

Molecular dynamics simulation of the water/1,2-dichloroethane interface

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Abstract

The interface between two immiscible liquids is a region with unique discontinuous properties. Knowledge of the structure and dynamics of this region plays a fundamental role in understanding, from a molecular point of view, many interfacial processes like, for example, charge transfer between the two phases. This paper reports the results of a molecular dynamics simulation of the interface between water and 1,2-dichloroethane (DCE). It is shown that this interface is very sharp at the molecular level, without a mixed region, but broadened by interpenetrating waves of one liquid into the other. In addition, an estimate of the frequency of these interpenetrating waves and a study of the dynamics of the global interface are presented. It is concluded that this dynamics is somewhat regular and has a long correlation time. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Liquid–liquid interfaces; Molecular dynamics simulation; Water; Dichloroethane

1. Introduction

The charge transfer reactions occurring across the liquid–liquid interfaces are very important in several areas of biology, chemistry and engineering. An understanding of the charge transfer mechanism is only possible if supported by a characterization of the structure and dynamics of the interfacial zone at the molecular scale. Experimentally, this is a difficult task because measurements must be done in a very restricted zone. In the last two decades several Monte Carlo and molecular dynamics simulations of liquid–liquid interfaces have been published [1–4]. Computer simulations are of fundamental importance for this problem because they can

provide a molecular characterization of the liquid interfaces, helping to understand charge transfer processes and to interpret experimental data. To clarify some important points of the behaviour of the interface, a molecular dynamics (MD) simulation of the water/DCE system was performed, focusing attention on the interfacial region.

This article begins with a brief description of the methods as well as the intermolecular and intramolecular potentials used in the simulation. In Section 3, some results of the simulation are reported, namely density profiles, interfacial position and width populations and a snapshot of the interfacial surface. Additionally, a simple study of the frequency of the position of the interface and a time autocorrelation analysis for these fluctuations are carried out. Finally, in Section 4, a short discussion of the results obtained is presented.

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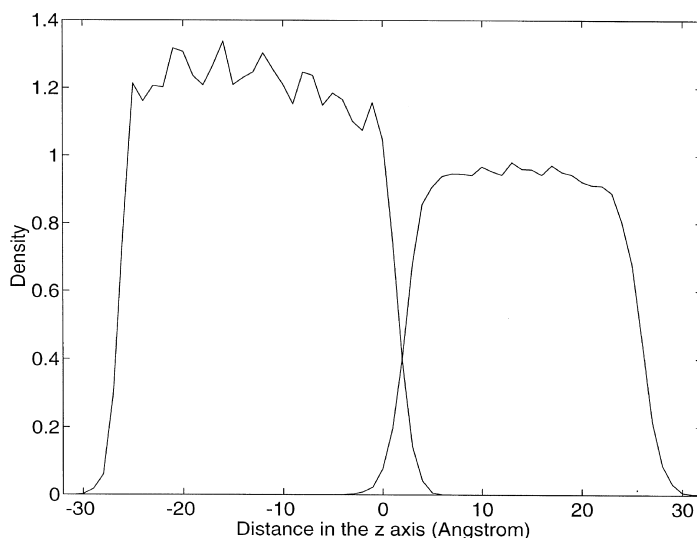


Fig. 1. Density profile of the water/DCE system. Water (right) and DCE (left).

2. Method and potentials

All MD calculations were carried out with the DL_POLY program [5].

The water/DCE system was represented by two separated parallelepipedic boxes, one containing 363 flexible water molecules and the other 100 flexible DCE molecules. Each box has a cross-section of $22 \text{ \AA} \times 22 \text{ \AA}$ on the x - y plane. The length of each box (along the z axis) was chosen in order to obtain the correct bulk density for the liquids. For the water system, a length of 22.5 \AA was used and for the DCE system the length was 27.2 \AA .

The two systems were equilibrated separately with a 250 ps run, in the canonical ensemble, using a Nosé-Hoover [6] thermostat. Periodic boundary conditions were applied in all directions. The integration step was 1 fs for the DCE simulation and 0.5 fs for the water simulation. After equilibration, the periodic boundary conditions along the z axis were removed and the box length was extended to infinity, thus producing two open boxes along the z direction. These open boxes were further equilibrated with a 250 ps run, under the same conditions as the precedent simulations. In each box, two liquid-vapour interfaces in the x - y plane and a bulk liquid region are obtained. The two boxes were then closed together to 5 \AA by their x - y cross-sections, forming one unified box with

both liquids inside. This has the same cross-section as used before and is open at both ends in the z direction. This was followed by an equilibration run of 500 ps with a timestep of 0.5 fs and under the same conditions as the previous equilibrations. After equilibration, a 250 ps run was performed without the thermostat, using a timestep of 0.5 fs. The results presented in this paper were taken from this last run.

