is likely to be wetted by the liquid molecules.

Figure 1 shows the calculation area. Periodical boundary condition is applied along the lateral direction, and solid surfaces are placed on the top and the bottom. The solid surface is constructed by putting solid molecules on a two-dimensional lattice with a lattice constant of $a = \sigma_{ss}$ and superposing 8 layers of the form along the *z*-axis (total number of the solid molecules, $N_{solid} = 17{,}424$). In the gap confined by the two solid surfaces, liquid molecules of $N_{liquid} = 1{,}083$ are placed so that observation of liquid bridge formation is possible.

To save computational time, two kinds of hypotheses are employed. One is that the solid molecules are fixed at the points on the two-dimensional lattice, which means the solid molecules are assumed to stay still. The other is that there is no kinetic energy transfer between the solid and liquid molecules. These hypotheses lead effectively to the fact that the solid surface is kept at 0 K. However it should be noted that this ultra-low temperature does not affect the liquid molecules abutting the solid molecules since there is no kinetic energy transfer between the solid and liquid molecules. Even though these hypotheses are different from the actual condition, the present study is considered to be effective for analyzing the effects of molecular-scale roughness as the first order approximation since the liquid molecules are not directly affected by the ultra-low temperature of the solid molecules. The temperature of the liquid molecules is maintained at 84 K by using the Nose method (Tuckerman et al. 1992). The cutoff distance for the interaction is set to be $R_c = 6\sigma_{ll}$.

To make the calculation results more realistic, the constants of molecules are set to be the same as those of argon. This is simply because that argon molecule is spherical just as in the simulation model and its characteristics are accurately identified. Even though the lattice arrangement employed in this study is different from the actual argon's crystal structure, that is, a face-centered cubic lattice, this treatment has an advantage of easy lattice formation for any two-dimensional roughness configuration, and we consider that the effects of roughness can be approximately encountered by continuously expressing the amplitude of the molecular-scale roughness amplitude.

In the simulations, all quantities are non-dimensionalized by setting $\sigma_{ll}$, $\tau = \sqrt{m\sigma_{ll}^2/48\varepsilon_{ll}}$, and 48 $\varepsilon_{ll}$as the unit length, the unit time, and the unit energy, respectively. Based on the values listed in Table 1, the unit time τ is calculated to be 0.31 ps. Using a time step of $\Delta\tau = 0.015\ \tau$ (4.65 fs), the equations of motion are solved numerically with the velocity Velret algorithm for 240 ksteps.

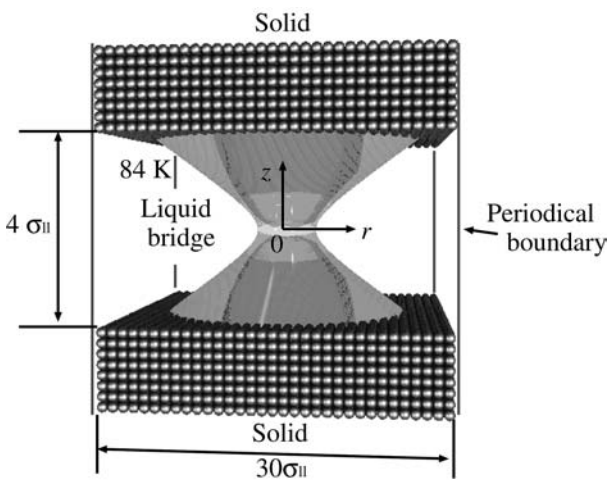


**Fig. 1** Calculation area

## 3 Simulation of liquid bridging

In a real system, since the solid surfaces are rough, it is expected that liquid bridge will be firstly formed on the top of an asperity. To realize this kind of condition, two-dimensional sinusoidal wave of one period as shown in Fig. 2 is used as the model of roughness. The spacing *h* between the solid surfaces is set at $4\sigma_{ll}$. Simulations are performed by varying the amplitude of roughness *d* to be 0 (smooth surfaces), $2\sigma_{ll}$, $4\sigma_{ll}$, $7.5\sigma_{ll}$, and by varying the

