Molecular Dynamic Simulations of Nano-Droplet Wetting on a Solid Surface

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ABSTRACT

Molecular dynamics simulations have been used to investigate wetting behavior of a nano-droplet using a rather novel configuration. An initially spherical liquid droplet, 6 nanometer in diameter, is located between two moving parallel surfaces (or walls) and surrounded by ambient gas. The shape of the droplet in contact with the solid surfaces is studied by applying continues pressure to the moving walls. The properties of the droplet and the surfaces are varied by suitably changing the liquid and wall molecular parameters, and their effect on the contact angle is studied. The parameters include interatomic interaction energies, wall porosity, and the droplet molecular diameter. Results indicate a complex relationship between the contact angle and the surface-liquid parameters. Comparison with the previous works demonstrates properties similar to the corresponding wetting phenomena on hydrophilic and hydrophobic surfaces for change in fluid interfaces, and were consistent with and macroscopic theory.

Keywords: contact angle, nano-droplet wetting, squeezing nanofluidics, interfacial tension

1 INTRODUCTION

Wetting and interfacial forces are responsible for behavior and properties of commonly used materials such as paints and lubricants. In studies of microfluidics and nano systems, droplet wetting has been shown to play an important role [1]. In spite of extensive study there is not sufficient information of wetting phenomena in micro and nano scale systems. Wetting in simple terms is the ability of a liquid to spread across its contact surface, and to produce a uniform, continuous interface. Spreading is due to the balance of the forces between liquid-liquid and liquid-solid molecules. At the liquid-solid interface, if the molecules of liquid have a stronger interaction with the molecules of solid, i.e., if the adhesive forces are stronger than the cohesive forces, then wetting of the surface occurs. Wetting is commonly characterized by the contact angle q, which is defined as the angle where the interface of liquid and gas contacts the solid surface. Contact angle indicates the degree of wetting. The lower the contact angle, the greater is the wetting. The usual description of surface wetting under ideal condition is based on Young's equation [2], which relates the contact angle q to the surface tension of the interfaces. In the present paper, we use the capillary bridge formed between two parallel solid surfaces to investigate the forced spreading of a nano-droplet on a surface. The configuration involves an initially spherical nano-size droplet squeezed between two walls that move in the opposite directions. This type of wetting plays an important role in lubrication and the design and operation of nano-machines.

2 METHOD AND THEORY

The simulation domain is a box contains 6379 argon atoms, of which 2123 atoms constitute the droplet, 3280 atoms the two walls, and 976 atoms constitute the ambient gas. The fluid particles can move freely in the 3-D box. The dimensions of the box L_x, L_y, L_z are $69.88s$, $34.94s$ and $34.94s$, respectively which are approximately equal to 24, 12, and 12 nm each. Here s is the characteristic length scale, and represented by the diameter of argon atom. The liquid droplet is initially placed between two walls parallel to x-z plane. Each wall consisted of two layers of atoms forming two planes of fcc lattice. The droplet initially has a spherical shape with a diameter $d = 17.47s$, or approximately $6.0nm$, and is located at the center of the two walls, i.e., the walls are initially tangent to the droplet surface. The droplet is then squeezed slowly between the walls by moving the walls at a constant speed V in opposite directions along the y-axis. The surrounding ambient gas has an initial density of $r_a = 0.0167 r_f$. Interactions between fluid atoms were modeled using the Lennard-Jones (LJ) potential.

$$U_{ij}(r) = 4e_{ij}[(s_{ij}/r\}^{12} - (s_{ij}/r)^6] \quad (1)$$

where e and s are characteristic energy and size parameters, respectively, and r is the center-center distance. For argon atoms, $e = 1.67\times10^{-21}$ J, and $s = 3.405$ Å. The potential was truncated at a cut off distance of $3s$. The fluid density and temperature are $0.75s^{-3}$ and $0.72e/k$, respectively. The wall-wall interactions were also modeled with the LJ potential. To

