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Wetting of Water and Water/Ethanol Droplets on a Non-Polar Surface: A Molecular Dynamics Study

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Spreading of sessile water droplets on a solid graphite surface has been studied using atomistic molecular dynamics techniques. The system is in the partial wetting regime and a straightforward scheme is applied to extract the contact angle from the atomistic simulations. Even for droplets containing a thousand molecules, the calculated contact angle for water is 83°, which is close to the experimental macroscopic value. On addition of ethanol, the contact angle decreases to 30° and we approach complete wetting. Time-averaged structural analyses show that the ethanol molecules form a monolayer on top of the solid surface. A few Å above the solid surface, the ethanol molecules are preferentially located at the liquid/vapor interface rather than in the bulk of the droplet.

Introduction

The contact of liquids with solids is encountered in a large variety of phenomena in daily life and is of considerable importance in both industrial and biological processes. Almost two centuries ago, Young,[1] studying wetting at a macroscopic level, was able to relate the surface tension, γ, of a sessile drop on a surface to the contact angle, θ:

$$\gamma_{\mathrm{s/l}} \cos \theta = \gamma_{\mathrm{l/v}} - \gamma_{\mathrm{v/s}} \tag{1}$$

where s, l, and v signify solid, liquid, and vapor, respectively, and "/" denotes an interface. Young's equation assumes the drop is spherical and that gravitational effects are negligible. Contact angles are accessible experimentally via optical microscopy and play a fundamental role in any treatment of wettability.

To date, most theoretical work has focused on pure liquids, and surprisingly there have been few studies of the effects of additives in liquid droplets on surfaces despite their evident industrial importance. For many industrial applications, the wetting requires to be rapid and uniform. To achieve such spreading, wetting is modified by lowering the surface tension through addition of surface-active species such as surfactants, polymers, or alcohols.[2−5] The use of sugar-based surfactants is, for example, used to improve the wetting properties of pesticides. Without such additives, droplets of pesticide solution are likely to bounce off the hydrophobic surfaces of the leaves,[6] leading to a lack of absorption and loss of applied product.

Computer simulations have been shown to be a useful tool for the investigation of wetting phenomena. An early attempt to model a water droplet on a solid surface by Klein et al.,[7] who carried out simulations of 90 water molecules on the hydrophobic and hydrophilic surfaces formed by adsorbed monolayers of long-chained molecules with different end groups. Calculated contact angles even for these very small droplets were similar to the macroscopic values. Rapid developments in computer technology have led to the possibility of simulating larger droplets. De Coninck et al.[8,9] have simulated droplets consisting of more than 10^4 atoms, with all atom−atom and atom−surface interactions described by Lennard-Jones potentials. Dynamic contact angles and flow fields were determined from the simulations and their results support the molecular-kinetic model[10] of wetting for this system.

De Ruijter et al.[11] have studied a mixture of long-chain and short-chain molecules. The short-chain molecules partially wetted the solid surface while longer chains led to complete wetting. The segregation of the two types of molecules to the solid surface and the influence of the solid/liquid interaction were studied. This segregation was dominated by the long-chain molecules, which formed the major component of the precursor film which spreads out quickly in front of the main body of the droplet.

In this paper, we present molecular dynamics simulations at the atomistic level of droplets of water on a model graphite surface, taking proper account of the long-range electrostatic forces. A cluster of pure water is placed on top of a graphite surface and forms a sessile drop with a given contact angle. We relate the atomistic behavior to relevant macroscopic parameters such as the contact angle and examine the dramatic effect of addition of ethanol molecules to the droplet.

Methods

The potentials and charges to describe the water molecules were taken, as in our previous work on the behavior of water at clay surfaces,[12] from the TIP-3P model

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of Jorgensen et al.[13] This model reproduces the structural and dynamic properties of water relatively well despite its simplicity. The water molecule is treated as rigid. The OH bond length and HOH angle were set to 0.98 Å and 109.5°, respectively, and were fixed with the SHAKE technique.[14]

The intramolecular and intermolecular potentials for the ethanol molecules were taken from the all-atom OPLS model,[15] which is designed for simulation of organic liquids and includes parameters for torsional and nonbonded interaction as well as angle bending and bond stretching. Point charges, located at the nuclei, were assigned to the ethanol molecules using the charge equilibration method[16] as implemented in the molecular graphics program *Cerius^2*.[17]

The solid graphite surface consisted of one layer of hexagonally arranged carbon atoms at a density of 0.384 $Å^{-2}$, separated by 1.53 Å. This surface layer was kept fixed during all simulations.

