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Computational study on the effect of alkyl chain length on alkane–water interfacial width

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ABSTRACT

The influence of alkyl chain length on the interfacial width of the *n*-alkane–water interface was examined with molecular dynamics simulations. We examined systems of *n*-hexane–water and *n*-nonane–water and also investigated the effect of different systems sizes. The electron density profiles of the systems were extracted from our simulations, along with corrections made for capillary waves, to estimate the X-ray reflectivity and the interfacial width. It was consistently found that increasing the alkyl chain length decreased the interfacial width in contrast to X-ray reflectivity experiments. Some of the potential reasons for this discrepancy are examined and discussed.

1. Introduction

It is important from both a technical and a theoretical point of view to gain detailed insight into the properties of interfaces [1], as they are ubiquitous in the environment, industry, and biology. Aqueous interfaces are known to exhibit properties that significantly distinguish them from bulk environments. The air–water interface is fairly well characterized, in which numerous studies have been carried out to better understand the neat air–water interface, along with how ions and different species are affected by them [2–8]. When another liquid comes in contact with water, it further affects the behavior of water molecules, ion specificity, and general reactivity [9,10]. Alkane–water interfaces are considered a prototypical system for studying the interaction of water with hydrophobic liquid surfaces [11], especially since the molecular structure of alkanes can be easily modified by varying chain length and their degree of branching. Of particular interest is the importance of alkane–water interfaces in the flooding of oil wells with steam, which is a common technique for secondary oil recovery [12].

One aspect of the alkane–water interface that may play a fundamental role in its ability to influence interfacial properties is the interfacial width. Previous X-ray reflectivity experiments have found that the interfacial width increases with *n*-alkane chain length [13–15]. However, recent work by us has found an opposite trend, that the longer the chain length, the smaller the interfacial width [16]. The molecular simulations results only investigated the separate water and alkane interfacial widths extracted from specific densities. In contrast, X-ray reflectivity experiment is related to electron density profiles [13–15]. Furthermore, due to the finite size of the simulation systems investigated previously, capillary wave broadening was not accounted for and may influence interfacial widths [17–21]. Electron densities can be extracted from simulation data, and a structure factor can be calculated based on them. This can be used to make direct comparisons with X-ray reflectivity data [22]. In this Letter, we calculate the X-ray reflectivity of the *n*-hexane/water and *n*-nonane/water interfaces and compare their differences with experiment.

2. Models and simulation details

Water was simulated using the rigid Dang-Chang water model [23,24], which has four sites, including a single Lennard–Jones (LJ) site at the oxygen atomic position. There are also partial positive charges at the hydrogen atomic positions, and both a negative partial charge and point polarizability located at an *m*-site, which is along the bisector of the oxygen-hydrogen bonds. Alkanes were simulated using a previously developed polarizable model [16]: the model included LJ, point charges, and point polarizabilties on all atomic sites. The model had similar parameters (with differing charges) for the methyl and methylene carbons and the same parameters for all hydrogen atoms. The charges were taken from the OPLS-AA [25] force field, and all intramolecular bonded interactions (harmonic bond bending, dihedral potentials, and bond stretching) were taken from the GAFF force field [26]. Each atom had an associated point polarizability taken from the work of Applequist [27].

MD simulations were carried out for the alkane–water interfacial systems in the NpT ensemble, with the temperature (298 K) and pressure (1 atm) controlled by the Berendsen thermostat and barostat, respectively [28]. A total of six systems were investigated, which included two different types of *n*-alkanes: *n*-hexane and *n*-nonane. The smallest of the *n*-hexane/water interfacial systems is

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denoted 1HEX and the smallest *n*-nonane/water system denoted 1NON, which both had 2000 water molecules and 200 *n*-alkane molecules. The approximate dimensions of these systems were 36 × 36 × 80 Å, with the 1NON system being somewhat longer in the *z*-dimension. Because the system was elongated in the *z*-dimension, two alkane–water interfaces formed bisecting the *z*-axis. Water occupied approximately 45 Å of the simulation box while alkane occupied the remaining. A second type of system had 400 *n*-alkane water molecules and the same number of water molecules (2000), which is denoted 2HEX and 2NON. This particular system was more elongated in the *z*-dimension with the water phase the same size and the alkane phase twice as long in the *z*-dimension, but with the same approximate *x* and *y* dimensions. Finally, a third set of systems were simulated with 8000 water molecules and 800 *n*-alkane molecules, denoted 4HEX and 4NON. These systems had the same *z*-dimension as the 1HEX and 1NON systems, but were replicated in the *x* and *y* dimensions, creating systems four times larger. As a result, the dimensions were twice as large in both the *x* and *y* dimensions. A total of 4 ns of production were carried out for each system, following extensive equilibration of at least 1 ns with a timestep of 1 fs. The alkane carbon-hydrogen bond lengths and the water geometries were kept rigid with the SHAKE and RATTLE algorithms [29]. A Lennard–Jones potential truncation of 12 Å was enforced with analytical tail corrections employed. Long-ranged electrostatics was handled with the particle mesh Ewald summation technique [30].

