Molecular Dynamics Study on the Dependence of Contact Angle on the Speed of Contact Line*

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Abstract
The flow in the vicinity of a moving contact line is characterized by a steep increase in the fluid slipping relative to the solid surface owing to fluid stress concentration at the contact line. In this study, molecular dynamics (MD) simulations are made to investigate the dependence of microscopic configuration of the fluid-fluid interface, in particular the contact angle, on the speed of contact line relative to the solid surface \( \Delta V \). While \( \Delta V \) increases when the solid surface velocity relative to the bulk fluid, \( V \), is increased from zero, \( \Delta V \) starts decreasing when \( V \) exceeds a certain upper limit for the given material combinations. The contact angle dependence on \( \Delta V \) (and \( V \)) was predicted from the microscopic stress balance near the contact line using the fluid distribution obtained from the continuum hydrodynamic theory. It is also shown that the stress balance prediction agrees with the MD results when appropriate slip velocities are assumed in the hydrodynamic calculation.

Key words: Contact Angle, Contact Line, Molecular Dynamics, Wetting, Interface

1. Introduction
Dynamic wetting or dewetting of a solid surface occurs in numerous industrial processes involving such phenomena as boiling, condensation, coating, drying, dropwise or rivulet flow, and wave-wall interactions. Of primary importance to these phenomena is the speed of the wetting/dewetting front, commonly referred to as the contact line, where the fluid-fluid (gas-liquid or liquid-liquid) interface meets the solid surface. The interface configuration near the contact line, generally dependent on the speed of the contact line, can also have significant influences on these phenomena.

The moving contact line problem, i.e., predicting the interface configuration as a function of the contact line speed as shown in Fig. 1, has been a challenge to continuum theories. The most crucial difficulty has been that the no-slip boundary condition used in such theories leads to a non-integrable singularity in the stress at the contact line\(^{(2)}\). To avoid such stress singularity, ‘local slip’ models of various kinds have been proposed.

The most common approach in these models has been to assume a fluid-wall slip velocity to be proportional to the shear stress on the wall surface\(^{(3)}\). This approach is based on Navier’s proposal\(^{(4)}\) in 1823 for fluid-dynamic problems in general. He used a
simple molecular hypothesis in attaining the idea of linear slip.

In the local slip models, empirical proportionality constants are used to describe experimental results on the macroscopic configuration of the interface. One may also want to employ a very large slip-length, on a non-physical basis, for calculation convenience such as to avoid numerical instabilities due to stress concentration.

More rigorous approaches have been made on the basis of microscopic considerations. Cox\(^5\) proposed an asymptotic expansion theory that can connect the interface configuration in the molecular-scale vicinity of the contact line to the macroscopic one. Additional theories are required to determine the microscopic interface configuration in the molecular scale. Indeed, several authors\(^6,7\) used the Cox theory with various assumptions on the value of microscopic contact angle as well as on its dependence on the speed of contact line. Some authors\(^6\) assumed that the microscopic contact angle is fixed independent of the contact line speed; on the other hand, others\(^7\) claim that the prediction of experimental results requires an assumption that the microscopic contact angle depends on the speed of the contact line.

Today, molecular dynamics (MD) simulations are rapidly expanding our knowledge on the velocity and stress fields in the molecular-scale vicinity of the moving contact line, as well as the interface geometry in such a small scale.\(^8-11\) Thompson et al.\(^10\) have shown the interface inclination angle, measured about six fluid molecular diameters away from the contact line, to be dependent on the relative velocity between the wall and the contact line, and the variation in the contact angle to agree with the estimation by Cox\(^5\). Qian et al.\(^11\) derived the stress balance among the interfacial tension, the wall-fluid tangential stress and other hydrodynamic stresses near the contact line. They have shown their formulation to be valid in both molecular and continuum scales.

In this paper, we first present the dependence of the microscopic contact angle on the relative velocity between the wall and the contact line by means of MD simulations. A model is then developed for prediction of such dependence. In the model this is realized by substituting the velocity distribution obtained by the hydrodynamic theory of Huh and Scriven\(^12\) into the stress balance formulation derived by Qian et al.\(^11\).

