Computer simulation study of water/hydrocarbon interfaces: effects of hydrocarbon branching on interfacial properties

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Abstract. We review here the results of our molecular dynamics (MD) simulation study of water/hydrocarbon liquid/liquid interfaces. In order to examine the effects of chain length and branching on interfacial properties, we considered five different alkanes (n-pentane, 2-methyl pentane, 2,2,4-trimethyl pentane, 2-methyl heptane, and n-octane) as the hydrocarbon phase. We used a recently-proposed procedure to identify molecular surface sites and constructed intrinsic density profiles, in addition to the more familiar laboratory-frame profiles, in order to determine the effects of interface fluctuations on the structure and dynamics of the two phases. We found that interfacial properties of the aqueous phase are relatively insensitive to the molecular structure of the hydrocarbon, even though both branching and chain length have significant influence on the hydrocarbon interfacial properties. We found that translational and rotational mobilities of molecules of both phases are affected by the presence of the interface and that rotational relaxation of water molecules is significantly more anisotropic in the interfacial region than in the bulk.

1. Introduction
Liquid/liquid interfaces are ubiquitous in nature and are technologically important for processes such as surfactant self-assembly, oil recovery, and phase-transfer catalysis. Oil/water interfaces are among the most familiar examples of this type and represent a prototypical manifestation of hydrophobicity on an extended length scale. Computer simulation provides a great deal of insight into the molecular origin of the properties of liquid interfaces.[1] Several alkane/water liquid/liquid interfaces have been studied by molecular simulation, usually focusing on the interface of water with a particular alkane species[1,2][2,3]. Our work was undertaken in part in order to examine how the properties of the aqueous phase depend on the molecular structure of the adjacent hydrocarbon phase [4,5]. We were also interested [6]in investigating how the
molecular relaxation processes in the interfacial region differ from the bulk phases and, in the case of water, how these differences are related to the interfacial hydrogen bond connectivity and lifetimes [5]. Another focus of our study was to use water/alkane systems to gain insight into the properties of the capillary waves arising at interfaces of immiscible liquids [7].

In this article, some of our main findings about the properties of water/alkane interfaces are reviewed, with the emphasis on the properties of the aqueous phase. Details of our work on water/alkane interfaces have either been published [4,5] or submitted for publication [8] elsewhere. We start by describing the model systems in Sec. 2. Structural features of these systems are presented in Sec. 3 and the results on the mobility of the molecules in the interfacial region in Sec. 4. The article is concluded in Sec. 5.

2. Model and simulation details
In this work we used effective potentials of the Lennard-Jones + Coulomb type to represent interaction sites of the molecules. In the case of water we used the SPC/E model [9] and for the alkanes the united-atom OPLS potential [10] in which the methyl and methylene groups are represented as single carbon-centered sites. Molecular dynamics (MD) simulations of five water/alkane systems under ambient conditions were carried out as described in Refs. [4,5]. Information on the specific systems studied is summarized in Table I. One of the goals of our work was to determine how the properties of the interfaces are affected by the extent of hydrocarbon branching and the chain length. For this purpose, we have classified the alkanes studied into two series: The molecules in Series 1 (n-pentane, 2-methyl pentane (2MP), and 2,2,4-trimethylpentane (TMP)) have the same chain length and different amounts of branching. Molecules in Series 2 (n-octane, 2-methyl heptane (2MH) and TMP) have the same mass and different amounts of branching. Our MD data were analyzed to determine the structural features of these alkanewater interfaces and the mobilities of the molecules in the interfacial region. In the case of water, these studies included the properties of the hydrogen bond network in the interfacial region.[4,8]

Table 1. Simulation setup

| Alkane           | No. of mols | Series | $\langle \rho \rangle$ (g/cm$^3$) |
|------------------|-------------|--------|----------------------------------|
| n-pentane (P)    | 91          | 1      | 0.625                            |
| 2-methyl pentane (2MP) | 79          | 1      | 0.650                            |
| 2,2,4-trimethylpentane (TMP) | 64          | 1, 2   | 0.692                            |
| 2-methyl heptane (2MH)       | 64          | 2      | 0.698                            |
| n-octane (O)     | 64          | 2      | 0.702                            |

* The number of water molecules is fixed at 586. The temperature and pressure are maintained at 1 atm and 298 K.