All short-range intermolecular interactions are assumed to be of the Lennard-Jones form:

$$U_{ij}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (2)$$

where σ is the collision diameter, ϵ the well depth, and r the distance between the atoms i and j. A cutoff of 9 Å was applied to the short-range intermolecular potentials. Surface/water and surface/ethanol potential parameters were determined using the Lorentz−Berthelot geometric mixing rules[18] and values of σ and ϵ for the surface carbon atoms from the OPLS force field. The long-range Coulombic interactions are handled with the Ewald summation.[19] Direct summation with a large cutoff distance (40 Å) was also employed to evaluate the significance of the choice of method for calculating the Coulombic interactions. Differences are negligible for the structural properties of the system studied in this paper

The program DL_POLY[20] was used for the molecular dynamics simulations, which were performed at constant volume and temperature (NVT). The temperature was set to 298 K and kept constant using the Berendsen[21] thermostat, with a temperature relaxation time of 1.0 ps. A three-step scheme was set up for the simulation. First, the liquid phase was set up by randomly distributing 900 water molecules in the simulation cell (100 Å × 100 Å × 100 Å) at the appropriate density (1 g cm^{-3}). All molecular positions and orientations were set at random with no atomic overlap. An equilibration run of 50 ps was then carried out on these molecules with a time step of 1 fs, at the end of which a single spherical droplet had been formed. The solid graphite surface was then introduced into the simulation cell, and the water droplet placed on top of the surface (Figure 1a). A second equilibration period, again of 50 ps and with the same time step, was carried out with a weak surface/liquid interaction. Finally, the interaction between the water and the graphite surface was increased to its final value and the drop began to spread spontaneously. Production runs all used a time step of 1 fs and the configuration of the molecules was monitored as a function of time. Typical lengths of production stage runs were 400 ps, although some runs were as long as 1000 ps to check that the system had reached equilibrium and that no further spreading occurred. In some runs, too, the initial configuration of the production runs was not the droplet as described above, but a uniform layer of molecules at the surface. The final results were independent of this choice of initial configuration. A positive slope of the calculated mean square displacement of the water molecules indicates the system is in a liquid state, which is also confirmed by rotational correlation times calculated as in ref 12. Where appropriate, ethanol molecules were introduced into the droplets as described in the next section.