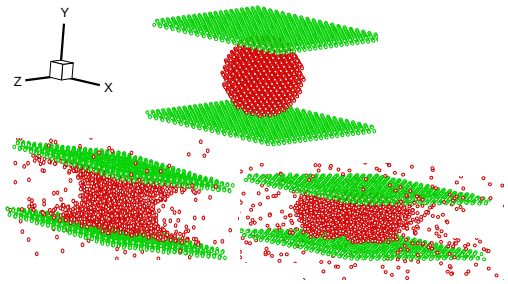

Figure1: Nano-droplet wetting on hydrophilic and hydrophobic surfaces

maintain a well defined solid-structure, each wall atom was attached to the lattice site with a simple harmonic potential, with a spring constant of $k = 200e / s^2$, and is allowed to oscillate due to thermal fluctuations around its lattice position. The density of wall considered as $r_w = 0.75s^{-3}$. The dimensions of the two walls were taken as one-half of the cube size in x direction, and equal to the cube size in z direction. Each wall consisted of two layers of atoms, which corresponds to a thickness of $0.64nm$. The initial distance between the walls is $17.47s$, or one-half of the cube size in the y direction, while the final distance is one-half of the initial distance, or ¼ of the cube size in the y direction. The equations of motion were integrated using Gear's fifth order predictor-corrector algorithm. The time step is $\Delta t = 0.005t$ or 1.078×10^{-2} ps where $t = (ms^2/e)^{1/2}$ with m, e, and s being the corresponding parameters for the atom. The reduced temperature is kept at $T^* = kT/e = 0.72$. The porosity of the moving surfaces was fixed to prevent any diffusion of atoms across the solid surfaces. The system was stabilized for approximately 500 time steps before the walls begin to move. The coordinates of all molecules were subsequently sampled every 500 steps for later analysis. The two walls move towards each other with a constant speed of $V = 0.218\times10^{-3}s$ per time step, or approximately 7.0 *m/s*.

A series of simulations were performed to determine the effects of droplet and surface parameters on the contact angle (cf. Table 1). The first set of simulations focused on the dynamics of droplet wetting and contact angle with the solid surface. In the second part, the effect of molecular size of droplet particles on the contact angle is studied while in the third part effect of wall porosity in contact angle is investigated. In the fourth part, the influence of liquid-liquid interaction energy parameter (e_f) on the contact angle is discussed and at the end, the effect of degree of droplet squeezing on contact angle is investigated.

Case	e_f	e_w	s_f	s_w	d
1-Ref.	1.0	1.5-0.01	1.0	1.0	$0.5d_i$
2	1.0	1.5-0.01	0.9	1.0	$0.5d_i$
3	1.0	1.5-0.01	1.0	1.0	$0.5d_i$
4	0.75	1.5-0.01	1.0	0.9	$0.5d_i$
5	1.0	1.5-0.01	1.0	1.0	$0.4d_i$

Table 1: Parameters used for different series of simulations.

3 RESULTS AND DISCUSSION

For the results in this paper, all variables are reduced with argon parameters reported earlier. In the first set of simulations, which is referred to the reference set, as is shown in Table 1, the reduced s for the wall and droplet atoms have the same value. The wetting properties of the system were investigated by varying the LJ energy parameter e_w of the wall, while e_f remains constant. This affects the surface-liquid interaction via the mixing rule, $e_{wf} = (e_w e_f)^{1/2}$. By changing e_w the e_{wf} and thereby the contact angle will be changed. The instantaneous snapshots of the droplet wetting for two extreme values of e_w are depicted in Figure 1, corresponding to highly wetting surface ($e_w = 1.5$) and dry surface ($e_w = 0.01$). As the two walls move at a fixed velocity in the opposite directions, the liquid droplet between the walls forms a capillary bridge. The surface of the interface initially has a spheroidal shape to satisfy the minimum energy requirement. As the droplet is squeezed further its surface (interface between the droplet and ambient gas) assumes a concave or a convex shape corresponding to a wet or dry surface. The contact angle (q) of the interface between solid, liquid and vapor can be determined by measuring the slope of the curve passing through the interface. After 20000 time steps the system was allowed to further equilibrate while the two walls remained stationary. Figure 2 demonstrates the temporal dependence of contact angle as the simulation proceeds. It shows a rapid decrease in the contact angle within the first 10000 steps which approaches to equilibrium in the next 10000 steps. The equilibrium was reached in about 20000 steps. Over the last 30000 steps we observe only expected thermal fluctuations. The equilibrium contact angle depends on the strength of the interaction between solid and liquid e_{wf}, and can vary from 0 to 180 degree.

