Molecular Dynamics Simulation of Wetting Behavior: Contact Angle Dependency on Water Potential Models

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The underlying principle of surface wettability has obtained great attentions for the development of novel functional surfaces. Molecular dynamics simulations has been widely utilized to obtain molecular-level details of surface wettability that is commonly quantified in term of contact angle of a liquid droplet on the surface. In this work, the sensitivity of contact angle calculation at various degrees of surface hydrophilicity to the adopted potential models of water: SPC/E, TIP4P, and TIP5P, is investigated. The simulation cell consists of a water droplet on a structureless surface whose hydrophilicity is modified by introducing a scaling factor to the water-surface interaction parameter. The simulation shows that the differences in contact angle described by the potential models are systematic and become more visible with the increase of the surface hydrophilicity. An alternative method to compute a contact angle based on the height of center-of-mass of the droplet is also evaluated, and the resulting contact angles are generally larger than those determined from the liquid-gas interfacial line.

1 Introduction

Wettability is an inherent properties of solid surface that plays significant roles in diverse fields such as biological science1–4 and material manufacturing5–7. From nature, the so-called “lotus effect” inspired the development of super hydrophobic surface that found its application in self-cleaning surfaces7, corrosion inhibition8, and rainproof mirror coating for automotive9. On the other side, nature also demonstrate the presence of super hydrophilic surfaces such as those in spider silks2 and desert beetle’s back3. This super hydrophilic surface is also actively investigated for its potential in oil/water separation10 and biological cell adhesion11. One of the research pinnacle emanated from the wettability of solid surface is the reversible hydrophilic-hydrophobic switching surface12–14. In such materials, the wettability of surface is adjusted by altering the configuration of surface molecules through a simple physical or chemical treatment. Therefore, a molecular-level understanding of surface wettability has important implications to the development of surface technology.

The wettability of a solid surface is commonly quantified in term of the contact angle formed by a liquid droplet on the surface. A surface is defined to be hydrophobic when the contact angle of liquid droplet is larger than 90°, otherwise it is defined to be hydrophilic. A theoretical framework to describe the relation between a static contact angle of liquid droplet and the surface free energy is given by Young equation15. When the surface roughness is included in the picture, Wenzel model and Cassie model are the two most commonly employed framework16. In case of complete wetting, the contact angle is dynamically expressed as the advancing contact angle and the receding contact angle.

Molecular dynamics (MD) simulation is a powerful tool to obtain the microscopic details of atomic system, and it has been widely used to investigate the physiochemistry of surface and the wetting behaviors17–33. One of the key issue in MD simulation is the potential models adopted to describe the interaction between molecules. The parameters of interaction between water molecules and surface atoms, such as σws and εws, are known to significantly affects the contact angle of water droplet, and thus have become the subject of fine tuning to reproduce the experimental observation29–33. On the other hand, the effects of the

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adopted potential model for water-water interactions to the contact angle measurement were scarcely reported. In one report, compared to the SPC/E water model, TIP5P was observed to give a smaller contact angle by 17.4°, while TIP5P was smaller by 4.1°. The sensitivity of contact angle with the adopted potential models under various degree of surface wetting remains unexplored. In order to clarify this issue, MD simulations of a water droplet on a solid surface at various degrees of wetting are performed and three potential models for water: SPC/E, TIP4P, and TIP5P, are adopted for comparison. The potential models are known to reproduce many important properties of liquid water, along with certain set of limitations that characterize any rigid and non-polarizable models. Two methods for determination of contact angles, one based on the liquid-gas interfacial line and the other based on the height of center-of-mass of the droplet, are also evaluated.

2 Simulation methods

2.1 Simulation cell and potential models

The simulation cell is a cubic box with 20 nm length. The dimension is chosen to effectively remove the interaction between the droplet and its periodic image. A structureless surface is located at the bottom of the simulation cell and a stack of 8000 water molecules is positioned on the surface. The top of simulation cell is enclosed with a single graphene layer. Two dimensional periodic boundary condition is applied to the directions that are parallel to the surface plane.

