INVESTIGATION OF INTERFACIAL PROPERTIES AT A-QUARTZ/ALKANE INTERFACES USING MOLECULAR DYNAMICS SIMULATIONS

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ABSTRACT

In this paper, molecular dynamics simulations were used to study density, orientation order parameter of liquid decane and tetracosane in the vicinity of (100) OH- and H- terminated silica (α-quartz) surfaces at various temperatures. Decane and tetracosane molecules were modeled using NERD united atom force field. Silica wall was modeled using Lopes et al. force field. Typical Hydrophobic and hydrophilic silica surfaces were generated by terminating the surface with hydrogen and hydroxyl. Adsorption of alkane molecules on both the solid surfaces was observed to be more remarkable at lower temperature. Orientation of the molecules was studied by examining the orientation order parameter. It was found that molecules in the first adsorption layer close to the hydrophilic surface are arranged more parallel to the interface than the molecules close to the hydrophobic surface. At a particular temperature decane and tetracosane molecules have similar kind of alignment near hydrophilic/hydrophobic quartz surfaces.

Index Terms: α-quartz, alkane, interface, ordering parameter, density.

1. INTRODUCTION

Examination of liquids adjacent to solid surfaces play an important role in lubrication, wetting, chemical and biological processes, heterogeneous catalysis, corrosion, catalysis adhesion, and surface modification in a variety of industrial processes. For a wide range of above applications, molecular level understanding of interfaces is important. Molecules show a unique behavior close to interfaces which is different from that of bulk region. In the vicinity of solid/liquid interfaces migration of liquid molecules is lower than in the bulk liquid region and viscosity is higher than the bulk liquid region [1]. This is related to the difference in the interaction between the molecules in the bulk liquid and in the interface region.
Silica is an abundantly available compound in the form of α-quartz. Because of the importance in geology, nanotribology, biomineratization, biomimetic filed and molecular engineering, silica interfaces were extensively studied by many researchers [2-15] at a molecular level. Liquids of hydrocarbon chain molecules have many industrial applications, and hydrocarbon chains are major building blocks for long polymers. Interfaces of polymer coating on solid surfaces have many applications such as structural adhesives used in aerospace, paints, MEMS, polymers used in microelectronics and laser printers. For the proper function of above devices interfaces should be carefully designed. Molecular understanding of transport and structure characteristics at solid/liquid interfaces of the microstructures built on a silicon wafer have a significant impact on the success or failure of various processes such as chemical coating and cleaning. One of the important things to examine is how the liquid polymer molecules are arranged in the presence of silica wall. The molecular-scale structure of the system will influence the properties of the nanoscale system. So their knowledge is important to realize optimal thermophysical and mechanical properties.

Few researchers investigated liquid interfaces with silica surfaces using experiments [3, 11]. But it is still difficult to understand the interfacial structure at the molecular level. Therefore, computer simulations are also performed to study the molecular-scale structure at solid/liquid interfaces. Computersimulations also provide better understanding of the experimental result. To analyze the molecular-scale structure and transport phenomena, molecular dynamics (MD) simulation is the best suitable method. Number of studies have been reported for polymers with reliable inter- and intramolecular potential models. NERD force field is one of them, which is used by many researchers to simulate coexistence properties of n-alkanes [16-17] and heat conduction [18]. Recently, quartz-water system was studied by many researchers with different force field for silica [3, 4, 8]. Skelton et al. [8] reported that ClayFF force field accurately describes the structure of water at the quartz interface. Wright et al. [11] examined the adsorption strength of amino-acid analogues on different surfaces of quartz. Lopes et al. [3] optimized the empirical CHARMM force field parameters for silica from abinitio calculations. In the force field of Lopes et al. [3] parameters for bulk and surface atoms are given in a different manner. This allows flexible slab surface simulation. Lopes et al. force filed [3] is compatible with NERD force field to build the system of α-quartz solid and alkane liquid. In the present work, α-quartz was modeled using Lopes et al. force field [3].