In Section 2, the method of MD simulation is described. In Section 3, the simulation results of the contact angle dependence on the speed of the contact line are shown. Subsequently, Qian et al.'s stress balance formulation and Huh-Scriven hydrodynamic theory are introduced and combined to reproduce our MD simulation results. Section 4 gives a summary of this paper.

2. Simulation Method

We simulate moving contact lines in a Couette flow geometry shown in Fig. 2. The flow consists of two immiscible fluids confined between two parallel walls that move in
the opposite directions.

All the interactions among the particles are represented by a modified Lennard-Jones (LJ) potential,

$$\Phi = 4\varepsilon_{ij} \left[ (\sigma_{ij} / r)^{12} - \delta_{ij} (\sigma_{ij} / r)^{6} \right],$$

where $\varepsilon$ and $\sigma$ are the characteristic energy and length scales of the interaction, respectively, and $r$ is the distance between the particles. The subscripts $i$ and $j$ denote the species of the interacting particle ("1" for fluid 1, "2" for fluid 2 and "w" for the wall). The philicity coefficient $\delta_{ij}$ is set to unity as in the usual LJ potential, except that $\delta_{12} = -1$ for ensuring the immiscibility of the two fluids. A similar approach has been taken in dealing with two-liquid problem $^{10,11}$.

The length scale $\sigma_{ij}$ is given the same value of 0.316 nm for all the interactions. The two fluids have identical properties; i.e. the mass of the fluid particle is $2.99 \times 10^{-26}$ kg, or 18 g/mol. The energy scales of $\varepsilon_{11}$, $\varepsilon_{12}$ and $\varepsilon_{22}$ are equivalent to $\varepsilon = 0.63$ kJ/mol, except that $\varepsilon_{2w} = \varepsilon_{1w} = 2$ where $\varepsilon_{1w} = \varepsilon$. This causes fluid 2 to wet the solid wall better than fluid 1 does.

The simulation cell is $4 \text{ nm} \times 2.1 \text{ nm} \times 18 \text{ nm}$ in size, with periodic boundary condition imposed on the $y$ and $z$ boundaries. The cell contains 2000 particles of each fluid. The distance between fluid particles is 0.31 nm, corresponds to a number density of $3.5 \times 10^{28}/\text{m}^3$, close to that of water in the standard condition.

Each of the walls consists of two ((100) and (200)) layers of body-centered cubic (bcc) lattice. The mass of wall particle is set to be $9.30 \times 10^{-26}$ kg (= 56 g/mol). Each particle is bonded to a lattice site by the Morse bond. The lattice constant is set to be 0.3 nm, a value chosen intentionally to be close to the average distance between the fluid particles. The lattice is forced to move at a constant speed to simulate a moving wall.

Our MD simulations were performed under a constant temperature condition of 300 K obtained with the NVT ensemble technique where the number of particles, the volume of the simulation system and the fluid and wall temperatures were kept constant. The temperature of the whole system was controlled by Nose thermostat $^{13}$. In order to confirm the influence of the temperature control in the present system, another set of calculations for several wall-velocity conditions was made in which only the temperature of the wall was controlled. The difference in the temperature distributions and the contact angles of the two control methods was within the statistical error.

Both the number density of the fluid and the temperature used in the present studies are considerably higher than those at the critical point of the LJ fluid with corresponding
ε and σ (the critical density and the critical temperature are $1.0 \times 10^{28}/m^3$ and 107 K, respectively)$^{(14)}$. Even in this supercritical condition, a definite interface between fluids 1 and 2 was formed in our calculation, as seen between two liquids.

The bulk viscosity and the interfacial tension between the two fluids are $2.3 \times 10^{-4}$ Pa·s and 0.168 N/m, respectively, obtained by the calculations conducted for the same temperature and density conditions.

The sampling of quantities was made for $1 \times 10^6$ to $6 \times 10^6$ steps after an equilibrium condition was reached with a $3 \times 10^5$ step calculation. The time step was set to be 0.7 fs.