3. Results and discussion

Figure 1 shows the density profiles for the different alkane–water systems with zero representing the Gibbs dividing surface (GDS) of water. The GDS of the alkane phases are shifted to greater *z*-coordinate than the GDS of water, with the distance often being referred to as the intrinsic length. The experimental bulk densities for *n*-hexane and *n*-nonane are 0.654 and 0.718 g/cm^3 respectively [31], corresponding closely to the liquid densities away from the GDS. It can also be observed that the systems have very similar bulk densities despite the different system sizes, except the 2NON system has a slightly lower density than the 1NON and 4NON systems. This may be a systems size effect due to the interfacial width in the *z*-direction, but as can be observed it is rather small. There are density oscillations present near the interface for the alkane phases, as described in our previous work [16]. Of interest is how the different systems behave at the interface. While the 1HEX and 2HEX, along with the 1NON and 2NON systems have similar density oscillations at the interface, the 4HEX and 4NON systems behave quite differently, having much broader interfacial density profiles and smaller oscillations at the interface. They still have density oscillations in phase with those of the 1 and 2 sized systems, but they are much smaller. If we take a model of an intrinsic width, broadened by capillary waves, the interfacial width should become broader with a greater lateral boxlength [17–21] due to capillary waves, consistent with our results. This will be discussed in greater detailed later.

To be able to make comparisons with experimental X-ray reflectivity experiments, the electron density needs to be computed [22,32]. The total electron density was computed from the sum over the product of atomic number density $n^i(z)$ along the surface normal direction multiplied by the atomic number, Z_i of each atomic species i [22,32,33],

$$\rho_e(z) = \sum_{i=1}^{n} n^i(z) Z_i \tag{1}$$

The atomic density was calculated in a histogram with bins of 0.25 Å in length.

The electron density profiles computed across the alkane/water interface for the different systems investigated are shown in Figure 2. There are noticeable oscillations in the electron density profiles, just as in the specific density profiles, while the 4HEX and 4NON systems are more smeared out due to capillary waves. A simple model has been used for electron density to estimate the interfacial width of the alkane–water interface [34],

$$\langle \rho(z) \rangle = \frac{1}{2}(\rho_w + \rho_a) + \frac{1}{2}(\rho_w - \rho_a)\mathrm{erf}(z/\sigma\sqrt{2}), \tag{2}$$

where σ is the interfacial width, ρ_w and ρ_a are the electron densities of the water and alkane phases, respectively. To be able to estimate the X-ray reflectivity, the structure factor needs to be calculated by making the Fourier transform of the position dependent derivative of the electron density [22,33,35],

$$\Phi(q_z) = \frac{1}{\rho_w} \int_{-\infty}^{\infty} [\frac{d\rho_e(z)}{dz}] \exp(iq_z z) dz \tag{3}$$

where ρ_w is the bulk electron density of water. This can be used to estimate the X-ray reflectivity [34],

$$R(q_z) = R_F(q_z)|\Phi(q_z)|^2 \tag{4}$$

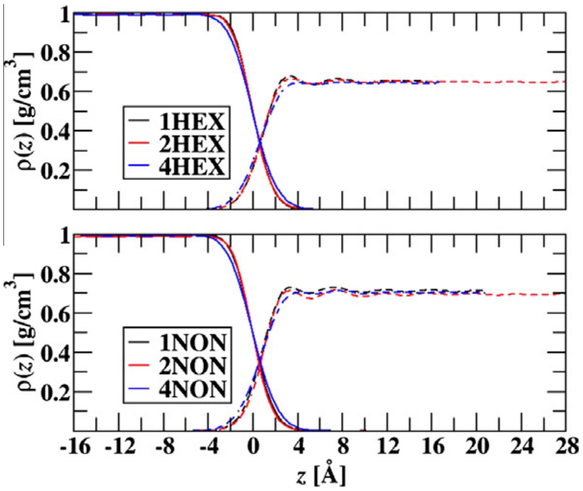

Figure 1. Density profiles for water (solid lines) and alkanes (dashed lines) for the systems described. The GDS for the water is represented as zero.

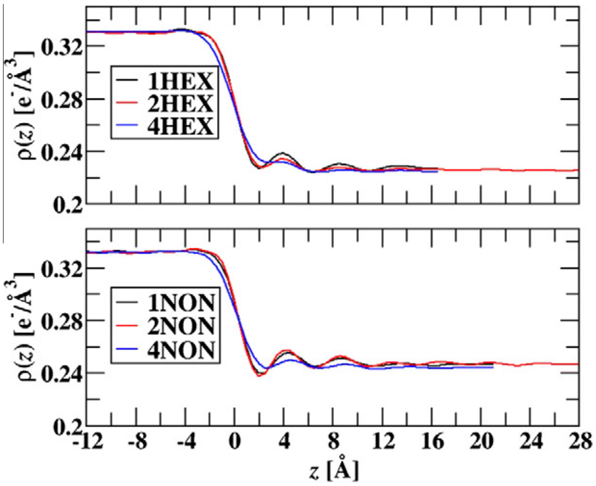

Figure 2. Electron density profiles for the *n*-alkane–water systems studied. The GDS for the water is represented as zero.