**Table 1** Characteristic values of argon

| | | |
|---|---|---|
| $\varepsilon_{ll}$ | $1.7\times10^{-21}$ J | Liquid–liquid interaction |
| $\sigma_{ll}$ | $3.4\times10^{-10}$ m | Liquid diameter |
| $\varepsilon_{ss}$ | $5.8\times10^{-22}$ J | Solid–solid interaction |
| $\sigma_{ss}$ | $3.0\times10^{-10}$ m | Solid diameter |
| *m* | $6.6\times10^{-26}$ kg | Mass of argon molecule |

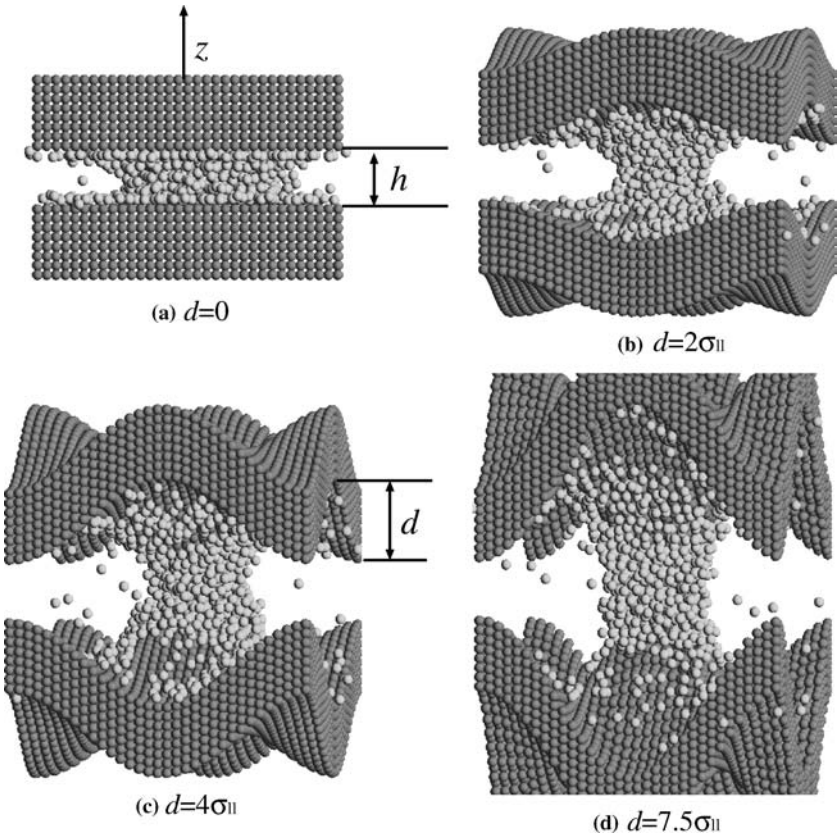


**Fig. 2 a–d** Liquid bridge formation between solid surfaces after 240 ksteps. ($\alpha = \sqrt{2}$ and $h = 4\sigma_{ll}$)

interaction ratio $\alpha$ to be 1, $\sqrt{2}$, respectively. Hereafter the case of $\alpha = 1$ is simply referred to as weak interaction condition, and the case of $\alpha = \sqrt{2}$ as strong interaction condition.

The calculation for amplitudes of $d = 0$ to 4 $\sigma_{ll}$ is divided into two stages as follows. Initially, the liquid molecules are arranged densely in the central region of the gap as a simple cubic lattice with a lattice constant of $a = 1.2\ \sigma_{ll}$. At the first stage, calculation is carried out from 0 step to 16 ksteps with the liquid–solid interaction ratio $\alpha$ kept at 0.5. Because of the small interaction ratio, the liquid molecules do not wet the solid surfaces at this stage. At the second stage, $\alpha$ is changed to be 1 or $\sqrt{2}$ and the liquid bridge formation is simulated until the equilibrium state is reached at 240 ksteps.