Simulations start with $e_w = 1.5$ corresponding to a highly wetting surface. By reducing e_w the contact angle will be changed. As e_w is reduced further, interaction

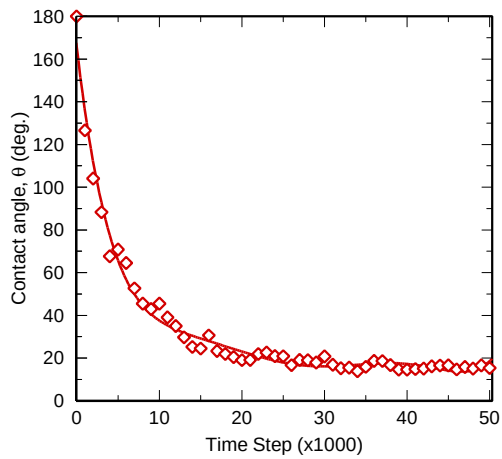

Figure 2: Droplet spreading on a hydrophilic surface and equilibrium contact angle

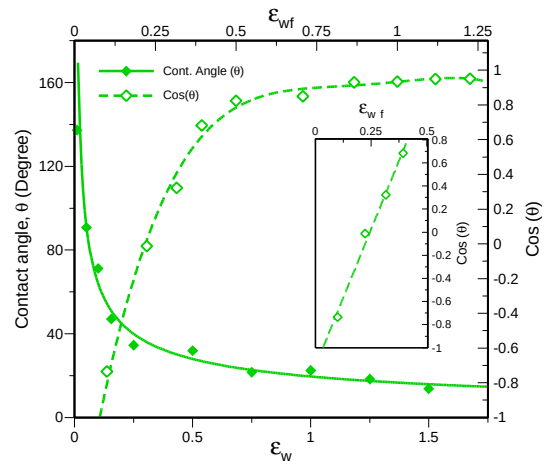

Figure 4: Contact angle and its Cosine as a function of surface-liquid interaction energy.

between the liquid atoms, e_{ff} becomes stronger than that between the liquid-solid atoms, and the contact angle moves toward $p/2$ for partially dry and eventually p for complete dry surface.

To calculate the contact angle, an algorithm was developed to track the interface based on the computed density profiles. The simulation box was divided into a large number of 3-D bins with 40, 80, and 40 bins in x, y, and z directions respectively. The interface was determined by identifying the bins that belong to the droplet surface. For this purpose planes of layers of the bins parallel to the x-z plain were considered. Each layer consisted of 160 bins (40 bins in x direction, 40 bins in z, and 1 bin in y direction). The average density profiles were determined by counting the number of particles in each bin. The liquid-vapor interface was then determined by comparing the density in each bin with the density in the core bin (at the center of the droplet) in each layer, defining the interface at the position where r_{bin} is reduced to at least $0.2\,r_{core}$. Considering the symmetry of the system, the surface obtained was smoothed by fitting a curve through the interfacial bins. The contact angle was obtained by determining the slope of the curve at y_{wall}. Figure 3 shows a typical plot of finding interface and its contact angle.

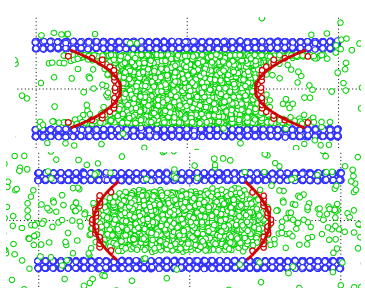

Figure 3: Average position of the particles and the interface for e_w, 1.5 (top) and 0.01 (bottom)

The first series of the simulations was performed using the parameters set as reference in Table I, and e_w ranging from 1.5 to 0.01. Figure 4 presents the contact angle plotted as a function of e_w. The droplet was observed to spread with a contact angle $q = 12.78^\circ$ for $e_w = 1.5$ with a large spreading area to $q = 137.3^\circ$ for $e_w = 0.01$ with a small spreading area. The transition of the surface from wet (hydrophilic) to dry (hydrophobic) occurred at $e_w < 0.1$ when q passes through $p/2$. For $e_w = 0.01$, the contact angle of $q = 137.3^\circ$ indicates a highly dry surface. Figure 4 further indicates the contact angle would vary from $q = 0$ (completely wet) to $q = p$ (completely dry surface), by suitably changing e_w. The relation between contact angle and wall interaction energy e_w was observed highly nonlinear. Comparing with previous works [3], the transition from dry to wet regime has occurred very suddenly. For e_w < 0.1, the contact angle changes quite rapidly with e_w, while for e_w > 0.1, the rate of change of q becomes small. It leads us to the fact that the nano-droplet wets the surface over a wide range of e_w while the dry surface has a narrow and tiny domain. The relationship between Cos(q) and e_{wf} also is plotted in Figure 4. It exhibits a non-linear relationship for the entire range of the simulation. However, comparing with previous works [3], [4], [5], in the partially wetting regime where $e_{wf} = 0.075 - 0.375$, as indicated in the inset of the figure, the relationship could be considered linear. Ultimately Cos(q) approaches a value of unity corresponding to a completely wet surface.