3. Results and discussions

3.1 Contact angle behavior in MD simulation

Figure 3 shows the distribution of the particle number density along the x axis under the static condition ($V=0$). The fluid atoms form a layered structure near the plate surface, and the fluid layer next to the wall is referred to as the ‘first layer’ hereafter. Sampling of the velocity, stress and other quantities were made for finite volumes, or bins. The thickness of the bin, $\Delta x$, was chosen to be the same as that of the fluid layer that ranged from 0.22 to 0.28 nm, and the length $\Delta z$ of the bin was fixed to be 0.03125 nm. The interface between fluid 1 and fluid 2 was defined by finding the z-coordinate on each fluid layer where the number density becomes the same for the two fluids. A linear interpolation of the number density distribution along the z-axis was used to find the precise location. The position of the contact line was defined to be the interface position in the first layer and the contact angle was calculated as the angle between the wall and the plane connecting the interface location of the first and second layer.

Figure 4 shows the x-z distributions of the fluid particles for the wall velocity $V$, relative to the simulation cell, of 0, 10 and 20 m/s. At $V=0$ m/s, the fluids are almost stationary and a static condition, in which the contact angle for fluid 2 is 79 deg., is achieved. As represented in the Young’s equation$^{(15)}$, the static contact angle can be determined from the stress balance among the fluid1-fluid2, fluid1-wall and fluid2-wall interactions.
interfacial tensions, namely among the interfacial energies. For the present system with $\varepsilon_{2W} = 2\varepsilon_{1W}$, the interfacial energy between fluid 2 and the wall is lower than that between fluid 1 and the wall. This makes the static contact angle for fluid 2 to be 79 degrees that is smaller than 90 degrees.

At $V = 10$ m/s, the contact lines are kept stationary, relative to the stationary frame of the simulation cell, and the system reaches a steady state with its particle distribution only slightly deformed from that under the static condition. At $V = 20$ m/s, in contrast, the contact line fails to be stationary relative to the simulation cell, and starts moving in the direction of the wall motion. The fluid particle distribution changes drastically, including the formation and stretching of a fluid-2 film that is terminated by the receding contact line of fluid 2.

The time trends of the contact line position and the contact angle at the receding contact line under such non-steady condition are depicted in Fig. 5. (In the present paper, the contact angle is always measured through fluid 2. Likewise, a receding contact line means that of fluid 2, i.e., a contact line moving in such direction that fluid 2 is forced to recede from the wall surface, being replaced by fluid 1. The opposite is true for an advancing contact line.)

The contact line velocity relative to the simulation cell, $V_{CL}$, is almost constant for the 300 ps time interval shown in this figure. The contact angle also remains constant. The averaged value of $V_{CL}$ is 15 m/s. In this case the wall velocity relative to the contact line, $\Delta V (= V - V_{CL})$ is 15 m/s.

Figure 6 shows the contact angles as functions of $\Delta V$ at the advancing (upper symbols) and receding (lower symbols) contact line. For $V < 17.5$ m/s (open symbols in the figure), in the present case $V_{CL}$ is zero. The advancing contact angle increases and the receding contact angle decreases monotonically as $\Delta V$ is increased. For $V$ beyond 17.5 m/s (solid symbols in the figure), the receding contact line starts moving relative to the simulation cell, in the direction of the wall motion, i.e., $\Delta V$ there becomes less than $V$. It is worth noting that the value of $\Delta V$ does not exceed ~18 m/s and decreases as $V$ increases beyond 17.5 m/s. The receding contact angle under such unsteady condition is almost constant at 40 degree. On the contrary the advancing contact angle continues to increase even after the advancing contact line started moving relative to the simulation cell. The change does not cause, however, fluid 1 to form a film at this contact line.