On the other hand, for $d = 7.5\sigma_{ll}$, calculation using the 2-stage method results in a deviation of the central axis of the liquid bridge from that of the roughness. The reason is considered as that in the case of small $\alpha$, the surface tension of the liquid drop becomes dominant, making the liquid surface a spherical shape by excluding the solid surfaces. Thus in this case, by setting the lattice constant the same as other cases ($a = 1.2\sigma_{ll}$) but fixing the interaction ratio at $\alpha = 1$ or $\sqrt{2}$ from 0 step, the simulation is performed till 240 ksteps.

As one example, side views of the liquid bridges after reaching an equilibrium state (at 240 ksteps) are shown in Fig. 2 for the case of strong interaction ($\alpha = \sqrt{2}$). It is seen that the radius of curvature of the liquid bridge tends to increase with increasing amplitude of roughness. Hereafter the side view of the liquid bridge is referred to as projected profile, and the top view as cross section.

Up to present, the surface of a liquid bridge formed between solid surfaces has been basically approximated by an arc. However, it is improper to directly compare the profiles obtained in the simulations with those obtained from a real system. This is because that the profiles from a real system are averaged by the number of molecules and time whereas the profiles shown in Fig. 2 are snapshots at 240 ksteps, i.e., at the instant of $\Delta\tau = 4.65$ fs. To make the comparison possible, it is necessary to convert the discrete projected profile to a continuous curve by using some kinds of averaging methods.

Here the continuous projected profiles are obtained through effective averaging process by using the following three methods.

1. The molecular number density is calculated by assuming that the position of a molecule at every step can be expressed by Gaussian distribution with its center at that position.
2. The molecular number density obtained after reaching the equilibrium state is averaged by time.
3. The liquid surface is determined from the points where the number density is nearly half of the density of the continuous liquid.

In next section, the methods will be described in detail respectively.

## 4 Calculation of number density

### 4.1 Spatial and time averaging

The number density of molecules is calculated by scanning an infinite small volume consecutively in the calculation area while counting the number of molecules inside the infinite small volume. Considering that liquid bridge is symmetrical with respect to its central axis, a small ring shown in Fig. 3 is selected as the infinite small volume. To improve the spatial resolution of the calculation, the width $\Delta r$ and the height $\Delta z$ of the ring are set as $0.1\sigma_{ll}$. The scanning of the infinite small volume inside the calculation area is accomplished by expanding the radius $r$ of the ring and shifting the ring along the $z$-axis. The number density at the point with coordinates of $(r, z)$ is calculated by dividing the number of molecules whose mass centers lie inside the ring by the volume of the ring.

Because of the high speed motion, the positions of molecules change rapidly such that the local number density varies significantly at each step. The variation is more remarkable at high spatial resolution, making it difficult to understand the characteristics of a liquid bridge. The reason for the variation on density is that the width of the ring is smaller than the diameter of the molecule, and the molecule with a certain volume is simply regarded as a point. To circumvent this problem, taking the molecular volume into consideration, a method in which the ratio of the common volume between the molecule and the ring to that of the molecule is totalized for all the molecules in the ring can be used. This however makes the algorithm complicated, thereby consuming a great deal of computational time. In this research a spatial averaging method is introduced in which the positions of molecules are expressed with a probability distribution. The spatial distribution of the molecules is expressed as a three-dimensional Gaussian function,

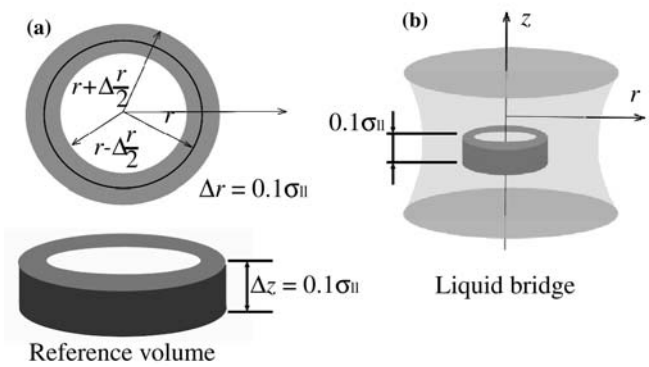


**Fig. 3** **a, b** Procedure for counting number density of molecules. **a** Is an infinitely small volume and **b** is scanning image of infinitely small volume

