# Drop Size Dependence of the Contact Angle of Nanodroplets

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*The contact angle of nanosized non-polarized argon sessile droplets on a solid substrate is studied by using molecular dynamics simulations. It is found that the drop size dependence of the contact angle is sensitive to the interaction between the liquid molecules and solid molecules. The contact angle decreases with the decreasing drop size for larger interaction between the liquid molecules and the solid substrate, and vice versa. This observation is consistent with most of the previous theoretical and experimental results.*

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The classical contact angle and wetting phenomena have been studied for more than one century.[1] With the development of new experimental facilities and theoretical methods, the contact angle of the micro-sized droplet has attracted much attention recently.[2−8] Understanding the wetting phenomena is particularly important in the micro- to nanofluidic applications, such as soft lithography techniques and labs on chips.[1] Considering a small scale sessile droplet sitting on an ideal solid surface in equilibrium with its vapour phase, we can describe the size-dependent apparent contact angle at small scales using a modified Young equation:[9]

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} - \frac{\tau}{\gamma_{lv} r_B}, \tag{1}$$

where $\gamma$ refers to the interfacial tension and subscripts $l, s$, and $v$ refer to liquid, solid, and vapour phases, respectively; $\theta$ is the equilibrium contact angle; and $\tau$ is the line tension, defined as the specific free energy of the three phase contact line, in analogy to surface tension: i.e., the excess free energy of a solid-liquid-vapour system per unit length of the contact line.[3,9] Here $1/r_B$ is the local curvature of the three phase contact line. The contact angle varies with respect to the drop size for micro-sized droplets.

When $r_B \to \infty$, Eq. (1) will be replaced by the classical Young equation:[3]

$$\cos\theta_\infty = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}. \tag{2}$$

Combining Eq. (1) with Eq. (2) yields

$$\cos\theta = \cos\theta_\infty - \frac{\tau}{\gamma_{lv} r_B}. \tag{3}$$

Although great effort has been devoted to it, there is still controversy regarding the size dependence of contact angle.[2,3] Both positive[4,5,7] and negative[2,6,8] values of $\tau$ have been reported. Wang *et al.*[6] once showed that $\tau$ was temperature dependence. It has been argued that the above observations were the results of different heterogeneity or surface roughness of the solid substrate surface.[2,7]

In this Letter, we study the wetting behaviour of micro-sized droplets by numerical simulations. Explicitly, a liquid argon droplet placed on an ideal solid surface is simulated by molecular dynamics.[10−13] The contact angles are computed from the density profile for different radius of the droplets. It is found that $\tau$ can be positive and negative, and even a negligible value, depending on the intensity of the interaction between the liquid molecules and the solid substrate. The tendency of the $\tau$ values with respect to the intensity is consistent with most of the experimental and theoretical results.

The interactions between molecules are expressed by the Lennard-Jones potential function

$$\phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], \tag{4}$$

where $\sigma$ and $\varepsilon$ are the length scale and the energy scale of the Lennard-Jones potential, respectively; the parameters are taken to be $\sigma_l = 3.4$ Å and $\varepsilon_l = 1.67\times10^{-21}$ J for argon-argon interactions. For liquid-solid interaction $\sigma_{sl} = \sigma_l$ is set, and the parameter of $\varepsilon_{sl}$ is implicitly specified through a non-dimensional parameter $\varepsilon^* = \varepsilon_{sl}/\varepsilon_l$.[14]

The computation box in our simulations has the size of $22\sigma_l \times 22\sigma_l \times 23\sigma_l$. The solid substrate contains 7200 solid molecules, composed of two layers of the $fcc$ lattice structure at the bottom of the box. The lattice constant of the solid substrate is $1.5496\sigma_l$, which is the equilibrium lattice spacing of the LJ potential. Initially argon molecules formed a crystalline $fcc$ structure, located on the solid substrate surface, with a lattice constant of 1.5496 $\sigma_l$ and a maximum random displacements of $0.01\sigma_l$ for each particle. In our series of simulations, the system contains $N = 400$,

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500, 864, 1372, 2048 and 2916 argon molecules, respectively. The motion of the atoms of the solid substrate is ignored.[14] The bounce back boundary condition is applied for the top boundary while periodic boundary condition is used in the $X$ and $Y$ directions. In the simulations the number of molecules, the volume and total energy of the system are kept to be constant as those in Ref. [14].