### 3.2 Microscopic stress balance

The stress balance in the molecular-scale vicinity of the contact line has been formulated by Qian et al. They show that the tangential force in a thin fluid layer on the wall surface, referred to as the ‘boundary layer’ by these authors, dictates the motion of the contact line. The net force exerted in the z-direction upon the fluid-wall interface...
is given by
\[
\int_{\text{INT}} dz \tau_{xz}^{WF}(z) = \int_{\text{INT}} \int_{0}^{x_0} dx dz \frac{\partial}{\partial z} \tau_{xz}(x,z) + \int_{\text{INT}} dz \tau_{xz}^{V}(x_0,z) - \gamma_{12} (\cos \theta - \cos \theta^0),
\]
where \(x_0\) is the thickness of the boundary layer, \(\gamma_{12}\) the interfacial tension between fluid 1 and 2, \(\theta\) the contact angle measured at \(x=x_0\) and
\[
\tilde{\tau} = \tau - \tau^0,
\]
is the deviation of the stress from its static value, denoted by superscript 0, at \(V=0\). The normal stress \(\tau_{xz}\) is the pressure along the \(z\)-axis, and \(\tau_{xz}^{V}\) is the viscous tangential stress as,
\[
\tau_{xz}^{V}(x_0,z) = \mu \left[ \frac{\partial \nu_x(x_0,z)}{\partial x} + \frac{\partial \nu_z(x_0,z)}{\partial z} \right]
\]
and ‘INT’ denotes integration along the \(z\)-axis over the length of the interface region. The contact angle \(\theta\) (or its deviation from the static contact angle \(\theta^0\)) affects the stress near the contact line through the last term in the right hand side of Eq. (2) that is termed the unresolved Young’s stress.

The left hand side of Eq. (2) represents tangential stress caused by the relative motion between the wall and the fluid in the boundary layer. Qian et al. affirmed through their MD simulation that the tangential stress is proportional to the slip velocity between the fluid and wall, \(v_s\), as
\[
\tau_{xz}^{WF}(z) = -\beta v_s
\]
which was first suggested by Navier\(^{[4]}\). The slip velocity \(v_s\) is given as the velocity difference between the wall and the \(z\)-component of the fluid velocity in the boundary layer.

The unresolved Young’s stress takes part in the force balance only in a control volume containing the fluid-fluid interface. If a distance \(z_i\) is chosen such that the interface in the boundary layer \((x \leq x_0)\) is located within a region \(|z|< z_i\), then the near-wall force balance outside this region is,
\[
\int_{0}^{x_0} dx dz \tau_{xz}^{WF}(x,z) + \int_{0}^{x_0} dz \tau_{xz}^{V}(x_0,z), \text{ for } |z|> z_i.
\]
We can therefore rewrite Eq. (2) as
\[
\int_{x_1}^{x_i} dz \tau_{xz}^{WF}(z) = \int_{x_1}^{x_i} dz \tau_{xz}^{V}(x_0,z) - x_1 \left[ \bar{p}(z_i) - \bar{p}(-z_i) \right] - \gamma_{12} (\cos \theta - \cos \theta^0),
\]
where
\[
p(z) = -\frac{1}{x_0} \int_{0}^{x_0} dx \tau_{xz}(x,z).
\]
We use this form for the following discussion.

The stress components \(\tau_{xz}^{WF}(z)\) and \(p(z)\) were measured by direct summation of the molecule and momentum transfers across the bin boundary and then averaged for 6 million steps to obtain time-averaged values.

The value of \(x_0\), the thickness of fluid layer where the concentration of the tangential stress occurs near the contact line, was taken to be the thickness of the first layer (0.22 nm in the present study), because \(\tau_{xz}^{WF}(z)\) in the second layer was found to be less than 3% of \(\tau_{xz}^{WF}(z)\) in the first layer. The value of \(z_i\), the half range of the contact line integrations Eq. (7), was chosen to be 4.5 nm to encompass the fluid-fluid interface in the first layer.

Figure 7 depicts the spatial variation of the wall-fluid tangential stress under the static condition, \(\tau_{xz}^{WF}(z)\). The stress distribution shows periodic, high-amplitude
fluctuations along the $z$-axis, with a characteristic wavelength identical to the wall lattice constant $a_0$. This occurs due to epitaxial ordering of fluid particles near the wall surface. Such ordering or crystallization of fluid molecules has been observed in MD simulations conducted for cases with fluid number density $\rho_f$ close to the number density of wall atoms\cite{16,17}, as in the present study. The ordering can be seen as spatial changes, bound to the wall lattices, in such parameters as $\rho_f$ and $\tau_{zz}^{\text{WF}}$.

The spatial distribution of the tangential stress under dynamic conditions, $\tau_{zz}^{\text{WF}}(z)$, is much smoother than the static stress $\tau_{zz}^{\text{WF}}(0)$ above, as shown in Fig. 8 for $V=10$ m/s. Although the dynamic stress $\tau_{zz}^{\text{WF}}(z)$ measured at each location fluctuates with time, as the structures in the fluid pass over the location of measurement, the measured fluctuations are smoothed out in time averaging.