The intramolecular potential for water contains two harmonic stretches and one harmonic bending and the potential for the DCE has three harmonic stretches, two harmonic bendings and one torsional potential. The parameters of those potentials were all taken from the CHARMM [7] forcefield except the torsional potential, which was taken from Jorgensen [8]. This particular torsional potential was chosen because it is more specific for the DCE molecule and gives better *trans/gauche* ratio in the liquid and gas phases. The intermolecular potentials used are a sum of pair-wise coulombic plus 6–12 Lennard-Jones terms. The intermolecular parameters were taken from the CHARMM forcefield for water and from Ref. [3] for DCE. The water–DCE interaction parameters were found using the standard combination rules, $\sigma_{ij} = 0.5(\sigma_i + \sigma_j)$ and $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$. A switching method to deal with the truncation of the long-range forces was used [9].

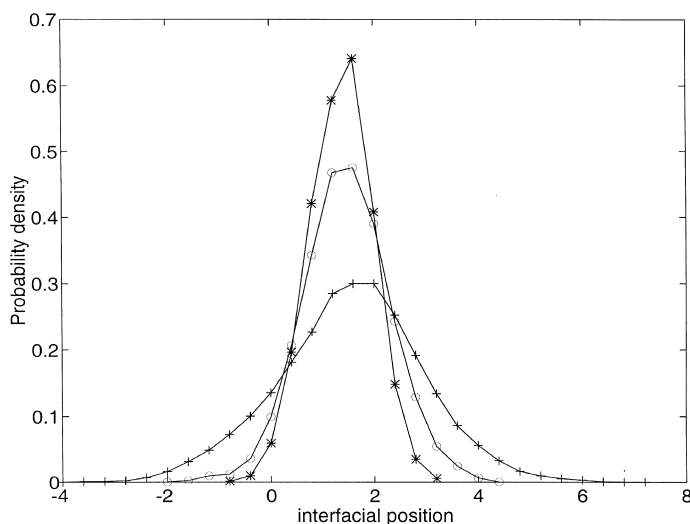


Fig. 2. Density probability of the interface position for several N (* $N = 1$, ° $N = 2$, + $N = 4$).

3. Results

3.1. Density profile

The simulation box was divided in slabs of 1 \AA length and parallel to the x - y plane and the density of the system was calculated separately for each slab. Fig. 1 shows the density profile determined in this way. It can be seen that the bulk densities agree quite well with the experimental values

($\rho(\text{DCE}) = 1.246$) and $\rho(\text{H}_2\text{O}) = 1.0$). The noisier profile of DCE is likely to be caused by the small number of molecules used. This was confirmed by increasing the number of molecules which was found to reduce the noise. The plot in Fig. 1 is that of a static averaged density profile, where a gradual change in composition along the z direction seems to appear, with a zone of strong mixing. This mixing is, however, totally illusory as will be seen later.

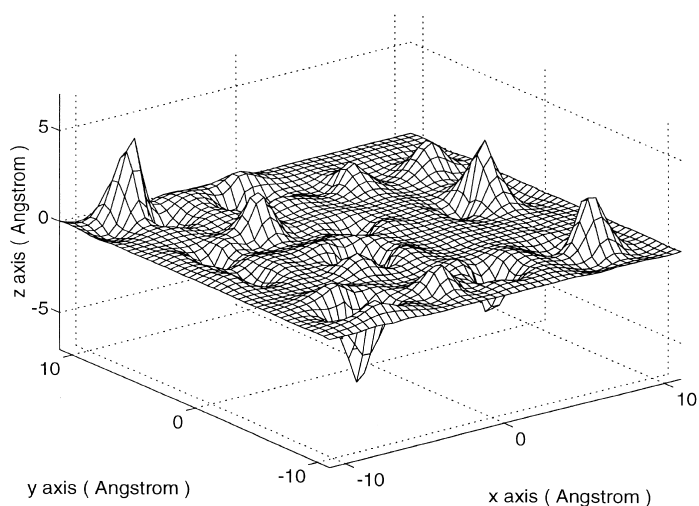


Fig. 3. Snapshot of the interfacial position for the water/DCE system. Water (top) and DCE (bottom).