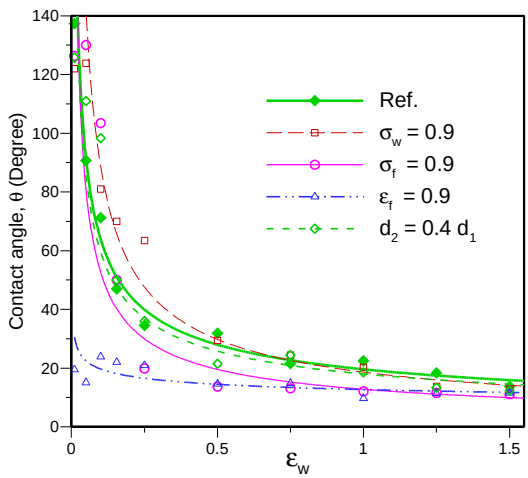

Figure 5: Effect of factors influencing the surface wetting

3.1 Effect of Influencing Factors on Wetting

Effect of various factors on wetability of the surface was studied by changing the following parameters. Figure 5 illustrates the results comparing to the reference case.

The effect of droplet molecular size (s_f) on the contact angle is investigated by changing the size of droplet diameter s_f, while other parameters of the system are kept unchanged. The parameter e_w is varied from 1.5 to 0.01 the same as before. In figure 5 the contact angle for $s_f = 0.9$ and $s_f = 1.0$, (the reference case) are shown. It can be seen that for e_w < 0.1, the contact angles are nearly the same for the two cases, while for e_w >0.1, the contact angle decreases, i.e., the wetability increases when droplet molecules become smaller. This is due to the fact that, lowering the value of s_f effectively increases the relative distance between the droplet molecules ($r_{ij}^* = r_{ij} / s_{ij}$), making cohesive energy weaker than the adhesive energy.

The effect of wall porosity on contact angle was examined by reducing the size of wall molecules (s_w), and keeping the other parameters same as the reference case. Figure 5 demonstrates that for e_w < 0.75, the contact angle increases as the wall porosity is increased, while for e_w > 0.75, the contact angle is relatively insensitive to the variation in wall porosity. Moreover, the transition from wet to dry surface occurs at a higher e_w. This result indicates that wall porosity has inverse effect on wetability of the surface. In the other words porosity makes a surface more dry or hydrophobic. It can be explained that, by reducing the size of the wall molecules, the interaction strength of the wall-fluid is lowered due to the increase in relative distance between wall-fluid molecules., making the adhesive energy weaker, while the fluid cohesive energy remains essentially unchanged.

The effect of interaction energy of the fluid atoms on the wetting and contact angle is studied by reducing e_f to the e_f = 0.75. As Figure 5 indicates, e_f has a strong influence on the surface wetting. This is primarily due to the fact that interaction energy between the droplet atoms is reduced 25% from its reference value, while the liquid-wall interaction energy is decreased by only 13%. As a result we observe significant wetting for even low values of e_w.

Simulations were performed to examine the sensitivity of the contact angle to the degree of droplet squeezing. For this purpose, the walls were allowed to continue their motion toward each other until their final distance between them reached to 40% of the original distance and the results were compared with the reference case where the distance between the walls were 50% of the original distance. Results indicate that the wetting of surface is relatively insensitive to the amount of droplet squeezing.

4 CONCLUSIONS

MD simulations of the wetting and spreading associated with a nano-droplet are performed by a relatively small amount of argon atoms. The effects of factors influencing the wetting phenomena were studied by squeezing an initially spherical droplet between two moving walls. Results indicate a highly nonlinear relationship between the contact angle and liquid-solid interaction energy. It was observed that the fluid-fluid energy has a strong influence on surface hydrophobicity. The liquid molecular size affect wetability in the way that liquid with smaller molecules wets the surface more. Surface porosity has inverse effect on wetability and it makes a surface more dry or hydrophobic.

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