Nanoscale Wettability of Water-Alcohol Mixtures on Graphite Surface: Molecular Dynamics Study

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Abstract

The ability to predict and control surface wettability at the nanoscale is crucial and rapidly evolving, particularly in the fields of microfluidics and nanotechnology. Typically, the contact angle is measured in simulations by creating a liquid droplet on a solid surface, fitting a curve to the droplet's interface, and determining the angle at the triple-phase contact line. However, at the molecular level, the triple-phase contact line becomes ambiguous due to the continuous motion of molecules, making conventional measurements difficult. This study reports the molecular dynamics simulations to determine the contact angle of water mixed with four primary alcohols (R_N-OH, where R = (C_NH_{2N+1}), N varies from 1 to 4) on a graphite substrate, using the Hautman and Klein method, which links the microscopic contact angle to the droplet's average centre of mass height through the concepts of equivalent contact area and volume. The water concentration is varied from 50% to 90% in the alcohol mixture. ContactAngleCalculator code is modified to calculate the contact angle of binary liquids. Results show that increasing alcohol concentration leads to greater spreading.

Keywords: Wetting, Contact Angle, Molecular Dynamics Simulation, Binary Mixtures.
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Introduction

Understanding the wettability of aqueous mixtures on solid surfaces is crucial for unravelling interfacial phenomena, with wide-ranging applications in material science, microfluidics, and processes like coating, adhesion, drug delivery, and fluid transport [1-3]. This paper reports the contact angle (CA) of water-alcohol binary mixture (R_N-OH, where R = (C_NH_{2N+1}), N varies from 1 to 4, R =1(methanol), R = 2(ethanol), R = 3(1-propanol) and R = 4(1-butanol) on a graphite substrate using molecular dynamics (MD) simulation. The water concentration is varied from 50% to 90% in the alcohol mixture.

Methodology

The MD simulation is carried out using large-scale atomic/molecular massively parallel simulator (LAMMPS) [4]. The alcohols are modelled using optimized potential for liquid simulation/all atom (OPLS/AA) [5, 6] force field and the water molecules using SPC/E model [7]. Two layers of graphene sheet are used to prepare the graphite. It has been found that two layers of graphene were sufficient to reproduce the CA [8]. The graphene sheets are generated using the nanotube builder plugin in VMD [9]. The graphene sheets are built with the dimension of 15 nm in both the x and y directions. The distance between the two graphene layers is 0.335 nm. The simulated water-alcohol binary mixture is centered above the graphite surface. The methodology used to simulate binary mixtures is same as our previous works [10,11]. The pair interactions are modeled using the lj/charmm/coul/long style with a cutoff of 10 Å for Lennard-Jones and 12 Å for Coulomb interactions. Long-range Coulombic interactions are handled using the particle-particle particle-mesh (PPPM) method with a precision of 1.0×10^{-4}. The simulations are performed in the NVT ensemble, maintaining a temperature of 298.15 K through the Nosé-Hoover thermostat, with a time step of 1 fs. Atomic positions are recorded every 1 ps. The simulation is run for 1 ns (i.e. 100000 time steps).

Discussion

In simulations, the CA is typically calculated by simulating a liquid droplet on a solid surface, allowing it to reach equilibrium, and analysing its shape. The angle is measured at the triple-phase contact line by fitting a curve to the droplet's interface. However, at the molecular level, CA becomes ambiguous, as shown in Figure 1.

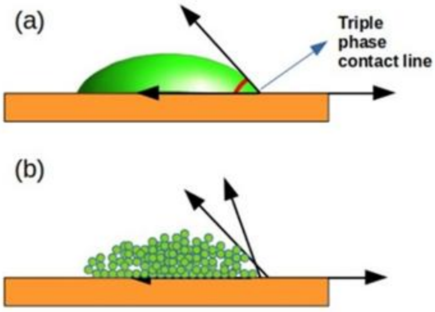

Figure 1: Schematic images of (a) macroscopic droplet, (b) microscopic droplet.

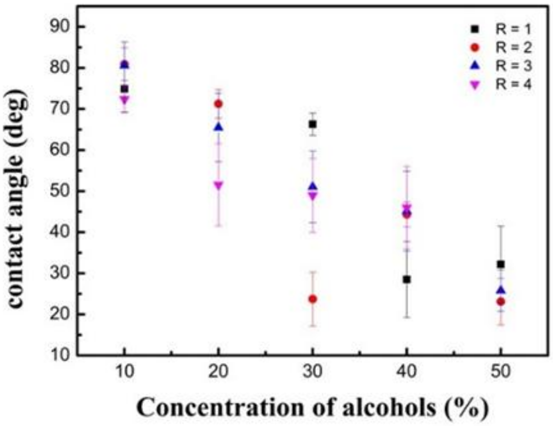

Figure 2: CA versus concentration of alcohols (%).

Hautman and Klein introduced a method for estimating the microscopic CA from the simulations, this approach uses the concepts of equivalent contact area and volume to create a quantitative link between the CA and the average height of the droplet's center of mass. The CA of the water-alcohol binary mixture on a graphite substrate is calculated using a flexible estimation tool called "ContactAngleCalculator" [12] which is specifically designed to function within VMD. The code is versatile and can be used with different MD codes. It was written only to work with a single molecular system. The code was modified to calculate the CA of the binary mixture. The modified version of the code is available at

https://github.com/akareem28/ContactAngleCalculator/blob/main/cac-cg-mult

The CA calculation using the ContactAngleCalculator code consists of four steps (i) coarse-graining the all-atom model of a molecule into a single bead and removing the evaporated molecules (ii) calculating the circular contact area from the real contact area, (iii) constructing the droplet from the real liquid volume and (iv) calculating the CA. Prior to the calculation of CA, the number density is calculated from the simulation. A detailed description of calculating CA using the Hautman and Klein method is available in reference [12, 13].

Figure 2 shows the CA versus concentration of alcohol in water-alcohol binary mixture on graphite surface. As the concentration of alcohol increases, the droplets spreads more on the graphite surface.

Conclusion and Future Prospective

The ability to predict and control surface wettability at the nanoscale is crucial and rapidly evolving, particularly in the fields of microfluidics and nanotechnology. Typically, the CA is measured in simulations by creating a liquid droplet on a solid surface, fitting a curve to the droplet's interface, and determining the angle at the triple-phase contact line. However, at the molecular level, the triple-phase contact line becomes ambiguous due to the continuous motion of molecules, making conventional measurements difficult. This study reports the MD simulations to determine the CA of water-alcohol binary mixtures on a graphite substrate. The Hautman and Klein method, which links the microscopic CA to the droplet's average center of mass height through the concepts of equivalent contact area and volume is used to calculate the CA at nanoscale. ContactAngleCalculator code is modified to calculate the contact angle of binary liquids. Results show that increasing alcohol concentration leads to greater spreading. Liquid spreads on a solid if it lowers the system's surface energy. On graphite, water-alcohol mixtures show better spreading with increasing alcohol concentration. Graphite's dispersive interactions are weak with polar water but stronger with alcohols, especially long-chain ones, reducing the contact angle at higher alcohol concentrations.

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