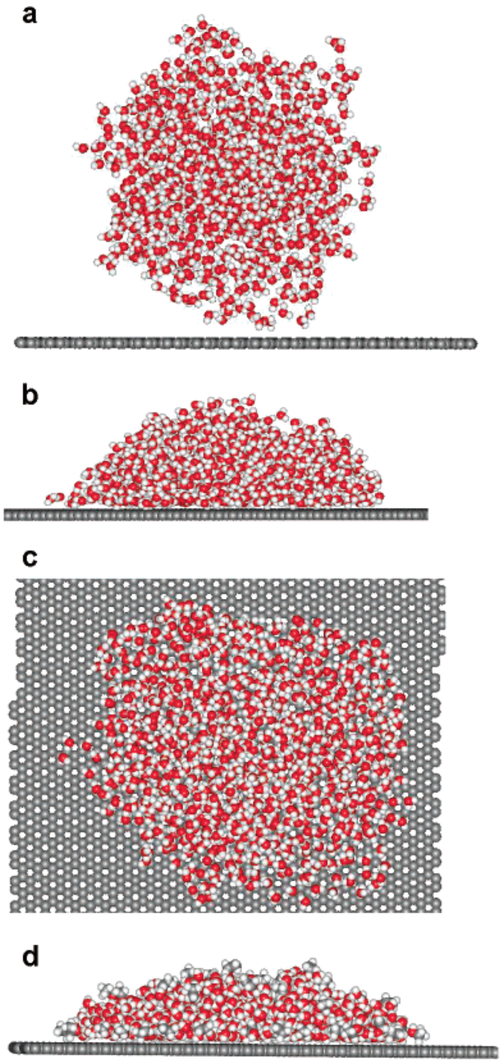

Figure 1. Representative snapshots from the simulation of pure water and water/ethanol mixtures on the graphite surface. (a) is a snapshot of the starting configuration, $t = 0$, for a water droplet and (b) and (c) are a side view and a top view, respectively, of the configuration after $t = 400$ ps. (d) is a 30 wt % water/ethanol blend at $t = 400$ ps. The oxygen, hydrogen, and carbon atoms are colored red, white, and gray, respectively.

Results

We show in Figure 1 snapshot views from the side and the top of a typical droplet of pure water in contact with

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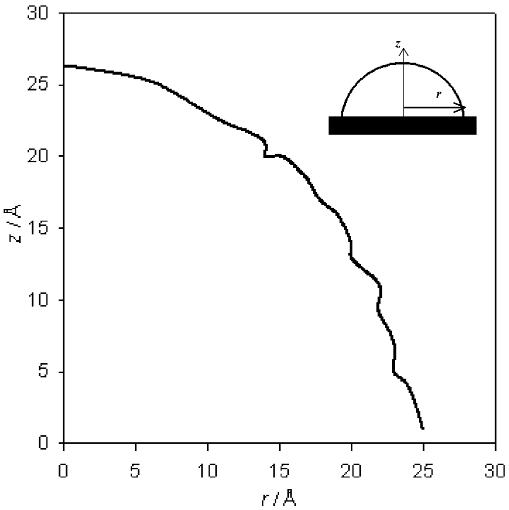

Figure 2. Time-averaged liquid/vapor boundary profile for a water droplet on a graphite surface. The radius, *r*, refers to the distance to the symmetry axis of the drop perpendicular from the surface. *z* is the distance above the surface.

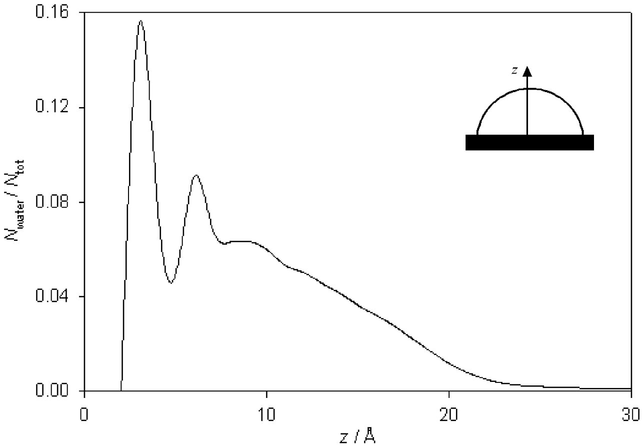

Figure 3. Fraction of the total number of water molecules, N_{water}/N_{tot}, at distance *z* above the surface. N_{water} is the number of water molecules in a 1 Å thick slice at distance *z* from the solid surface. N_{tot} refers to the total number of water molecules in the droplet.

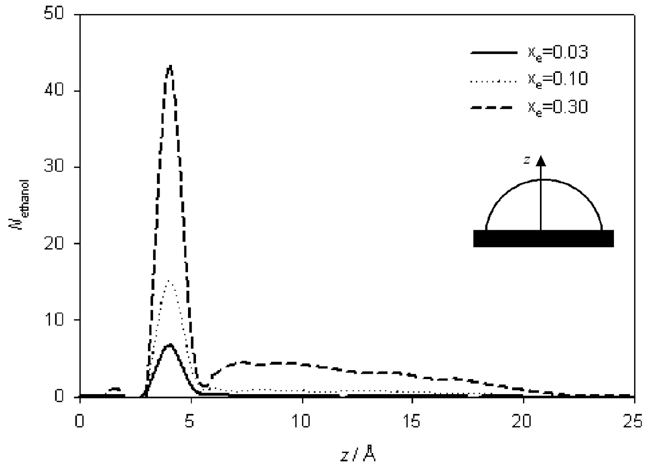

Figure 4. The number of ethanol molecules $N_{ethanol}$ present at a distance *z* above the surface for water/ethanol blends on graphite is plotted, as described in the text and x_e is the weight fraction of ethanol in the solution.

the graphite surface before and after spreading was complete. This is an instantaneous picture and the drop is not quite spherically symmetric. A time-averaged profile for the liquid/vapor boundary is given in Figure 2. This shows the droplet is much closer to spherical symmetry, compared to the instantaneous picture, where the atomic positions are time-averaged over 100 ps.

