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An all-atom simulation study of the ordering of liquid squalane near a solid surface

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ABSTRACT

An all-atom molecular dynamics study using the OPLS force field has been carried out to obtain new insights in to the orientation and ordering of liquid squalane near a solid surface. As observed in previous experiments, the squalane molecules closest to a SiO_2 substrate are found to be tightly bound with their molecular axis preferentially parallel to the interface. Unlike linear alkanes, the squalane molecules are also found to lie preferentially parallel to the liquid/vapor interface. The simulation results predict that the molecular plane orientation of the squalane molecules changes from mainly parallel to perpendicular to the substrate in going further away from the substrate.

1. Introduction

The structural, dynamical, and rheological properties of liquids near solid surfaces have been the main focus of many theoretical and experimental studies due to the important role liquid/solid interfaces play in a wide range of practical applications [1–4]. Liquid/vapor interfaces are also equally important. In general, the consensus from the literature is that order parameter of liquids near interfaces deviate considerably from their bulk values. An atomic or molecular level understanding of such interfaces is found to be crucial for predicting the structural and thermodynamic properties of liquids near surfaces and remains a major focus of ongoing research [2,5,6].

Understanding the effect of interfaces is particularly crucial for nanoscale materials, such as thin polymeric films, since their behavior is dominated by surface effects. The main focus of many of the investigations on interfaces for the last three decades has been on the interfacial properties of alkanes at the molecular level [1]. This is understandable in view of their simple structure, their use as prototypes for more complex polymers, and they are the building blocks of many biologically important molecules. The emergence of surface and interface sensitive experimental techniques have now pushed the focus to the study of the structure and thermodynamic properties of multi-branched alkanes at interfaces [3,7,8]. Early on, there was some confusion about the degree of disruption of molecular order (layering) due to the effect of side chains in multi-branched alkanes that are near solid surfaces. Molecular dynamics (MD) simulations predicted that branched alkanes confined between two substrates form layered structures, like linear alkane systems but with less degree of ordering [9,10]. However, early surface force apparatus (SFA) measurements indicated that side chain branching can completely disrupt molecular layering [11,12], thereby contradicting the simulation results. This confusion was straightened out after a series of recent experiments using a variety of experimental techniques, including SFA, were conducted and confirmed that confined branched alkanes indeed form layered structures near solid surfaces [3,7,8].

Our present work was motivated by one of the recent experimental results on squalane near a solid surface [7]. Squalane $C_{30}H_{62}$, is a highly branched alkane molecule consisting of 24 backbone carbon atoms along with six symmetrically placed methyl groups. The experimental results show that the first two layers closest to the substrate are tightly bound whereas, unlike in the linear alkane systems, layers further away from the substrate showed a broadening in the solvation force peaks resulting from increased interlayer spacing [7]. In the absence of any direct experimental observation of the chain orientations, they ascribed this broadening in the solvation force peaks to interdigitation of the branched methyl groups between the solvation layers. Their conclusion was based on an earlier united-atom MD simulation study that clearly showed a high degree of interlayer interdigitation in a confined squalane film compared to a confined *n*-hexadecane film [9]. It is important to note that, in united-atom models the hydrogen atoms of the squalane molecules are not explicitly considered. The major question is whether interdigitation is the main mechanism that is fully responsible for the broadening in the solvation force peaks. The main focus of the present study is thus to identify the mechanisms that are primarily responsible for this observed behavior.

Accurate modeling of the adsorption behavior of squalane on a surface may require explicit inclusion of all the atoms in the simulation, as done in the present study. In particular, the explicit interaction of hydrogen atoms with a surface is expected to be the main factor controlling the adsorption process. Such atomistic

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details are also expected to be significant if we are to reliably quantify the degree and manner of interdigitation between chains on different layers in a confined squalane film. Since all the atoms are treated explicitly in all-atom models, the requirements in terms of computer time is significantly larger than for united-atom models. Despite the computational cost, the current study has shown that a detailed description of interatomic potentials and dynamics is essential to capture the effect of hydrogen on the interfacial and bulk properties of squalane. This level of details has only been possible recently due to the development of parallel molecular dynamics algorithms and the availability of increased computational power.

In this study, atomistic MD simulations using the optimized parameter for liquid simulation-all atom (OPLS-AA) force field [13] have been utilized to elucidate the atomic basis for the structure and orientation of liquid squalane on hydroxylated SiO_2 surfaces, both crystalline and amorphous. Attention is also given to the structure and orientation of the squalane molecules near the squalane liquid/vapor interface.

2. Molecular dynamics simulation details

We have performed MD simulations of the squalane/silica systems using the OPLS-AA potential which has been optimized for carbohydrates and has been recently used by us [14–16] to study the free surface properties of normal and branched alkanes. The OPLS-AA force field represents the total potential energy of the system as a sum of four types of potentials: nonbonded interactions, bond stretching, angle bending, and torsion potentials. Nonbonded interactions are evaluated for all intermolecular interactions and for intramolecular interactions between atoms separated by three or more bonds. The OPLS-AA force field parameter values used for the squalane system can be found in Ref. [13] and for the silica system in Ref. [17].