The dynamic deviation of local stress, $\tilde{\tau}$, if obtained through the direct subtraction Eq. (3), therefore, includes as large spatial fluctuations as that in the static stress $\tau_{zz}^{\text{WF}}(0)$. The fluctuations are not physically meaningful since the $z$-coordinates for $\tau_{zz}^{\text{WF}}(z)$ and $\tau_{zz}^{\text{WF}}(0)$ refer to origins located at different positions on the wall depending on the position of the contact line relative to the wall lattice. The influence of these fluctuations on the force balance calculation, Eq. (7), can be eliminated effectively by using the periodicity of the fluctuations in the static stress. We start by writing the integral of Eq. (3) as

$$\int_{z_1}^{z_2} \int_{z_1}^{z_2} \int_{z_1}^{z_2} dz\tilde{\tau} = \int_{z_1}^{z_2} dz\tau - \int_{z_1}^{z_2} dz\tau^0. \quad (8)$$

The integral of the dynamic stresses does not require any further manipulation, but the integral of the static stress, $\int_{z_1}^{z_2} dz\tau_{zz}^{\text{WF}}(z)$, shows a strong, oscillatory dependence on $z$. This dependency can be eliminated by using the fact that $\tau_{zz}^{\text{WF}}(z)$ is a purely periodic function of $z$, except in the close vicinity of the contact line, leading to that $\langle \tau_{zz}^{\text{WF}}(z) \rangle_z = 0$ where $\langle f(z) \rangle_z$ represents the averaging of $f(z)$ around $z = \zeta$ for $L=10$ with $L$ being an arbitrary integer. It is hence known that $\langle T(z) \rangle_{\zeta}$ for $|\zeta| >> 0$ no longer depends on $\zeta$ where $T(z) = \int dz\tau_{zz}^{\text{WF}}(z)$. Thus $\int_{z_1}^{z_2} dz\tau_{zz}^{\text{WF}}(z)$ can be replaced with $\langle T(z) \rangle_{z_2} - \langle T(z) \rangle_{z_1}$. In this study $L$ was chosen as 10.

The static pressure $p^0(z)$ also indicates spatial fluctuations due to the fluid ordering. We thus used $\langle p^0(z) \rangle_{z \pm z_i}$ instead of $p^0(\pm z_i)$.

To obtain the quantities of the components in Eq. (7), the fluid properties at $x = x_0$ ($\mu = 2.7 \times 10^{-4}$ Pa s and $\gamma = 0.184$ N/m), slightly different from the bulk value, were used.

The magnitudes of the terms in Eq. (7), for $V=10$ m/s, are plotted in Fig. 9 in terms of integral parameters defined by,
By substituting Eq. (9) into Eq. (7), \( W_{WF} = W_V + W_P + W_S \) is obtained. As shown in the figure, this relation is well satisfied. This means that the force balance near the contact line, Eq. (7) holds in our calculational case.

The values of \( \beta \) in Eq. (5) were obtained for \(|z| > 1.7 \text{ nm}\) where net tangential stress which exerts on the fluid disappears in the static condition. The obtained values were 3.74 MPa·s/m and 2.94 MPa·s/m for fluid 1 and 2 respectively. To confirm applicability of Eq. (5) for the whole range of \( z \) including the interfacial region, we compare the integrated value \( \int_{z_1}^{z_2} \beta(z) \Delta V \) with \( W_{WF} \). As shown in Fig. 9, they are consistent well, indicating that Eq. (5) can be applied to our system.

### 3.3 Hydrodynamic model and its applicability to the present microscopic system

From Eqs. (5) and (7), the contact angle \( \theta \) (or deviation of \( \cos \theta \) from its static value) can be obtained if the velocity and pressure distribution in the first layer are known. In this study, hydrodynamic model by Huh and Scriven\(^{(12)}\) is used to estimate such hydrodynamic quantities. The model is briefly reviewed here.