3. Interfacial Structure
A simple way to characterize the interfacial structure is in terms density profiles of the molecules of the two phases in the 'laboratory' frame, i.e., the frame defined by the simulation cell. Figure 1 depicts these profiles, based on the locations of the water oxygen and alkane carbon sites, in the
case of the water/TMP system. As can be see from this figure, the laboratory density profiles, especially the one of water, exhibit very little structure. This is a consequence in part of the fact that the liquid surfaces are not perfectly flat, but deviate from planarity due to the presence of capillary waves [11]. The extent of broadening of the density profiles due to capillary waves can be gauged by identifying the interfacial molecules, i.e., molecules for which the nearest neighbour belongs to the other phase. The distribution, which is approximately Gaussian, along $z$ of these molecules is shown as dashed lines in figure 1.

![Figure 1](image1.png)

**Figure 1.** Density profiles for the water/TMP system. The density profile of molecules in the interfacial region is shown as dashed lines.

In order to determine the intrinsic structure from which these broadening effects have been removed, we follow the procedure developed by Pandit et al.[3] to locate the intrinsic interface. This procedure identifies the surface site relative to the location of the molecules of the other phase and uses Voronoi tessellation to determine the distance of molecules from the intrinsic surface location.

![Figure 2](image2.png)

**Figure 2.** Water density profiles for water/alkane Series 1 interfaces. Left: density profile in the laboratory frame; right: intrinsic profile relative to the hydrocarbon phase.

As figure 2 illustrates in the case of water in the water/Series 1 alkane systems, the intrinsic density profile of water relative to the hydrocarbon surface exhibits much more pronounced interfacial structure than the corresponding laboratory profile. Figure 2 also illustrates the weak dependence of the water interfacial structure on the extent of branching in the hydrocarbon phase. The intrinsic profile $\rho_{w-H}^I(z)$ resembles water structure next to a solid hydrophobic wall [12].
Figure 3 shows that the density profile of the hydrocarbon phase relative to water, \( \rho_{i}^{H-w}(z) \), exhibits more pronounced interfacial structure than the laboratory profile \( \rho_{j}(z) \). The profiles for different alkanes differ substantially from each other, as shown in Figure 3 for the Series 1 liquids. Increased branching at fixed chain length leads to less efficient packing, as evidenced by a broader first peak and a larger distance between first and second peaks of the corresponding \( \rho_{i}^{H-w}(z) \). These effects are less clear in the case of \( \rho_{j}(z) \), for which increased branching mainly leads to larger peak amplitudes.

As water molecules approach the interface, they cannot participate in as many hydrogen bonds as in the bulk liquid. Next to a flat hydrophobic surface, some of the O-H bonds are approximately normal to the interface, with the H pointing towards the other phase.[12] We have shown that this is also true for the intrinsic O-H orientations at the liquid water/alkane interfaces.[4] These results are not shown here, but we illustrate in figure 4 how the average number of hydrogen bonds varies with the distance from the interface.

As can be seen from figure 4, the extent of hydrogen bonding within the aqueous phase is essentially independent of the molecular structure within the hydrocarbon phase. There are, however, significant differences in the hydrogen bond profiles, \( N^{iH}_{w}(z) \) and \( N^{jH}_{w}(z) \) in the laboratory and intrinsic frames. In the intrinsic frame, the range of distances over which the average number of hydrogen bonds decreases from its bulk value is significantly shorter and reaches a larger value than in the laboratory frame. As in the case of density profiles, \( N^{iH}_{j}(z) \) resembles more closely the behaviour of water next to a flat hydrophobic interface than does \( N^{jH}_{w}(z) \).

**Figure 3.** Alkane density profiles for water/alkane Series 1 interfaces. Left: density profile in the laboratory frame; right: intrinsic profile relative to the water phase.
4. Dynamics in the interfacial region

We have investigated the interfacial mobilities of the molecules of the two phases and their residence times in different interfacial layers. For this purpose, we have used both the intrinsic and laboratory-frame density profiles to determine the locations of molecules relative to the interface. The procedure used to identify the three regions (interfacial, intermediate and bulk-like) is illustrated for the laboratory-frame density profile of water. In the case of the intrinsic profile, the interfacial and intermediate regions corresponded approximately to the same ranges of $z$-values \[5\]

We refer the readers to our paper on interfacial dynamics for the results on the distributions of residence times and survival probabilities of the molecules in the different regions \[5\].