Simulated systems here consist of a squalane layer over a silica substrate with periodic boundary conditions in all directions. The box dimension in the *z*-direction, i.e., normal to the substrate, is large enough so that interaction between molecules across the vapor phase is negligible. In order to understand how the roughness of a substrate affects the structure and orientation of the squalane liquid near the interface, an atomically flat {0 0 1} α-quartz and an amorphous substrate (about 4 Å roughness) were used. The crystalline substrate (α-quartz) was formed by generating a slab of the desired size from experimentally determined lattice parameters [18]. The crystalline slab was created such that the appropriate crystallographic direction was aligned along the *z*-axis and an oxygen-rich plane was exposed on the top and bottom surfaces. All dangling bonds on oxygen and silicon atoms in the surface planes were then capped with –H or –OH atoms, respectively. The hydroxylated amorphous slab was generated by following a previously reported procedure [19,20]. The α-quartz and amorphous substrates have the same surface size of 54×51 Å^2 in contact with liquid squalane. The separation between the two silica surfaces is large (about 20 Å) and can therefore neglect the interactions between the two surfaces.

The effect of film thickness on the structure and orientation of squalane molecules near the liquid/solid and liquid/vapor interfaces was also studied by preparing two films of the same surface area as that of the substrate but with system sizes of 100 and 200 squalane molecules. The thickness of both films were much larger than the cutoff distance used in the simulations so that the long-range Coulombic interaction between a chain and its mirror image in all periodic directions was minimal.

The simulations were run in the NVT ensemble using the LAMMPS parallel molecular dynamics code [21]. Velocity-Verlet algorithm was used to integrate the particles equation of motion with a time step of 1 fs. In order to investigate the temperature dependence of the ordering and orientation of the squalane molecules near an interface, simulations were performed at four different temperatures (300, 350, 400, and 450 K) that are above the melting temperature (235 K) but below the boiling point (623 K) of squalane [3,22]. A Nose–Hoover thermostat with a damping time of 100 fs was used to maintain the system temperature. The van der Waals interactions for all the simulations were cut off at 12 Å. It is important to note that results from a larger cutoff of 16 Å, tested for the case of 300 K and 450 K, matched very well, within the error of the simulation, with results from the 12 Å cutoff. Therefore, in this study we present only the results from the 12 Å cutoff simulations. Coulombic interactions were calculated using the particle–particle/particle–mesh (PPPM) algorithm [23]. The smaller and bigger systems were first equilibrated for at least 8 ns and 18 ns, respectively, and then the atom positions were recorded every 5 ps for at least another 1 ns for further analysis.

3. Results and discussion

One of the fundamental parameters for characterizing an interface is the density profile which is accessible to experiments and can be also easily determined in simulations. Average mass density profiles have been determined for each system at different temperatures. Fig. 1 shows average density profiles for the two film thicknesses on α-quartz substrate at four temperature values. The density at a given value of $z, \rho(z)$, was calculated by partitioning the simulation cell into bins along the *z*-direction, i.e., perpendicular to the interface, and adding the masses of atoms in each bin per partitioned volume.

As expected, the solid/liquid interface is characterized by an oscillatory density profile whose amplitude shows a strong dependence on temperature [5,24]. The amplitude of the density

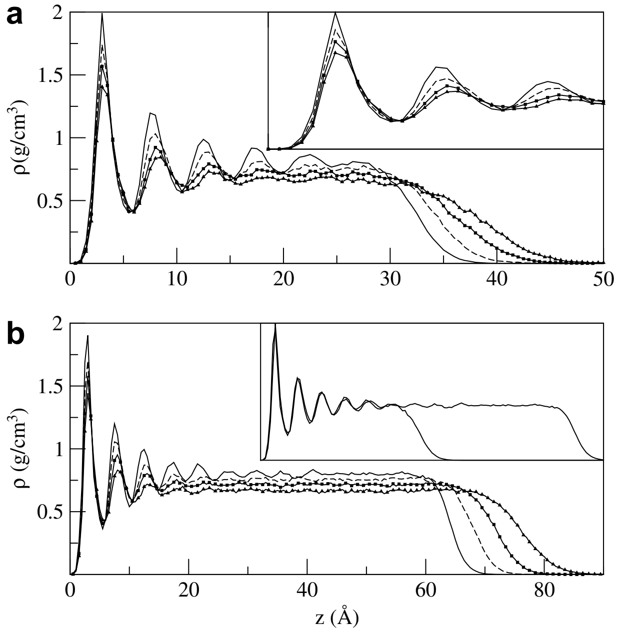

Fig. 1. Average mass density profiles of the squalane liquid as a function of distance from the α-quartz substrate for (a) the smaller film (100 squalane molecules) and (b) the bigger film (200 squalane molecules) at temperature of 300 K (solid lines), 350 K (broken lines), 400 K (squares), and 450 K (triangles). The inset in (a) is the magnification of the density profiles close to the substrate. The inset in (b) shows the density profiles of the smaller and bigger films at 300 K, for the sake of comparison.