The α-quartz solid wall has a trigonal crystal structure. Among the all possible reconstructed silicocrystallographic surfaces, only few are found to be more stable. Each crystallographic faces have different structural features. Depending upon the type of termination unit, different kind of surfaces was generated. Knowledge of how the liquid molecules are interacted with the quartz surface atoms will help to understand the structural properties of liquids near solid wall. It is also important to know how far the fluctuations caused by the solid wall extends into the bulk liquid from the solid wall, which might be influenced by the topology and termination of the crystallographic surface. Structural properties of solid substrate, such like atomic scaleroughness and distribution of partially charged groups on the surface, influence the hydrophobicity and hydrophobicity nature of the substrate [6]. In the present study we mainly focused on structure of liquid alkane in the vicinity of OH- and H- terminated (100) α-quartz surface. To investigate the structural characteristics of liquid decane and tetracosane in the vicinity of (100) α-quartz surface, we studied average density and orientation order parameter along the axis perpendicular to the solid surface z-axis. The simulations were performed for three temperatures and its influences were examined.
II. COMPUTATIONAL DETAILS

A. Molecular model

Mainly three kinds of models have been utilized to describe an alkane molecule for molecular dynamic simulations, which include the all atom (AA) model [19], the united atom (UA) model [20] and the anisotropic united atom (AUA) model [21]. In the UA model, each of CH$_2$ and CH$_3$ groups is represented by a pseudoatom with a spherical potential surface, which is connected to other pseudoatoms to represent linear chain molecules. The AUA is a sort of UA, although in the AUA model, the force center is moved away from the carbon for better accounting of interactions. The AA models reproduce the molecular structure including hydrogen atoms and flexibility of molecules related to them, although the computational time is significantly longer than the UA models. Mainly for computational reasons, most of the researchers used UA in studies of alkane properties. In the present work, we used a UA model to describe alkane molecules. From now on, we refer to the united pseudoatoms as atoms. The NERD forcefield [16] was used to define intra- and intermolecular interactions. In this force field, total potential energy of the system is written as the sum of nonbonded interactions, bond bending, bond stretching and torsion potential. In the NERD force field, interaction between two atoms which are located more than three atoms apart on the same molecule and atoms located on the different molecules are given by the Lennard-Jones (LJ) 12-6 potential.

\[
U^{12}(r_{ij}) = 4\varepsilon_{ij}\left[\frac{\sigma_{ij}}{r_{ij}}\right]^{12} - \left[\frac{\sigma_{ij}}{r_{ij}}\right]^{6}
\]

(1)

where $r_{ij}$ is the distance between atoms $i$ and $j$. The energy parameters for the methyl and methylene groups are $\varepsilon_{\text{CH}_3} = 1.4358 \times 10^{-21}$ J and $\varepsilon_{\text{CH}_2} = 6.3233 \times 10^{-21}$ J, respectively. The size parameter of CH$_3$ and CH$_2$ units are $\sigma_{\text{CH}_3} = 3.91$ Å and $\sigma_{\text{CH}_2} = 3.93$ Å respectively. Interactions between two different sites are described by the standard Lorentz-Berthelot combining rules.

\[
\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad \text{and} \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}
\]

(2)

The bond bending, bond stretching and torsion are the deformations defined by other interaction potential functions included within the chains. The bending takes place between any three neighbor atoms within a molecule and is modeled by the harmonic potential.
Fig.2 Number density distribution of α-quartz/decane system at 350K.

\[ U(\theta) = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \]  

(3)

where \( \theta \) is the bond angle. The constant \( k_\theta \) is \( 8.6291 \times 10^{-19} \) J/rad\(^2 \) and equilibrium angle \( \theta_0 \) is 114.0°.

The bond stretching potential is given as follows

\[ U(r_k) = \frac{k_r}{2} (r_k - b_{eq})^2 \]  

(4)

where \( k_r \) is \( 1.3323 \times 10^{-18} \) J/Å\(^2 \) and \( b_{eq} \) is 1.54Å. The torsion occurs between any four neighboring atoms in a molecule. The torsion potential that works between two atoms which are two atoms apart is defined by the following function.

\[ U(\phi) = V_0 + V_1 (1 + \cos \phi) + V_2 (1 - \cos 2\phi) + V_3 (1 + \cos 3\phi) \]  

(5)

where \( \phi \) is the dihedral angle, and \( V_0 = 0 \), \( V_1 = 4.9018 \times 10^{-21} \) J, \( V_2 = 9.4146 \times 10^{-22} \) J and \( V_3 = 1.0925 \times 10^{-20} \) J.