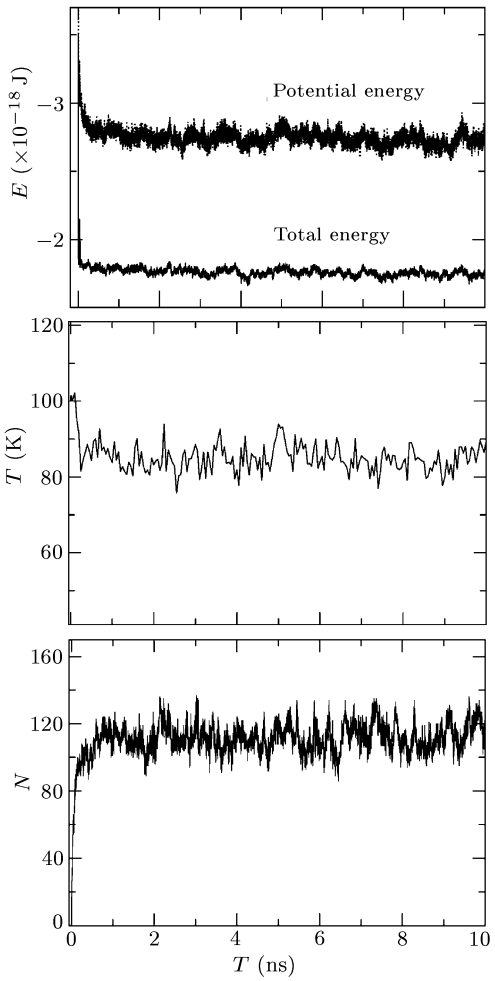



**Fig. 1.** The system energy ($E$) (potential energy and total energy), temperature ($T$) and the numerical evapouration ($N$) versus the simulation time.

We use the Verlet algorithm[15] with a time step of 0.01 ps. Typically first 50 ps of the calculation is spent for the temperature compliance and molecules are velocity controlled, then an idling period for the equilibration follows taking typically 100 ps without any operation on the velocity.[14] It is confirmed that the system has reached the equilibrium by monitoring the temperature, potential energy, and the number of vapour. A typical example for $N = 2916$ argon molecules, $\epsilon^* = 0.5$ and $T = 86$ K, is shown in Fig. 1. We can find that all the systems reach their equilibrium states after 1 ns. We collect the data every 0.5 ps for analysis for 10 ns after the first 1.5 ns.

The solid substrate can be changed from hydrophobic to hydrophilic by changing the liquid-surface coupling parameter $\varepsilon^*$.[14] We have performed numerical simulations for different $\varepsilon^*$ at three different temperatures. It has been indicated that a perfectly round shape droplet apart from the substrate surface is formed for about $\varepsilon^* < 0.1$, and the argon molecules completely spread out on the substrate surface for about $\varepsilon^* > 0.9$. A hemicycle-like droplet sitting on the substrate surface is generated only when the value of $\varepsilon^*$ fell in a certain range.[14] The simulations are carried out for $\varepsilon^* = \varepsilon_{sl}/\varepsilon_l = 0.6$, 0.554, 0.5, 0.45, 0.4, 0.35, 0.3, at temperatures of $T = 86$ K, 93.9 K, and 100 K, respectively.

To evaluate the contact angles, the system were partitioned into lattices of $100 \times 100 \times 100$. We calculate the three-dimensional density distributions, and plot the contour profiles in two dimensions. Figure 2 shows a density profile for $N = 2916$, $\epsilon^* = 0.5$, and $T = 86$ K. There are a circle-like profile in the liquid-gas interface while layered structure parallel to the solid surface inside the droplet. The layers closed to the surface of substrate are particular and cover a wider area compared to the size of the droplet,[14] which is usually ignored in the contact angle analysis.[4,5] Here, the layers below 7.8 Å from the solid surface are not taken into account.