$$f(\varepsilon_x, \varepsilon_y, \varepsilon_z) = \frac{1}{(2\pi\sigma)^{3/2}} \exp\left[-\frac{\varepsilon_x^2}{2\sigma^2}\right] \exp\left[-\frac{\varepsilon_y^2}{2\sigma^2}\right] \exp\left[-\frac{\varepsilon_z^2}{2\sigma^2}\right], \tag{4}$$

where $\varepsilon_u$ ($u = x, y, z$) is the difference between $r$ and $r_G$ ($\varepsilon = r - r_G$) which are the positions of the counting point in the ring and the mass center of the molecule, respectively, and the value of $3\sigma$ ($\sigma^2$: variance) is set to be equal to the radius of the liquid molecules $\sigma_{ll}/2$.

The number density profile obtained with the above spatial averaging is then further averaged with time. The averaging is conducted within the time interval from 160 ksteps to 240 ksteps in which the equilibrium state is considered to be reached.

### 4.2 Verification of the number density calculation

To verify the validity of the calculation method proposed in the previous section, the computational results are compared with the characteristics of argon. A liquid drop formed in vacuum as shown in Fig. 4 is selected as the calculation subject. The drop is composed of liquid molecules of $N_{liquid} = 1{,}083$ and its temperature is kept constant at 84 K. The snapshot of the liquid drop and the number density profile along the $z$-axis in the equilibrium state (240 ksteps) are shown in Fig. 4a and b, respectively. Figure 4b is plotted by varying the radius of the ring to be $r = 0.05\sigma_{ll}$, $1.05\sigma_{ll}$, $2.05\sigma_{ll}$ as illustrated in Fig. 4c. The two broken lines along the $z$-axis indicate the non-dimensional actual number densities of liquid argon (90 K) and solid argon (40 K) (NAOJ 2002), respectively. In the case of $r = 0.05\sigma_{ll}$ (on the central axis of the ring), the number density profile fluctuates remarkably, while in the cases of $r = 1.05\sigma_{ll}$, $2.05\sigma_{ll}$ (apart from the central axis), the fluctuation becomes less pronounced. The small values at the two ends of the number density curve indicate a phase transition from liquid state to vapor state, and the dependency of the density on the radius $r$ of the ring is attributed to the spherical shape of the liquid drop. Additionally, it is considered that the molecules tend to distribute regularly in the central part because of the axial symmetry, thereby resulting in remarkable fluctuation in the density profile for $r = 0.05\sigma_{ll}$. The number densities averaged in the range of $z = -4$ to $z = 4$ in Fig. 4b are almost the same for the three different values of $r$. It is evident from Fig. 4b that the averaged number density which was calculated at the temperature of 84 K lies between the two broken lines corresponding respectively to the number densities of liquid argon at 90 K and solid argon at 40 K. This demonstrates that the method for calculating density profile is valid.

### 4.3 Distribution of molecular number density inside liquid bridge

The distribution of molecular number density inside a liquid bridge formed between solid surfaces for the case

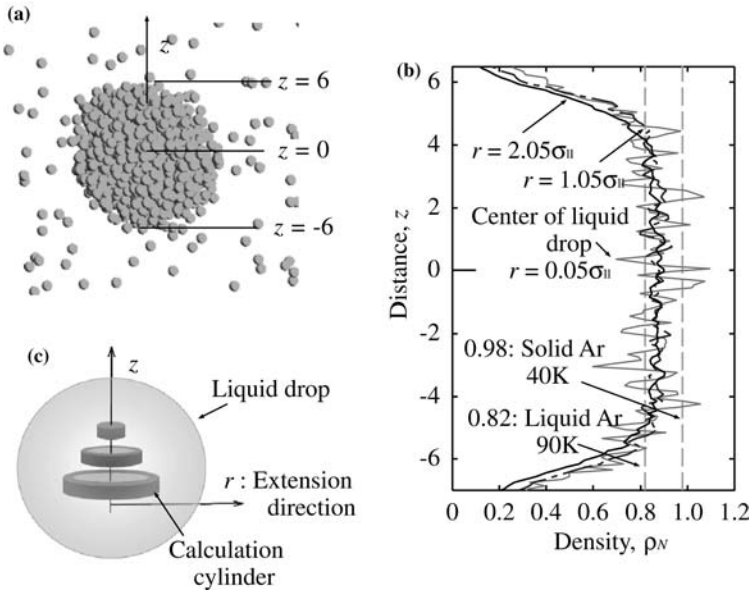


**Fig. 4 a–c** Number density profile of liquid drop. **a** Is a snapshot, **b** is number density profile of liquid drop and **c** is a scanning image in liquid drop