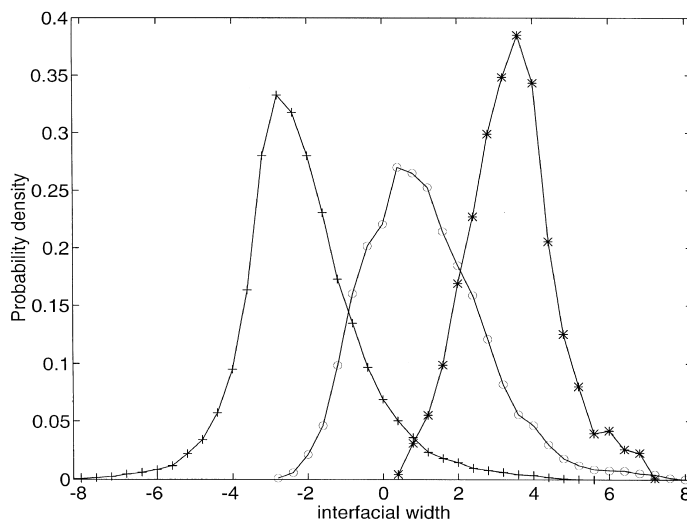


Fig. 4. Density probability of the interface width for several N ($^*N = 1$, $^{\circ}N = 2$, $^+N = 4$).

3.2. Interface width and location

To gain a better insight into the interface structure, the x - y plane was divided in $N \times N$ square areas, with a minimum side length not smaller than the bulk correlation length (about 5 Å for most liquids away from their critical point). For each of the $N \times N$ columns obtained, the interfacial position (p_{ij}) and width (w_{ij}) have been defined according to Eqs. (1) and (2) below:

$$p_{ij} = 0.5(\min(z_{ij}(\text{H}_2\text{O})) + \max(z_{ij}(\text{DCE}))) \quad (1)$$

$$w_{ij} = \max(z_{ij}(\text{DCE})) - \min(z_{ij}(\text{H}_2\text{O})) \quad (2)$$

In the equations z_{ij} is the z position of one molecule in the ij column. This allows us to define local, and not only global, interface positions and widths. The probability distribution of the interfacial position is shown in Fig. 2 for several N values. The increasing width of the distribution with increasing N shows that the interface is far from planar. In fact, if the interface was planar, then its position would be the same in every ij column defined and the position of the distribution would be independent of N . Fig. 2 gives a picture of a very irregular, corrugated surface.

In order to obtain a snapshot of the interfacial surface, a plot was prepared with the 16 independent positions of the interface, each one corresponding to the location of the interface in one of the 16

independent columns that result from the division of the x - y plane in 4×4 square areas. Then, a graphical interpolation of these points was made and the resulting picture of the interfacial surface is depicted in Fig. 3.

Fig. 4 shows what seems to be an even more important feature. It is clear from Eq. (2) that a positive width implies interpenetration of one liquid into the other, while a negative width means an effective separation between the two liquids. In Fig. 4, it can be seen that, as N increases, the width of the interface is shifted towards the negative values. This means that, when considering all the interface, the probability of some interpenetration occurring is very high, but taking the $N \times N$ interfacial areas independently, the probability of interpenetration for each one of them is very low. Or, in other words, for most of the interface fractional areas, interpenetration does not occur and the most probable value for the interfacial width is about -2.8 Å. This can be seen as a gap between the two liquids with an extension of a typical van der Waals radius. So, it can be said that not only at a macroscopic level but also at a molecular level, mixing is almost non-existent.

3.3. The dynamics of the interface position

To study the dynamics of the interface position, a probe square area of $5.5 \text{ \AA} \times 5.5 \text{ \AA}$ was built in the centre of the x - y plane, defining the cross-section of a