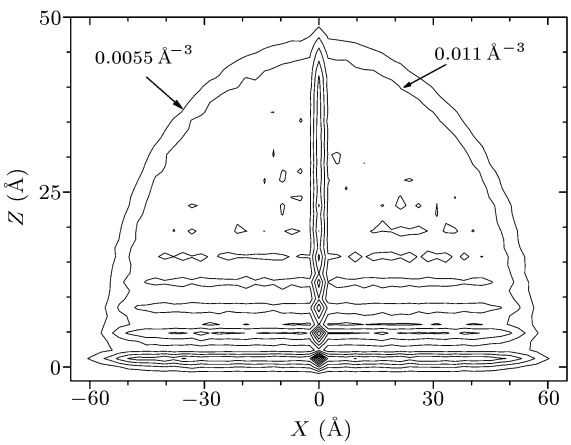



**Fig. 2.** A density profile for $N = 2916$, $\epsilon^* = 0.5$ and $T = 86$ K.

An argon molecule could be distinguished as in vapour and liquid state by the number of its neighbouring molecules $N_n$. An argon molecule can be determined to be the neighbouring molecule of the one within the distance of $1.4\sigma_l$.[16] The molecules are treated to be in a liquid cluster state when $N_n \geq 4$, otherwise the molecules are treated to be in a vapour state (including dimer and trimer states). One cluster includes the one as well as all the neighbouring molecules. We can find that nearly all the argon

molecules congregate into one big liquid cluster on the solid substrate surface, surrounded by the gas state molecules in our numerical simulations.

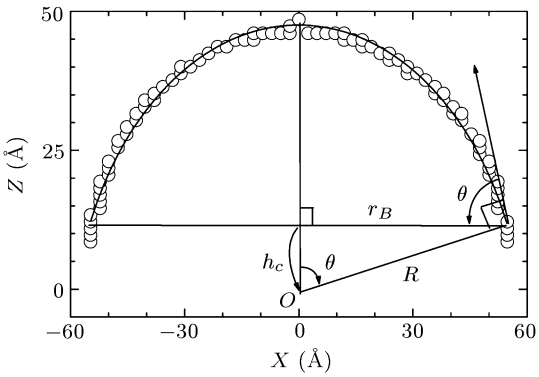



**Fig. 3.** The fitted profile to the droplet for $N = 2916$, $\epsilon^* = 0.5$ and $T = 86\,\mathrm{K}$ in two dimensions.

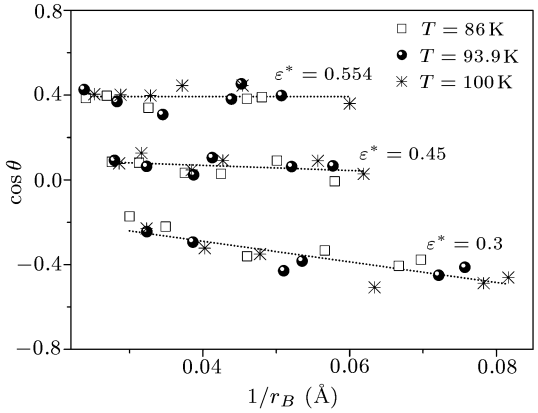



**Fig. 4.** Plots of $\cos\theta$ versus $1/r_B$ for droplets for $\epsilon^* = 0.554$, 0.45, 0.3 and $T = 86\,\mathrm{K}$, 93.9 K, and 100 K, respectively. The dotted lines are the linear fits.

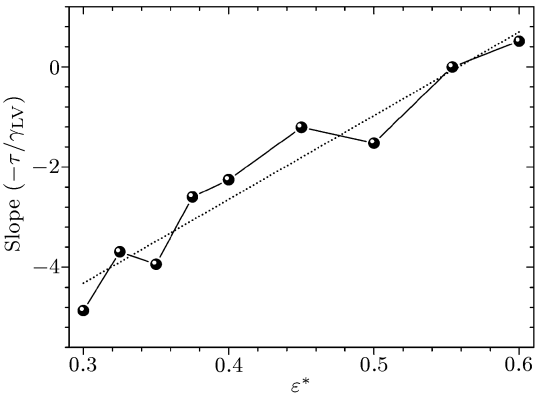



**Fig. 5.** The slope in Eq. (3) of a sessile nano-sized droplet versus the interaction between liquid molecules and the solid substrate. The dotted line is the linear fit $-\tau/\gamma_{lv} = -9.33 + 16.72\epsilon^*$.