of strong interaction ratio ($\alpha = \sqrt{2}$) is exemplified in Fig. 5, where the amplitudes of the roughness are (a) $d = 0$ (smooth surfaces), (b) $2\sigma_{ll}$, and (c) $7.5\sigma_{ll}$, respectively. In the figure, the solid surfaces are located at $z = \pm 2.0$, the origin of the $r$ axis lies on the central axis of the liquid bridge, and the half-tone lines indicate the lines which show their back side in applying the hidden-line elimination. The surface of the liquid bridge is in the region where the density decreases drastically. Since liquid–vapor phase transition occurs in this region, it is referred to as transition region hereafter. As for the thick solid lines in Fig. 5, the detailed discussion is given later.

For the case of smooth surfaces shown in Fig. 5a, a layered structure is exhibited distinctly, indicating that the molecules arrange regularly in layers. This structure extends to the transition region and as a result, periodical ripples appear on the surface of the liquid bridge. While for the case of rough surfaces shown in Fig. 5b, with increasing roughness the layered structure in the number density distribution of liquid molecules is disrupted, resulting in a superposition of ripples in two dimensions. In Fig. 5c, the layered structure as observed in Fig. 5a is almost invisible and two-dimensional ripples are exhibited instead. Additionally, the density distribution is averaged and as a result, the amplitude of the ripples become small and the transition region is smoothed.

To observe the continuous transition of the number density distribution, simulation was performed by using a model in which a liquid drop was confined between a smooth upper surface and a lower rough surface. Figure 6 shows the results for amplitude of roughness $d = 7.5\sigma_{ll}$ and interaction ratio $\alpha = \sqrt{2}$, where (a) is the snapshot at 240 ksteps and (b) is the distribution of the number density. A layered structure is observed distinctly near the smooth surface (the upper surface), while as approaching the rough surface (the lower surface), the