To determine properties such as densities and contact angles, we began the averaging of the positions of the atoms in the droplet only when it had stopped spreading, that is, when the distance of the center of mass of the droplet above the surface remained constant. In the following analyses, the radius of the droplet is obtained from the average distance from the symmetry axis perpendicular to the solid surface. The number of molecules as a function of height above the surface was first examined by locating the center of mass of each molecule. The droplet was divided into thin slices of width 1 Å parallel to the surface. In simulations on bulk water, all such slices have uniform density. To check our choice of slice width, thinner slices were also used and the results were identical. In Figure 3, we plot the number fraction of water molecules as a function of the distance above the surface *z*. In agreement with previous simulations of water and graphite,[22] there are two distinct peaks indicating some ordering of the liquid close to the surface. The first layer of water molecules is located a distance of 3 Å from the surface. Further out, ≈8 Å, from the surface the density increases to 0.8 g cm^{-3}, which is slightly lower than that of bulk liquid water (0.98 g/cm^3).

Occasionally, spontaneous evaporation from the droplet into the vacuum takes place. However, very few water molecules escape from the drop and the evaporated molecules eventually return to the main body of the droplet, and the volume of the cluster remains effectively constant.

To study the spreading of a blend of water and ethanol on the surface, the simulations were repeated placing a droplet of uniform density containing 3, 10, or 30 wt-% (corresponding to molar fractions 0.01, 0.03, and 0.13, respectively) ethanol on the surface. A droplet of pure ethanol wets the hydrophobic surface completely,[23] and the spreading of droplets of each of the three mixtures is greater than that of droplets of pure water containing the same number of molecules as shown in Figure 1d.

A short time after the start of the simulations of the blends, the ethanol molecules segregate toward the solid surface. Consequently, as displayed in Figure 4, which plots the number of ethanol molecules in 1 Å thick slices at a given height above the surface, there is a large density gradient close to the surface. For the lowest concentration of ethanol studied, the majority of the ethanol molecules are located at the solid surface and the remainder solvated in the bulk of the droplet. Although the number of ethanol molecules at the graphite surface increases as the overall concentration of ethanol increases, the *fraction* of the total number of ethanol molecules close to the surface decreases markedly and the number of solvated molecules in the bulk increases.

To investigate this segregation further, density profiles were calculated up to 8 Å above the surface. The system was divided into 1 Å thick slices perpendicular to the surface. We show in Figure 5 two number density profiles parallel to the surface for the droplet with the highest concentration of ethanol. In Figure 5, the ethanol densities have all been scaled by a factor of 10. The density is plotted as a function of distance from the symmetry axis of the