Mean squared displacements for molecules in the plane of, $\langle (\Delta r_x(t))^2 \rangle$, and perpendicular to, $\langle (\Delta r_z(t))^2 \rangle$, the interface represent a simple measure of the translational mobility of molecules. In figure 6, these are shown for water in the water/TMP system in the laboratory frame. These results show that the translational mobility of water is enhanced in the interfacial region, leading to considerably faster in-plane diffusion. Given that the tendency of water to cross the interface towards the other phase is strongly suppressed, the longer-time slope of $\langle (\Delta r_z(t))^2 \rangle$ is actually somewhat smaller at the interface than further away from it, despite the higher short-time mobility. Figure 6 also shows that diffusion in the intermediate region differs very little from the bulk. Thus we focus on the interfacial region in our further examination of translational mobility.
In figure 7 are shown the in-plane mean squared displacements for water in the interfacial regions of Series 1 and 2 water/alkane interfaces. The dependence of $\langle [\Delta r_{xy}(t)]^2 \rangle$ on the molecular structure of the alkane phase is weak, but shows definite trends with branching and chain length. Within Series 1, increased branching at fixed chain length leads to lower water mobility. Within Series 2, the mobility decreases with increasing chain length.

Also fairly modest is the difference in water translational mobilities when computed in the laboratory and intrinsic frames. This is illustrated in figure 8, where the results for $\langle [\Delta r_z(t)]^2 \rangle$ in water/(Series 1)alkane systems is displayed. We see that the mean squared displacements are very slightly higher in the intrinsic frame and that in both frames, the translational mobility normal to the interface decreases with increasing alkane branching, following the same trend as for in-plane translation.

In addition to translational diffusion, orientational relaxation of molecules near the interface is expected to differ from the same process in the bulk liquid. We have investigated these differences by examining how they affect the orientational time correlations

$$C_l(t) = \langle P_l[\hat{u}(0) \cdot \hat{u}(t)] \rangle,$$

where $P_l$ is a Legendre polynomial of order $l$ and $\hat{u}$ a unit vector embedded in a molecule. In the case of water, we chose unit vectors along the three principal axes of inertia.
The results for the relaxation of the time correlations $C(t)$ for the three vectors in the water/TMP system in the interfacial and bulk-like regions are shown in figure 9. As can be seen from the figure, reorientation of water is more anisotropic near the interface than in the bulk liquid, with a significant speed-up near the interface of the relaxation of the H-H and out-of-plane vectors, while the dipole relaxation becomes somewhat slower.

The results for the relaxation of the time correlations $C(t)$ for the three principal axes of water in the water/TMP system in the laboratory frame are shown in figure 9. As can be seen from the figure, reorientation of water is more anisotropic near the interface than in the bulk liquid, with a significant speed-up near the interface of the relaxation of the H-H and out-of-plane vectors, while the dipole relaxation becomes somewhat slower.

The results for the water/TMP system are representative of all the water/alkane systems we studied. A comparison of the results for the dipole vector relaxation in interfacial region of all the systems, displayed separately for Series 1 and 2, is shown in figure 10. These data indicate very weak dependence of $C(\mu\mu)(t)$ on the molecular structure of the alkane phase. Within Series 1, a slight slowdown in the relaxation rate is seen as the extent of alkane branching increases.

We have also studied [5] interfacial orientational relaxation in the intrinsic frame and found that these results resemble closely the results for the laboratory frame. These results are reported in Ref. [5], but are not displayed here. The comparison of the results for the laboratory and intrinsic frames for water reorientation exhibits the level of agreement similar to that displayed in Figure 8 for the molecular mean squared displacements.

The most significant aspect of interfacial rotational mobility that our results display concerns the increased anisotropy in molecular reorientation in the interfacial region compared to the bulk liquid. We can gain further insight into this aspect of water interfacial mobility by examining the behavior of the time correlation of the hydrogen bond population in water/alkane interfacial systems. We have obtained the results for $C_{HBA}(t)$, the time correlation for the fluctuations in
the numbers of H-bonds in region $k$:

\[
C_{\text{HB},k}(t) = \frac{\langle [h_{ij}(t) - \bar{h}_k]' [h_{ij}(0) - \bar{h}_k] \rangle}{\langle [h_{ij}(0) - \bar{h}_k]^2 \rangle},
\]

where $h_{ij}(t) = 1$ if there is a hydrogen bond between molecules $i$ and $j$ at time $t$ and 0 otherwise.

\[
\bar{h}_k = \left\langle \sum_{i,j \in k} h_{ij} / N_k^2 \right\rangle
\]

is the average number of H-bonds and $N_k$ is the number of molecules in region $k$.