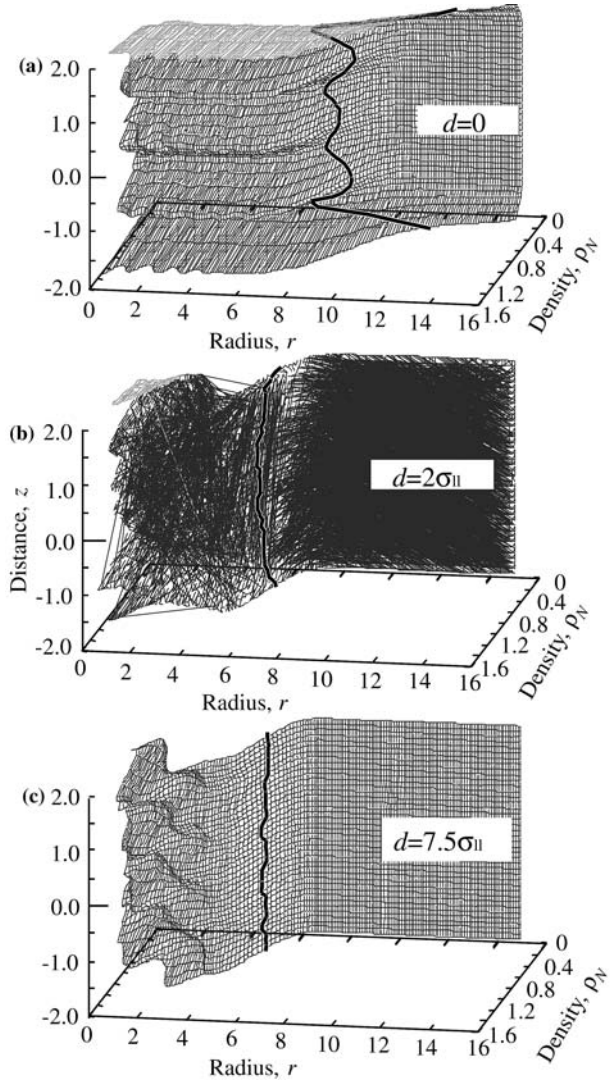


**Fig. 5 a–c** Two-dimensional distribution of number density of molecules ( $\alpha = \sqrt{2}$ and $h = 4\sigma_{ll}$)

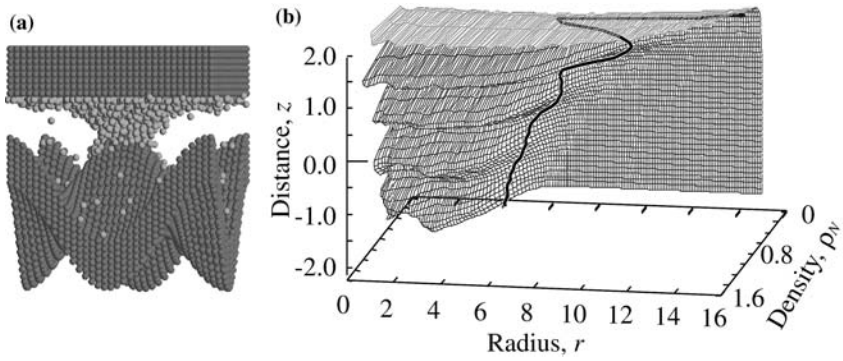


**Fig. 6** **a, b** Liquid bridge formation between smooth and rough surfaces ( $\alpha = \sqrt{2}$, $d = 7.5$ and $h = 4\sigma_{ll}$) **a** snapshot and **b** number density distribution

layered structure is smoothed gradually by averaging, and correspondingly the ripples in the transition region become less distinct and almost disappear in the part below the central line of the gap.

## 5 Projected profiles of liquid bridge

### 5.1 Determination of projected profile of liquid bridge

The method in which Gibbsian zero-adsorption dividing surface is chosen as the reference surface is generally used for determining the projected profile of a liquid bridge from the number density distribution (Mareschal et al. 1997). In this method, the density profile representing the change of number density with phase transition from liquid to vapor is approximated by a hyperbolic tangent (tanh) function, and its inflection point is defined as the point on the projected profile. However, the tanh function cannot be calculated accurately when the method is applied to nonuniform density distributions such as those presented in Figs. 5 and 6. As an example, the density profiles in the proximity ($z = -1.1$) to the smooth surface (Fig. 5a) and the rough surface (Fig. 5b) are plotted in Fig. 7a and b, respectively, and are approximated by tanh function. The density profile of the liquid bridge formed between smooth surfaces as shown in Fig. 7a can almost be approximated by a tanh function, although fluctuation is somewhat observed near the central axis. While for the case of rough surfaces as shown in Fig. 7b, because of the two-dimensional disturbance of the layered structure inside the liquid bridge, the density profile deviates from the tanh function significantly. We thus newly introduce a method that can simply describe the surface shape in the transition region by a curve showing the cross section of the bridge.

In Gibbsian method, the surface position is defined resultantly as the point where the density is equal to the half of the liquid density (i.e., 50% threshold value of liquid density). Extending the concept of threshold of liquid density, the region where the density is lower than a threshold is regarded as gas region, and the region where the density is larger than the threshold is considered as liquid region. Therefore, we simply apply the

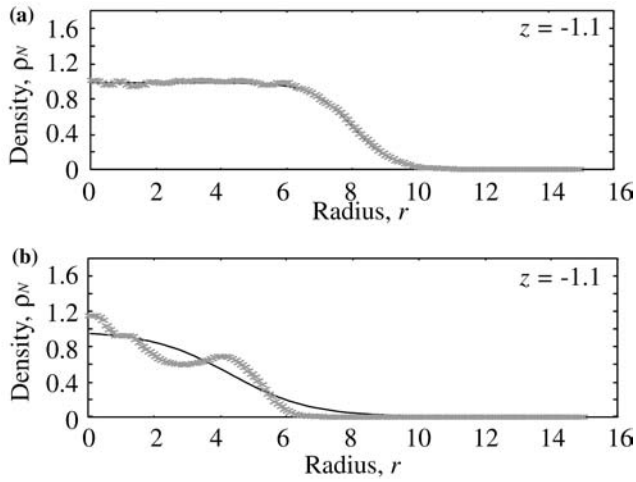


**Fig. 7** **a, b** Number density profile and hyperbolic tangent regression curve **a** between smooth surfaces and **b** between rough surfaces ($d = 2\sigma_{ll}$)