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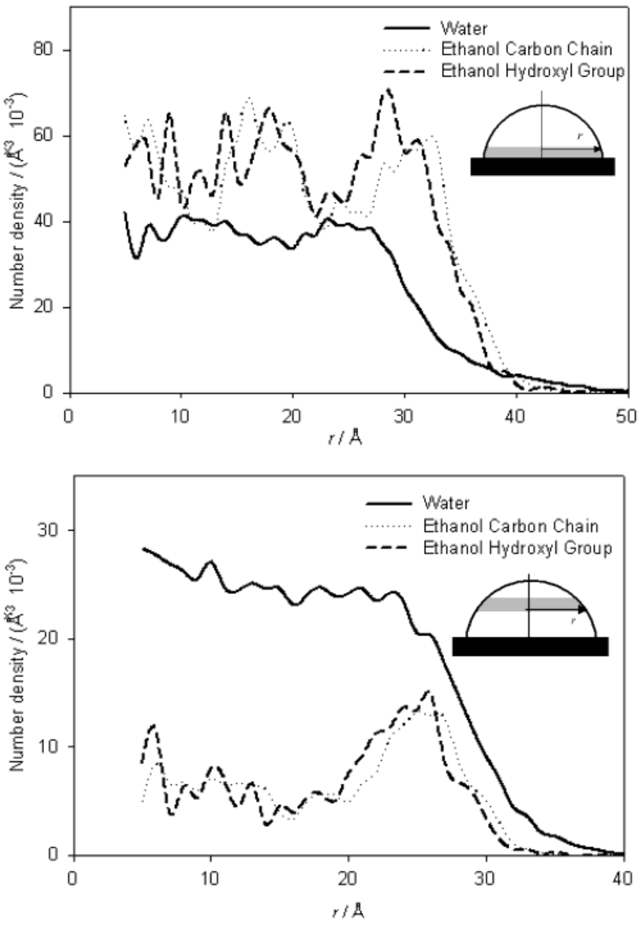

Figure 5. Number density profile for water (solid line), the carbon chain, and the hydroxyl group in the ethanol (dotted and dashed line, respectively) as a function of distance from the symmetry of the droplet (parallel to the surface). The top figure (a) is the density profile averaged over a distance range 0−8 Å above the surface. (b) is the profile for the bulk of the droplet averaged over 10−15 Å (shaded part of the inset) above the surface. For clarity, the ethanol atom densities have been scaled by a factor of 10.

time-averaged droplet; the top and bottom frames are for 0−8 Å and 8−13 Å above the surface, respectively. The shaded regions of the droplet in the inset in Figure 5 show which part of the droplet is considered. Figures 4 and 5a show the ethanol is distributed reasonably evenly in a monolayer above the solid surface. Following ref 24, we define the main body of the droplet as the region where the water density exceeds half the bulk density. It is clear from Figure 5a that the ethanol monolayer extends laterally well beyond the main body of the droplet by as much as 10 Å. Moving further up (≈10 Å) from the solid surface, (Figure 5b), the ethanol molecules are organized quite differently. First, a larger fraction of the ethanol molecules at this height from the surface is located preferentially at the liquid/vapor interface: the interface is identified as the region where the density falls from 90% to 10% of the bulk value of the particular droplet considered. It also shows that in the outer shell of the droplet (the liquid/vapor interface), the separation of the carbon chain and hydroxyl group peaks indicates that molecules orient themselves with the hydrophobic tail pointing out from the droplet and the hydroxyl group pointing toward the interior of the drop. There is no preferred orientation of the ethanol molecules in the center of the drop.

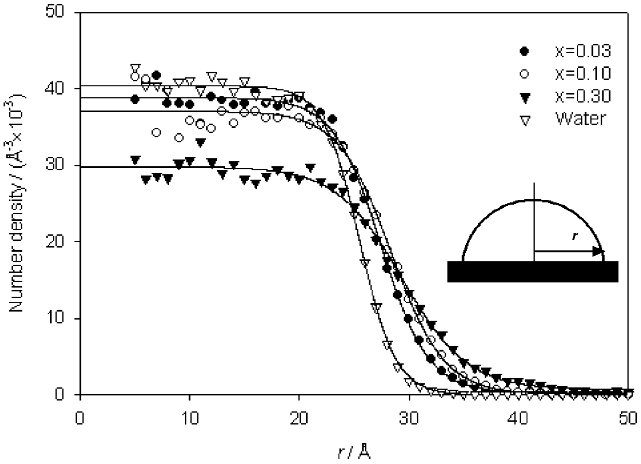

Figure 6. Number density profile for all molecules at the base of the droplets, time-averaged over 0−8 Å from the surface. The radius refers to the distance from the symmetry axis of the drop perpendicular from the surface. x_e is the weight fraction of ethanol in the solution. The solid lines are fits to eq 3. The positions of the hydroxyl and alkyl groups are defined by the positions of the oxygen atom and the center of mass of the two carbon atoms, respectively.