Figure 11 displays side by side $C_{\text{HB},k}(t)$ and $C_{\text{HB},k}(t)$ in the three regions. The figure indicates that the two time correlations exhibit the same trends as a function of the distance from the interface. In particular, their behavior suggests that slower relaxation of the water dipoles in the interfacial region is related to the longer H-bond lifetimes in this region.

The enhanced anisotropy in water reorientation at the interface is also related to the preferred molecular orientations relative to the interface and how they affect the three principal axes. This information is displayed in figure 12 for the dipole and H-H vectors.
Figure 12. Probability distributions of $\cos \theta = \hat{u} \cdot \hat{n}$, where $\hat{n}$ is the surface normal and $\hat{u}$ a unit vector along a water molecule principal axis (left figure $\hat{u} = $ along molecular dipole; right figure $\hat{u} = $ along molecular H-H distance) in the interfacial region of water/TMP.

Specifically, in this figure are depicted the distributions of $\cos \theta = \hat{u} \cdot \hat{n}$, where $\hat{n}$ is the surface normal along the positive z direction and $\hat{u}$ a unit vector along a molecular principal axis. The distributions of for the dipole and H-H vectors are strikingly different from each other. The dipole clearly has a preferred orientation relative to the interface, with a peak at about 107°, predominantly in the plane of the interface, with a slight tilt towards the hydrocarbon phase, while the H-H vector has essentially no orientational preference. This indicates that the faster reorientation of the H-H vector at the interface than in the bulk is due mainly to the reduced water density in the interfacial region, while the slower reorientation is related to the difficulties of disrupting interfacial the H-bond network.

Figure 13. The orientational time correlations for the main-chain end-to-end vector of alkane molecules within Series 1 in the interfacial region and in the bulk.

While our focus has been primarily in characterizing the aqueous side of water/alkane interfaces, we have also studied the structural and dynamical properties of the alkane side of the interface. In figure 13 are shown the results for $C_1(t)$ of the vector connecting the main chain ends [4,5] for alkanes of Series 1. These results indicate that orientational relaxation rate is strongly dependent on the extent of branching within this series, whereas within Series 2, for which the results are not displayed here, slower relaxation rate is observed with increasing chain
length. As can be seen from figure 13, the orientational relaxation rates of the three alkanes within Series 1 are only weakly dependent on the vicinity of the interface.

5. Summary and Conclusion

In this article, we have provided an overview of our MD simulation results for water/alkane liquid/liquid interfaces under ambient conditions. We have studied the properties of these interfaces for several different alkane phases in order to determine the effects of chain length and extent of branching. We have also studied how the interfacial structure and molecular mobility are affected by capillary waves. To this end, we determined the location of the intrinsic, nonplanar, interface using as a criterion the proximity of the molecules of the other phase [3]. We summarize here our main findings.

The diffuse nature of the density profiles in the laboratory-frame reflects the broadening due to capillary waves. The intrinsic density profiles reveal more pronounced structure. For the aqueous phase, this structure is essentially the same for all the alkane phases and resembles the structure near a planar hydrophobic wall [12]. By contrast, the intrinsic alkane density profiles are quite different from each other, reflecting the differences in molecular shapes and intermolecular correlations within this phase.

Water translational and rotational mobility is quite different near the interface compared to the bulk liquid. However, this difference does not persist deep into the aqueous phase. Molecules that are about 5 Å away from the interface exhibit essentially bulk-like dynamics.

Water interfacial dynamics is only weakly dependent on the molecular structure of the alkane phase. This conclusion is in general agreement with the experimental observations [6]. We have also found that interfacial dynamics are quite similar in the laboratory and intrinsic frames.

Water mobility near the interface reflects the fact that the presence of the alkane phase essentially blocks water motion in the direction towards this phase. Molecular mobility in other directions does not appear to be significantly hindered and is actually enhanced for some types of motion, such as translation in the plane of the interface.

Orientational relaxation of water molecules is significantly more anisotropic near the interface than in the bulk. This is a consequence of the preferred molecular alignments relative to the interface and of the somewhat longer hydrogen bond lifetimes in the interfacial region.

In the case of the alkane phase, molecular mobility varies considerably with chain length and the extent of branching, but shows more modest effects due to molecular alignment in the interfacial region.

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