concept of threshold to the case of rough surface instead of applying Gibbsian method. The problem is to find the best threshold for expressing the liquid surface exhibiting the characteristics as shown in Figs. 5 and 6. In this research the liquid density is set as 0.8 because the number density of a liquid drop formed in vacuum was calculated to be about 0.8 in Sect. 4. Notably, the density in the liquid region is larger than 0.8 in Fig. 7a. This is because the density profile is extracted along the ridge of the density distribution.

By varying the threshold to be 50%, 45%, and 40% of the liquid density, the projected profiles are plotted along the $z$-axis in Fig. 8, where (a) is the case of smooth-smooth surfaces shown in Fig. 5a, and b is the case of smooth-rough surfaces shown in Fig. 6. It should be noted that this is equivalent to identify the boundary between liquid and gas through weighted average of liquid and gas densities. In Fig. 8b, since there is the deepest valley in the density profile near the position of $z = 1.5$, even the maximum density does not reach the density thresholds of 50% and 45% and as a result, the surface is scissioned and expressed in an unrealistic shape. In the case of the threshold being decreased to 40%, the projected profile is able to be determined even

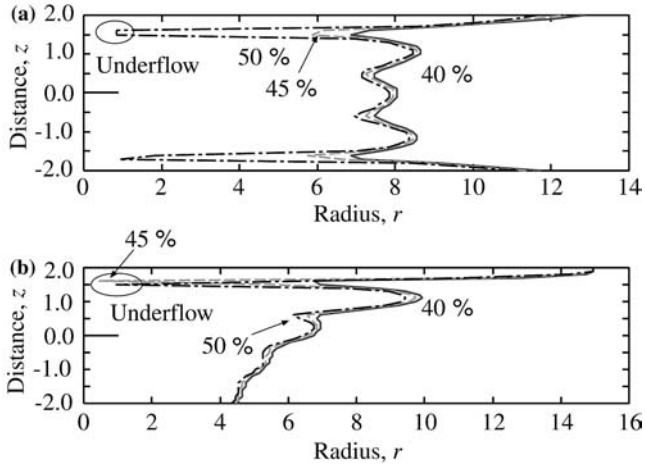


**Fig. 8 a, b** Projected profiles of liquid bridge with different threshold values **a** between smooth surfaces and **b** between smooth and rough surfaces ($d = 7.5\sigma_{ll}$)

in the region of low density. For all the cases the projected profiles are almost the same except in the region of low density. Thus the projected profile of a liquid bridge is determined by using the 40% threshold. In Figs. 5 and 6, the thick solid curves in the transition region represent the projected profiles. It is evident that the features in the transition region are well described by the one curve.