The potential energy is assumed to be pairwise additive, and the potential energy of system $\Phi$ is given by

$$\Phi = \sum_i \sum_{j>i} \phi_{ij} + \sum_i \phi_{ws,i}$$

(1)

where $\phi_{ij}$ is the potential energy arising from the interaction between two particles,

$$\phi_{ij} = 4\varepsilon \left( \frac{\sigma_{i,j}^6}{r_{i,j}} - \frac{\sigma_{i,j}^{12}}{r_{i,j}^{12}} \right) + \frac{Z_i Z_j}{r_{i,j}}$$

(2)

and $\phi_{ws,i}$ is the potential energy arising from the interaction between a water molecule with the structureless surface, which is modeled by

$$\phi_{ws,i} = \frac{4}{3} \pi \rho_s \varepsilon_{ws} \sigma_{ws}^3 \left[ \frac{2}{15} \left( \frac{\sigma_{ws}^3}{r_{\perp,i}} \right)^9 - \left( \frac{\sigma_{ws}^3}{r_{\perp,i}} \right)^3 \right]$$

(3)

where $\rho_s$ is the “atomic” density of the surface, $r_{\perp,i}$ is the normal distance of the $i$-th water molecule from the surface plane, $\sigma_{ws}$ and $\varepsilon_{ws}$ are the combined Lennard-Jones parameters from the water potential model and the surface model obtained using the Lorentz-Berthelot mixing rule as

$$\sigma_{ws} = \frac{\sigma_s + \sigma_w}{2}$$

(4)

$$\varepsilon_{ws} = \lambda (\varepsilon_w \varepsilon_s)^{1/2}$$

(5)

where $\sigma_s$ and $\varepsilon_s$ are the Lennard-Jones parameters whose values are opted from Ref. 33 for modelling the surface of a graphite. Here a scaling constant $\lambda$ is introduced to modify the hydrophilicity of the surface and, thus, to alter the contact angle of water droplet. The description of interactions between water molecules is varied using SPC/E, TIP4P, and TIP5P potential models.

2.2 Molecular dynamics simulations

MD simulations at constant temperature and volume are performed using GROMACS. The equation of motion is integrated using the leapfrog algorithm at 2 fs time step. The potential energy arising from the interaction between two particles is smoothly truncated at $r_{cut} = 8.65 \text{ Å}$ using a switching function that takes effect from 6.65 Å. The cutoff distance is chosen to be far beyond the radius of first and second coordination shell of pure water that are typically around 3 Å and 4.5 Å, respectively, as reported by both simulation and experimental works. Nosé-Hoover thermostat is applied to keep the simulation temperature at 298 K with a coupling time of 0.5 ps. The geometry of a water molecule is constrained using SETTLE algorithm. The position of all carbon atoms in the graphene layer at the top of simulation cell is fixed during the simulation. The system is equilibrated for 1 ns and the trajectory of water molecules is sampled from the 39 ns production run.

3 Results and discussion

The contact angle is calculated from the liquid-gas interfacial line determined using a cylindrical binning procedure followed by the circular least square fitting. In this method, for each configuration snapshot, the liquid droplet is divided into several horizontal layers. The layer thickness is chosen to be 0.5 Å to ensure that each layer contains enough water molecules to give
a uniform density. The center of symmetry of each layer is taken from the lateral position of the center of mass of the droplet. The local density \( \rho(r) \) as a function of the distance to the center of symmetry \( r \) is then calculated by applying cylindrical binning and averaged over the time. The location of liquid-gas interface of this layer is then defined as the distance \( r \) where the density falls into half, as shown in Figure 1.

The liquid-gas interfacial lines that corresponds to the shape of water droplets on a structureless surface are shown in Figure 2. The strength of water-surface interactions, described by \( \varepsilon_{\text{ws}} \) parameter in Eq. 3, is modified using a scaling factor \( \lambda \) according to the known experimental facts. \( \Phi_{\text{ws}} \) potential energy of water-water interaction of intermolecular interactions between water-water and water-surface. Since SPC/E model is known to have a negatively large water-surface interaction scaling factor \( \lambda \). The droplet shapes are seemed to be invariant to the water potential models at \( \lambda = 0.5 \) and 2.5, but a difference in droplet radius is observed at \( \lambda = 4.5 \) where SPC/E gives the smallest droplet radius and TIP4P gives the largest. Since the number of water molecule \( N_w \) is identical, larger droplet radius indicates that the wetting of surface is improved and a smaller contact angle can be expected.