A convenient way of calculating the wetting area is via the total density profile for the first layer of the adsorbed molecules (Figure 6). The density profile parallel to the surface for the first 8 Å above the surface is plotted for each droplet. Following ref 24, the resulting profiles $\rho(r)$ are fitted to a sigmoidal function:

$$\rho(r) = \frac{1}{2}(\rho^l + \rho^v) - \frac{1}{2}(\rho^l - \rho^v)\tanh\left(\frac{2(r - r_e)}{d}\right) \quad (3)$$

ρ^l and ρ^v are liquid and vapor density, respectively, r_e is a constant defining the position of the Gibbs dividing surface, and d is the width of the liquid/vapor interface. The sigmoidal function fits the profiles of all the droplets very well. The resulting values of ρ^l and ρ^v are physically reasonable with $\rho^v \approx 0$, profiles fit very well to this function. For the pure water droplet, the fitted value of d, that is, the width of the liquid/vapor interface near the solid surface is 6.7 ± 0.2 Å. The experimental value[25] of the water/vapor interface width (in the absence of a solid surface) is 3.3 Å with a corresponding theoretical value for an isolated TIP-3P water droplet of 3.0 Å. The interface widens with increasing ethanol concentration. Fitted values of d from the fits are 8.7 ± 0.3 Å, 9.7 ± 0.6 Å, and 12.0 ± 0.6 Å for 3, 10, and 30 wt-% ethanol, respectively. Increasing interface thickness is expected when surface-active molecules are present at the surface.

The base radius of the drop can be calculated by assuming, as above and in ref 11, that the liquid/vapor interface is located where the density falls to half its bulk value. The same approach can be used for the slice closest to the surface to extract the base radius of the droplet, R_s. The average surface area occupied per molecule, S, is then given by $\pi R^2_s/N_s$, where R_s is the base radius of the droplet and N_s the number of ethanol molecules at the surface. Values of S for water/ethanol blends are collected together in Table 1. S_{ethanol} decreases markedly as the concentration of ethanol increases and the ethanol molecules pack more closely together at the surface. Similar results are obtained if we use the fitted values of r_e (eq 3) instead of R_s.

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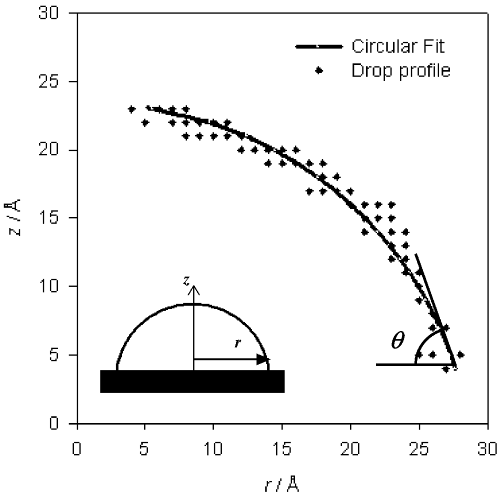

Figure 7. Simulated liquid/vapor interface profile. The profile is fitted to a circle to calculate the contact angle, θ, where liquid/vapor interface and solid meet.

Table 1. Values of the Molecular Coverage of Ethanol, S_{ethanol}, on the Graphite Surface, and the Base Radius of the Droplets, R_s

ethanol concentration/wt-%	0	0.03	0.10	0.30
S_{ethanol}/Å^2	0	250.6	117.1	48.8
R_s/Å	25	27	28	30

To link the simulations to macroscopic parameters, the contact angles have been estimated. A common approach[7] to extract the contact angle from nanoscopic droplets is to fit the liquid/vapor interface to a circle. As we have seen in Figure 2, the time average is nearly spherical, and as before the liquid-vapor interface is defined as where the density falls to less than half that of the bulk; this avoids the need for fitting a large number of density functions. The total boundary profile is then fitted to a circle and the contact angle calculated where solid and fitted circle meet, as shown in Figure 7. Because of the presence of the precursor film and large fluctuations in density, data points less than 8 Å above the solid surface are discarded. For a pure water droplet,[26] the estimated contact angle is 83 ± 5°. When ethanol molecules are added to the droplet, the contact angle decreases to 70 ± 5°, 63 ± 5°, and 30 ± 5° for 3, 10, and 30 wt-%, respectively, consistent with the increased wetting of the blends relative to pure water. Experimentally, contact angles of water/ethanol mixtures have been determined from a wetting study of hydrophobic powder beds,[23] finding drastically enhanced wetting properties with increasing ethanol concentration. Contact angles for one of the hydrophobic surfaces studied in this paper were estimated to 90° and 45° for pure water and 0.15 wt % ethanol solution, respectively, which is consistent with the values and trends seen in our simulations.