The liquid/vapour interface is located at the position where the density falls to about half the bulk value.[14] The points with the density in the range $[(1-\delta)\rho/2, (1+\delta)\rho/2]$ are selected to fit a circle by using of the Levenberg–Marquardt least squares fitting method,[17,18] where $\delta = 0.2$, $\rho$ is the average density of the droplet. We find that the estimation of the contact angle is insensitive to the choice of $\delta$ for the fitting.[4,14] The height of the centre of the circle $h_c$ and its radius $R$ could be obtained from the fitted circle. Thus the contact angle $\theta$ and the radius $r_B$ can be calculated by $\cos\theta = -h_c/R$ and $r_B = \sqrt{R^2 - h_c^2}$, respectively.[14] An example for the fitting is shown in Fig. 3. The circle is a good approximation of the density profile.[4,5]

Figure 4 depicts our results of $\cos\theta$ versus $1/r_B$ for some typical parameters $\epsilon^*$ at three different temperatures. It seems that $\cos\theta$ is temperature independent. Then, the data of all the three temperatures for each $\epsilon^*$ are used to fit a linear line as shown by the dotted lines in Fig. 4. Figure 5 displays the slopes of all the fitted lines for different $\epsilon^*$. It seems that the larger the value of $\epsilon^*$, the larger the slope. When $\epsilon^* \approx 0.55$, the slope can be close to zero, indicating that $\cos\theta$ is almost independent of the droplet sizes. In the figure, a linear fit of these slopes is plotted to guide the eyes. Those results show that the larger the size of the drop, the larger the value of $\cos\theta$ for $\epsilon^* > \epsilon_c^*$, and the larger the size of the drop corresponding to smaller value of $\cos\theta$ for $\epsilon^* < \epsilon_c^*$, where $\epsilon_c^* \approx 0.55$. We remind that larger $\epsilon^*$ means strong interaction between liquid and the solid substrate. Consequently, the drop size of contact angle depends on the interaction between liquid and the solid substrate, and thus the bulk contact angle $\theta_\infty$.

The slope represents the value of $-\tau/\gamma_{lv}$ from Eq. (1). The sign of the line tension $\tau$ has the opposite sign of the slope, since $\gamma_{lv}$ is a positive constant.[3] We find that $\tau$ can change its sign: i.e., $\tau$ is positive for $\epsilon^* < \epsilon_c^*$ and negative for $\epsilon^* > \epsilon_c^*$.

Werder *et al.* have used molecular dynamics to study the wetting behaviour of water droplets on graphite,[4,5] and found positive $\tau$ for $\cos\theta < 0.25$. This is consistent with our results. The experimental investigations on the long-atom-chain molecule liquid systems above the solid surfaces have shown that most of the $\tau$ is negative.[2,6,8] The values of $\cos\theta$ in those experiments are larger than 0.6.[2,6,8] The droplets are rather flat for larger value of $\cos\theta$. Consequently, a larger number of liquid molecules are needed in the simulations to study the wetting behaviour of those droplets with $\cos\theta > 0.6$. Because of the limitation of the computer capacity, we can only obtain the contact angle with an acceptable accuracy for $\cos\theta < 0.6$. However, from Fig. 5 a linear fitting line can effectively

reflect the trend of the value of $\tau$ versus $\cos\theta_\infty$ (or $\epsilon^*$) and the zero value of $\tau$ appears at $\epsilon^* \approx 0.55$. If this linear line can be extrapolated to larger $\cos\theta_\infty$ (or $\epsilon^*$), the value of $\tau$ can change from positive to negative when $\epsilon^* \geq 0.55$ and $\cos\theta > 0.5$ (see Fig. 4), consistent with those experimental results. We consider simple argon molecules used in our simulations while alkane, alkene, or other organic systems in the experiments, the value of $\epsilon^*$ (or $\cos\theta_\infty$) at $\tau = 0$ might be different between our simulations and those experiments.

In summary, the droplet size dependence of contact angles of nano-droplets have been determined to be sensitive to the interactions between liquid droplets and the solid substrate, and consequently, the bulk contact angle. The contact angles decreases with the decreasing drop size for larger interaction between the liquid droplets and the solid substrate, and vice versa. Our simulation results are consistent with many theoretical and experimental results on micro-sized drops. It should be noted that our conclusions on the contact angle for $\cos\theta > 0.6$ is obtained by extrapolation due to the limitation of our computer capacity. Numerical simulations on larger systems are needed to obtain the results directly for $\cos\theta > 0.6$ and we are working on this direction.

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