In the present work we modeled the α-quartz wall using the force field of Lopes et al. [3]. This is an optimized CHARMM potential for α-quartz. In this force field, total potential energy is comprised of bond stretching, bond bending, torsion, electrostatic and Lennard-Jones interaction. Silicon, oxygen and hydrogen are treated as interaction sites. For the potential parameters for the silica please refer to Lopes et al. [3].

B. Computational systems

To examine the structure of alkanes in the vicinity of α-quartz surfaces we have performed the molecular dynamics study. Fig.1 shows an example of the simulation system. System consists of a pair of α-quartz solid walls and a liquid alkane is sandwiched between solid walls. The α-quartz solid wall was created in such a way that 100 plane was perpendicular to the z-axis. The surface of the left wall was terminated by –OH (silanol) and the right wall by –H (silane). In this study, (100) crystal plane was used for the solid surface, and these surface was OH- or H-terminated, which gives hydrophilic and hydrophobic characteristics, respectively. There are generally two types of silanol (–OH) termination; one is called germinal silanol which has two –OH groups bonded to a Si atom. The other one is called vicinal silanol which has one –OH group bonded to a Si atom and forms a hydrogen bond with the...
adjacent silanol groups. Periodic boundary conditions were applied in three spatial directions. A liquid film is enclosed in a box of lengths $L_x=29.4\,\text{Å}$, $L_y=31.8\,\text{Å}$ and $L_z=150\,\text{Å}$ for decane, $L_x=49.1\,\text{Å}$, $L_y=53.0\,\text{Å}$ and $L_z=150\,\text{Å}$ for tetracosane. The LJ and coulomb interactions were truncated with a cut-off radius ($r_c$) of 12.0 Å. The time integration of equations of motion is implemented by the reversible reference system propagator algorithm (r-RESPA) method [22] with multiple time scales (MTS). An integration time step of 1fs for the intermolecular motion and 0.2fs for the intramolecular motion were used in all simulations. Initially, liquid densities of alkanes at three temperatures examined were calculated from bulk liquid simulations. Next, initial configuration was created by placing the required number of molecules randomly in between the two α-quartz solid walls so as to have the saturated liquid pressure in the direction normal to the film. After that, the system temperature was gradually raised to the required temperature and then simulations were performed for NVT ensemble, i.e. with constant number of particles, volume and temperature for $5\times10^6$ intermolecular time steps. The simulation system was maintained at constant temperatures using Nose-Hoover thermostat. Equilibrium averages were collected for about 2 ns.

![Position-z](A) Density (kg/m$^3$)

0 50 100 150
0 500 1000 1500
T=350K
T=400K
T=450K

Fig. 3 Density distribution along z direction for (a) decane at T=350 K, 400K and 450K (b) tetracosane at T=400K, 450K and 500K
III. RESULTS AND DISCUSSION