The most crucial part of any molecular simulation study is the choice of bonding and nonbonding potentials. Small changes in the interacting forces might affect the final results significantly. The sensitivity of the potentials used in these simulations have been tested by studying the change in wetting behavior of the water droplet when the liquid/surface potential is altered, that is, when the surface is made more hydrophobic or hydrophilic. The Lennard-Jones liquid/surface potential is altered by changing the well depth, $\epsilon_{\text{C-OW}}$, in eq 2. The collision diameter is kept constant. The resulting variation of the contact angle with perturbation of the liquid/surface interaction is shown in Figure 8. Small changes (~1%) of the original value of the well depth, $\epsilon_{\text{C-OW}} = 0.12$ kcal/mol, do not change the contact angle significantly. The variations are smaller than the uncertainty in the estimation of the contact angle. Wetting properties do change, as expected, when the well depth is increased or decreased by more than 0.01 kcal/mol (~10%). We have varied the strength of the interaction, $\epsilon_{\text{C-OW}}$, from 0.02 to 0.20 kcal/mol. Within this interval, both non- and complete wetting was seen. The droplet loses contact with the surface ($\theta > 180°$) when $\epsilon = 0.02$ kcal/mol, while the water forms a monolayer, $\theta = 0°$, on the surface when $\epsilon > 0.17$ kcal/mol. Contact angles as high as 160° were obtained, and it is interesting to note in this context that contact angles of this magnitude have been observed for water at a rough, highly hydrophobic surface.[27]

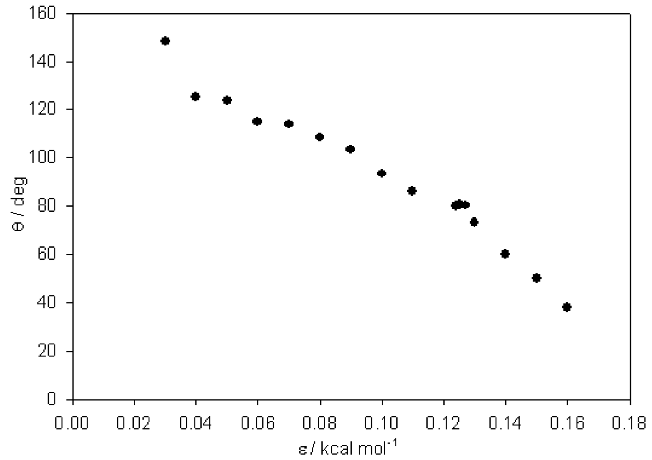

Figure 8. Contact angle of a water droplet, θ, vs the interaction Lennard-Jones parameter, ϵ (kcal/mol), as defined in eq 2.

Conclusions

Molecular dynamics simulations for droplets on a graphite surface have been carried out. In contrast to previous work, a fully atomistic approach is used to describe the system. Long-range Coulombic interactions are also taken into account. We have observed the formation of sessile droplets on top of the solid surface. The simulated contact angles indicate that the system is in the partial wetting regime and the value agrees well with the macroscopic measurements. On addition of ethanol, the wetting properties of the droplet increase and the contact angles decrease. The ethanol molecules are concentrated close to the hydrophobic solid surface and, at the top of the droplet, at the water/vapor interface with the hydroxyl group pointing toward the center of the droplet and the alkyl chain pointing toward the vacuum. When the characteristics of the surface are changed from hydrophobic to hydrophilic, a wide range of contact angles were seen. We are thus sufficiently encouraged to extend these studies to tackle more complex wetting problems and examine droplet formation in more detail.

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