The system is modeled by two-dimensional steady flow where a flat interface between two immiscible fluids contacts with planar wall as shown in Fig. 10. The curvature of the interface is not considered. Stokes approximation is applied, the stream function \( \psi \) then satisfies the biharmonic equation, i.e. \( \nabla^4 \psi = 0 \). This equation is solved under following boundary conditions: (1)no slip at the fluid-fluid and fluid-solid interfaces (2) continuity of tangential stress at the fluid-fluid interface (3) vanishing of normal component of fluid velocity at the fluid-fluid and fluid-solid interfaces. The obtained distributions are proportional to \( \Delta V \). For instance, the velocity and the pressure for the receding fluid are written in the form of

\[
\begin{align*}
\nu_r &= g_{\nu r}(\phi, \Delta V), \\
\nu_\phi &= g_{\nu \phi}(r, \phi, \Delta V), \\
\bar{p} &= g_{p}(r, \phi, \Delta V)
\end{align*}
\]

(10a–c)

where \( r \) and \( \phi \) are the polar coordinates, and \( g_{\alpha \beta}(\alpha=\nu r, \nu \phi \text{ or } p) \) given by

\[
g_{\alpha \beta}(r, \phi, \Delta \theta) = \left[ 1 + (\pi - \phi)c \right] \cos \phi - \left[ c + (\pi - \phi d \right] \sin \phi
\]

(11a)
with constants $c$ and $d$ which depend on the contact angle $\theta$. Note that the wall velocity here is represented by not $V$ but $\Delta V$ because the origin of axis is fixed at the contact line.

The applicability of Huh’s model to the present microscopic system was examined by comparing the velocity distributions Eqs. (10a) and (10b) with those obtained by the MD simulation.

The velocity and pressure distributions strongly depend on the distance from the wall surface; however, in the present MD simulation, the density distributions of fluid and the wall do not have cross point as shown in Fig. 3, thus determination of the position of wall surface involves unavoidable arbitrariness. We hence treat it as a fitting parameter for each fluid and it is taken as $x_{W1} = x_{W2} = 0.125$ nm for both fluid 1 and 2.

The slip (or locking) effect between the fluid and the wall is essential in the microscopic analysis, but is not considered in Huh’s model. To cope with this, we introduce an “apparent” value of the wall velocity alternative to $\Delta V$. The apparent value is chosen so as to be equal to the fluid velocity just on the wall surface, obtained by extrapolation of the $z$-component of the velocity distribution along the $x$-axis near the wall. For instance, to represent slip between the wall and the fluid, the apparent value of the wall velocity is taken to be smaller than the actual value of $\Delta V$. Hereafter, these apparent wall velocities for fluid 1 and 2 are represented with constants $c_{n}(n=1,2)$ as $c_{1}\Delta V$ and $c_{2}\Delta V$, respectively. For the present case we select $c_{n}$ as 1.05 ($n=1$) and 1.00 ($n=2$).

Shown in Fig. 11 are the velocity distributions of fluids along the $z$-axis in the first layer for $\Delta V = 10$ and 17.5 m/s. The distributions for Huh’s model are obtained by substituting $\theta$ and $\Delta V$ in the MD result into the model. The velocity distributions in the MD simulation is obtained as the averaged values in the first layer, while for Huh’s model they are represented by those calculated at $x = x_{n}$ where the particle number densities of the fluid $n$ in the MD simulations takes its peak value namely, at $x_{1} = 0.245$ nm for fluid 1 $x_{2} = 0.255$ nm for fluid 2. Their agreement is excellent except $|z|$ within 0.5 nm.

### 3.4 Combination of the microscopic stress model and the hydrodynamics model

Substituting Eqs. (5), (10a)–(10c) and (11) into Eq. (7), we obtain

$$
\int_{z_{1}}^{z_{2}} dz \beta v_{n} = \int_{z_{1}}^{z_{2}} dz \Delta V \left[ \frac{\partial g_{s\theta}(x_{n}, z, \theta)}{\partial x} + \frac{\partial g_{s\theta}(x_{n}, z, \theta)}{\partial z} \right] \\
- x_{n} \Delta V \left[ g_{s}(x_{n}, z, \theta) - g_{p}(x_{n}, z, \theta) - \gamma_{1}(\cos \theta - \cos \theta_{0}) \right] \\
(12)
$$

where $g(x,z)$ represents $g$ expressed in rectangular coordinates and the subscript $n$ (fluid 1 or 2) is chosen for the corresponding fluid at the location of $z$. After introducing $c_{n}$ and
where