Figure 3 shows the comparison of contact angles \( \theta \) of water droplets obtained from MD simulations using three different potential models of water at various levels of surface hydrophilicity. On this structureless surface, the boundary of hydrophobic/hydrophilic is observed when \( \varepsilon_{\text{ws}} \) is \( \sim 1.1 \text{kJmol}^{-1} \) for all the studied water potential models. The differences in contact angle between three potential models become more visible as the surface become more hydrophilic with the increase of \( \varepsilon_{\text{ws}} \). In accordance to Figure 2 water droplets described by TIP4P potential model have the smallest contact angle over the studied \( \varepsilon_{\text{ws}} \), and SPC/E potential model have the largest contact angle. This trend persists across the variation of surface hydrophilicity. The ability of water to wet the surface can be related to the competition of intermolecular interactions between water-water and water-surface. Since SPC/E model prefer to stay in the droplet phase, thus lower their tendency to wet the surface. However, when comparing between TIP4P and TIP5P potential models, the trend of contact angle does not always follow the trend of \( \Phi_{\text{ws}} \). For all models, the trend of contact angle resembles the trend of potential energy of water-water interaction \( \Phi_{\text{ww}} \) as shown in Figure 4. it is straightforward to argue that the water molecules of this model prefer to stay in the droplet phase, thus lower their tendency to wet the surface. However, when comparing between TIP4P and TIP5P potential models, the trend of contact angle does not always follow the trend of \( \Phi_{\text{ww}} \).

Another method to calculate the contact angle is based on a spherical geometry approximation that relates the contact angle \( \theta \) with the average height of the center of mass of the water droplet \( h_{\text{CoM}} \) according to:

\[
\langle h_{\text{CoM}} \rangle = (2)^{-4/3} R_0 \left( \frac{1 - \cos \theta}{2 + \cos \theta} \right)^{1/3} \frac{3 + \cos \theta}{2 + \cos \theta}
\]

where \( R_0 = 3N/4\pi \rho_0 \) is the radius of a spherical drop of \( N \) water molecules at a uniform density \( \rho_0 \) and the bracket \( \langle \ldots \rangle \) denotes the ensemble average. The method is less tedious since \( \langle h_{\text{CoM}} \rangle \) can be obtained immediately from the simulations. The contact angles obtained using this method are shown in Figure 5. When compared to the results from the liquid-gas interfacial line method, the center of mass method tends to give a higher value of contact angles, regardless of the adopted potential models of
water. Nevertheless, both methods are in agreement for the gradient line of \( \frac{\Delta \theta}{\Delta \epsilon_{ws}} \) and, thus, the center of mass method can be useful for a rapid assessment of contact angle of water droplet at various surface properties.

### 4 Conclusion

MD simulations of water droplet on a structureless surface have been performed to investigate the sensitivity of contact angle calculation to the adopted potential models of water. The investigation is carried out over the variation of surface hydrophilicity by introducing a scaling factor \( \lambda \) that modify the strength of water-surface interaction through \( \epsilon_{ws} \) parameter. Under a similar thermodynamics condition, the computed results shows that SPC/E model gives the largest contact angle, while TIP4P gives the smallest. This trend persists over all the studied variation of surface hydrophilicity. The difference in contact angle between potential models become more visible as the hydrophilicity of surface increases. Although the large contact angle for SPC/E can be argued by its negatively large potential energy of water-water interaction, the trend of contact angle between TIP4P and TIP5P resembles more to the trend of potential energy of water-surface interaction. An alternative method to compute a contact angle based on the height of center-of-mass of the droplet is shown to reproduce the contact angle trend with the change of surface hydrophilicity, although the method generally gives a larger contact angles compared to those obtained from liquid-gas interfacial line.

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Figure 5 Comparison between contact angles calculated from the height of center of mass of droplet with those calculated from the liquid-gas interfacial line. Data from the latter method are actually the same with Figure 3 but they are included here to make the comparison easier. The interaction between water molecules are modelled with: SPC/E (left), TIP4P (middle), and TIP5P (right).


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