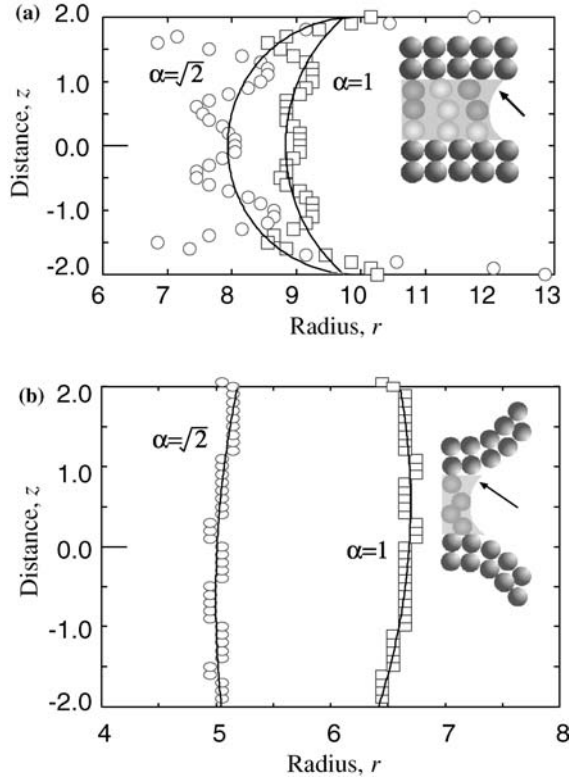


**Fig. 9 a, b** Projected profiles of liquid bridge ( $\alpha = \sqrt{2}$ and $h = 4\sigma_{ll}$) **a** between smooth surfaces and **b** between rough surfaces

## 5.2 Projected profile of liquid bridge

With the use of 40% threshold, the projected profiles for the cases of smooth and rough surfaces were determined and are shown in Fig. 9a and b, respectively. In the figure, the symbol (*circle*) represents the case of strong interaction ($\alpha = \sqrt{2}$), and the symbol (*square*) denotes the case of the weak interaction ($\alpha = 1$).

In the projected profiles of the liquid bridge formed between smooth surfaces, periodical ripples corresponding to the inner layered molecular structure are exhibited, and the ripples are more remarkable as the liquid–solid interaction becomes strong. Although it is no longer reasonable to make an arc approximation, the projected profiles are approximated with arcs by using the least squares method and the results are plotted with solid lines in Fig. 9a. It is seen that the projected profiles deviate significantly from the arcs.

On the other hand, for the case of rough surfaces shown in Fig. 9b, the periodical ripples on the projected profiles are almost smoothed out and the calculated values (indicated by (*circle*) and (*square*)) lie approximately on the arcs fitted with the method of least squares. In addition, the curvature of the projected profile is negative for the case of strong interaction whereas positive for the case of weak interaction, showing the same tendency as actual phenomenon.

Disappearance of the layered structure of the molecular arrangement inside the bridge in the case of molecularly rough surfaces can be attributed to two principal effects. One is that the irregular distribution of solid molecules can propagate from the solid surface to the liquid surface. The other is that the distance between the liquid molecules inside the bridge and the solid molecules becomes longer with increasing roughness amplitude except for the molecules located around the central axis of the bridge, which results in emergence of bulk-like properties. Since these two effects are related to each other, however, it is not reasonable to consider these effects separately.

Since there is molecular-scale roughness on a real surface, the layered structure of molecular arrangement will be disturbed eventually even if the size of the liquid bridge is in nanoscale. This suggests that due to the surface roughness arc approximation becomes applicable and as the result, the liquid bridge force measured on high-polished surfaces agrees comparatively with that predicted by the conventional theory.

## 6 Summary

The molecular dynamics was used to simulate the formation of a liquid bridge with a model in which a molecularly thin film is confined between two solid surfaces. Molecular number density inside the liquid bridge was calculated by using spatial and time averaging method and projected profile of the liquid bridge was

determined from the density distribution. By comparing the projected profiles of liquid bridges formed between solid surfaces with different roughness, it is clarified that due to the molecular-scale roughness on the surfaces, the layered molecular arrangement inside the liquid bridge is disturbed and the projected profile can be approximated by an arc.

## References


Chen Y, Weng J, Lukes JR, Majumdar A, Tien C (2001) Molecular dynamics simulation of the meniscus formation between two surfaces. Appl Phys Lett 79:1267

Gao C, Dai P, Homola A, Weiss J (1998) Meniscus forces and profiles: theory and its applications to liquid-mediated interfaces. ASME 120:358

Homola A (1991) The role of interfacial forces and lubrication in thin-film magnetic media. Adv Info Storage Syst 1:279

Mareschal M, Baus M, Lovett R (1997) The local pressure in a cylindrical liquid-vapor interface: a simulation study. J Chem Phys 106(2):645

NAOJ (2002) Chronological scientific tables, Maruzen

Tuckerman M, Berne BJ, Martyna GJ (1992) Reversible multiple time scale molecular dynamics. J Chem Phys 97(3):1990