All quantities were calculated after the system has reached equilibrium and interface has been formed. The density profile is one of the fundamental properties that represent the structure of the interface region. The local density was obtained by dividing the rectangular parallelepiped simulation box into slabs with a thickness of 0.1 Å in z direction. Time-averaged number density of atoms of decane molecules and α-quartz system at 350K is shown in Fig. 2. Where α-quartz density is shown in dashed line and decane density is shown solid line. Time-averaged density profiles of decane are characterized by oscillation in the vicinity of α-quartz substrate. The amplitude of peaks is related to the order of molecules at the interface. In adsorption layer, liquid molecules are adsorbed to solid a surface, which is described by the first peak in the density profile. If we observe the regions closely near the interfaces, a very slight overlap exists between number densities of solid and liquid molecules. This implies that very small amount of decane molecules get into the voids on the solid walls. When compared with hydrophilic surface, larger number of molecules gets into the hydrophobic surface. From now on, density distributions and distributions of the orientation order parameter are presented only for the portions of the liquid to study the structure of liquid in the vicinity of α-quartz. Density profiles for decane at T=350K, 400K and 450K, and tetracosane at T=400K, 450K, and 500K are shown in Fig. 3. The density profiles exhibit a flat region of a well-equilibrated bulk liquid phase away from the surface of the α-quartz walls. The amplitude of oscillations decreases when moving away from the wall and disappears after some distance. As expected, Fig.3 shows that with an increase in temperature, liquid density decreases. At 350K height of the first peak of the density profile is higher near hydrophilic side than the hydrophobic side for decane. The heights of the first peaks of the density profile near hydrophilic/hydrophobic surfaces are same at 400K. The decay of oscillation occurs in a similar manner when we compare decane and tetracosane at the same temperature. For a particular alkane, location of the first peak is slightly moved away from the surface with an increase in temperature. Heights of the peaks in the density profile are dependent on the temperature. It is also observed that distance between neighboring peaks is marginally depends on temperature. As temperature goes higher, density fluctuations far away from the wall are not prominent.

The orientation order parameter can be used to quantify the effect of interface on the chain ordering. A convenient orientation order parameter is defined as follows [5]

\[ P(z) = \frac{1}{2} \left\{ 3 \cos^2 \theta - 1 \right\} \]  

(6)

where \( \theta \) is the angle between a vector connecting two carbon atoms which are two units apart in a molecule and interface normal. The average is taken over all vectors and time steps. The range of this parameter is [-0.5, 1]. A positive value indicates preferential alignment normal to the interface. Negative value indicates preferential alignment parallel to the interface. Zero indicates completely random arrangement of molecules. To calculate spatial distribution of the orientation order parameter, the simulation box was divided into slabs with a width of 1 Å in z direction. A vector connecting between two atoms is assigned to the slab where the midpoint between two atoms is located. Fig. 4 shows the average orientation order parameter in z direction. In Fig. 4 density profiles for decane and tetracosane are shown as dash dotted lines at 350K and 400K. Approximate minimum orientation order parameter is -0.4 in the adsorption layer near the OH-terminated side which indicates that molecules are almost parallel to the interface. Molecules are less parallel to the interface in the adsorption layer near the H-terminated surface. In the adsorption layer close to hydrophilic surface, orientation order parameter is positive. That means a small portion of molecules in the first adsorption layer intrude into the solid wall in perpendicular direction to the interface near the hydrophilic side. On the other hand the intruded parts of the molecules near the hydrophobic side are parallel to the interface. This might be because of the difference in topology the hydrophilic and hydrophobic α-quartz surfaces. As expected, the orientation order parameter shows zero in the bulk liquid region, which means molecules are
randomly oriented. The orientation ordering parameter is positive in between the layers adjacent to hydrophobic/hydrophilic surfaces which mean molecules are perpendicular to the interface. This is a sign of interlayer interdigitation[5].With an increase in temperature molecules are preferentially less parallel/perpendicular to the interface in each internal layer. Both decane and tetracosane show similar kind of ordering close to the hydrophobic and hydrophilic surfaces.

Fig.4 Orientation order parameter as a function of distance for (a) decane at T=350K, 400K and 450K (b) tetracosane at T=400K, 450K and 500K
IV. CONCLUSIONS

We have investigated the molecular structure of liquid decane and tetracosane at different temperatures in the vicinity of (100) α-quartz surfaces terminated by OH- and H- groups, which are hydrophilic and hydrophobic surfaces, respectively. Time-averaged mass density profiles and ordering parameter are analyzed at different temperatures. For all cases studied, averaged density profile along z-direction consists of oscillations near the solid wall. Amplitudes of the fluctuations of the time-averaged density profile are slightly depending on the temperature for decane and tetracosane. Molecular orientation is investigated by examining the orientation order parameter. In the adsorption layer close to the hydrophilic side molecule are more parallel to the interface than the molecules in adsorption layer near hydrophobic surface. Alkane molecules are oriented randomly in the bulk liquid region. Liquid molecular orientation is almost independent of the chain length of molecule in the vicinity of α-quartz surface.

REFERENCES