$$F(\theta) = \int_{z_1}^{z_2} d\zeta \left[ \beta_n \left[ 1 - g_{wz}(x'_n, z, \theta) \right] + \mu \left( \frac{\partial g_{wz}(x'_n, z, \theta)}{\partial x'} + \frac{\partial g_{wz}(x'_n, z, \theta)}{\partial z} \right) \right]$$

and

$$\Delta V = \frac{\gamma_{12}(\cos \theta - \cos \theta^n)}{F(\theta)}$$

Equation (13) represents the relation between the contact line velocity $\Delta V$ and the contact angle $\theta$.

The values of $\theta$ and $W_{WF}$, $W_V$ and $W_P$ obtained with Eqs. (13) and (12) (prediction model) are depicted in Figs. 12 and 13 with those of the MD results. All of the indicated quantities show good agreement between the MD results and the prediction model for both advancing and receding contact angles.

It is worth to note that the solution $\theta$ of Eq. (13) exists only in a limited range of $\Delta V$ as shown in Fig. 12. This is consistent with the results for the receding contact line in the MD simulation shown in Fig. 6. When $V$ increases below $\Delta V_{\text{max}}$, the value of $\Delta V$ also rises with $V$. On the other hand, when $V$ increases beyond $\Delta V_{\text{max}}$, the solution of $\theta$ which satisfies Eq. (13) does not exist. The contact line thus moves in the direction of the wall motion, leaving film behind it, so that $\Delta V$ is kept below $\Delta V_{\text{max}}$. The motion of the advancing contact line should be induced by the hydrodynamic stress due to large deformation of fluid interface.

From the figure it is also known that $\theta$ estimated by Eq.(13) is not single-valued for $\Delta V$ over 10 m/s (receding contact line) or 20 m/s (advancing one). For instance,
the values of $\theta$ of 22 and 52 degrees are obtained from the equation for $\Delta V=15\text{ m/s}$ of the receding contact line. The larger one is reproduced by the present MD calculation but the smaller one is not.

The full-ranged behavior of $W_{WF}$, $W_V$, and $W_P$ for the receding contact line is shown in Fig. 14 as a function of $\theta$. They are continuous and seem to be physically meaningful for whole range. This indicates that the smaller contact angle below 38 degrees would physically exist. At this range, for instance $\Delta V=15\text{ m/s}$ and $\theta=22$ degrees, as shown in Fig. 15 the velocity decrease near the contact line is steeper than the other. This corresponds to the larger $W_{WF}$ for $\theta=22$ degrees than that for $\theta=52$ degrees.

However, when $\theta=22$ degrees, the difference of the interface position between first and second layers in the $z$-direction should be approximately 0.6 nm. This means that a stable thin layer of fluid should hold on the wall surface with the length of 0.6 nm. It is unclear whether such a thin layer can exist over that length.

4. Summary

In this study, molecular dynamics simulations were made to investigate the dependence of microscopic (molecular-scale) contact angle on the speed of contact line. A model to predict the microscopic contact angle in the MD simulations was developed. In the model, the contact angle is estimated by substituting velocity distribution obtained from hydrodynamic theory by Huh and Scriven\textsuperscript{(12)} into microscopic stress balance formulation near the contact line by Qian et al\textsuperscript{(11)}. The contact angle behavior in MD results was then compared with the estimated value by the model.

- By taking into account the slip or locking effect on the wall surface, hydrodynamic model by Huh and Scriven well estimates the molecular-scale velocity distribution in the boundary layer where wall-fluid tangential stress acts on the fluid.
- The present model developed in this study well reproduces the contact angle behavior for the change in the wall velocity in MD simulation.
- In the MD simulation, film formation behind the contact line is observed for high wall velocity as seen in previous studies. In such a case the contact line follows the wall motion and the relative velocity between them, $\Delta V$, is
suppressed below a certain value.

- By the present model, it is shown that the range of $\Delta V$ where the solution of the contact angle exists is limited below a certain value. This is consistent with the MD results. The maximum value of $\Delta V$ predicted in the model agrees well with MD simulation. It is also indicated that the contact angle would take two different values for a single value of $\Delta V$.

References