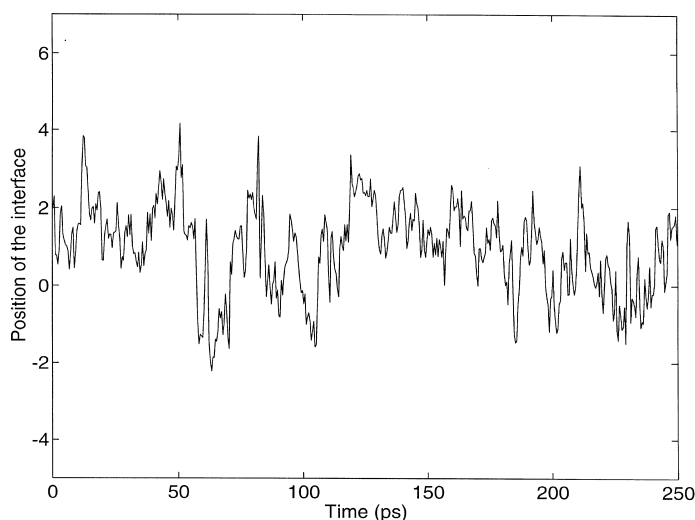


Fig. 5. Position of the water/DCE interface obtained during the simulation.

probe column, where the evolution of the interface position in time has been measured. The resulting position profile is shown in Fig. 5. As can be seen, the instantaneous position of the interface oscillates about $\pm 2 \text{ \AA}$ around its mean value. To estimate the relaxation time of these oscillations, the power spectrum of their wave-like movement has been computed. The power spectrum estimation is a classical powerful method for decoupling a narrow-band

signal buried in noise. Fig. 6 shows these results. One strong band can be detected, centered at 9.5 ps^{-1} , which corresponds to oscillations with a period of 0.11 ps. The other bands, observed at higher frequencies, are obviously associated with statistical noise.

The time correlation function ($C(t)$) for the interface position was also computed and is plotted in Fig. 7. This picture shows that the interface position is

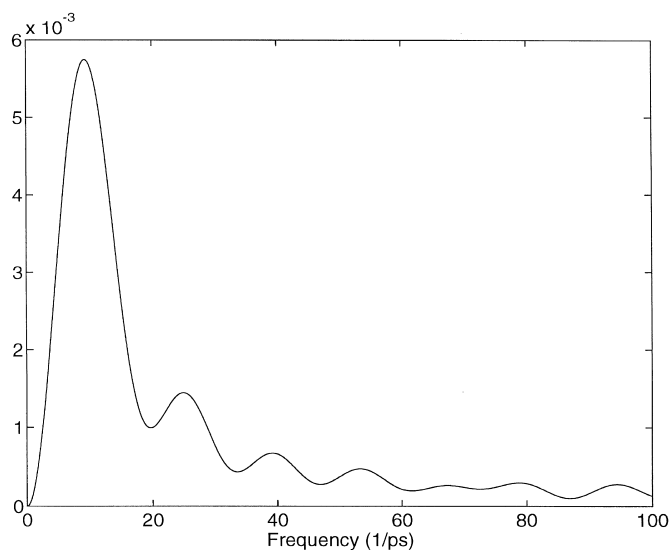


Fig. 6. Power spectrum estimation of the oscillations of the water/DCE interface.

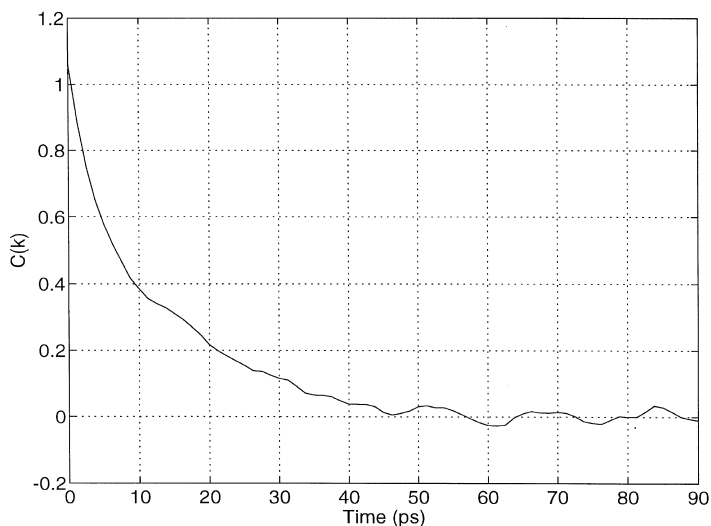


Fig. 7. Time autocorrelation function for the oscillations of the water/DCE interface.

highly correlated in time. The correlation time (given by $\int_0^{\infty} C(t)dt$) was estimated to be 12.0 ps which is a very long time at a molecular level.

4. Discussion

In the present work, it has been demonstrated that the interface between water and DCE is very sharp. It does not appear to exist in any mixed region, even at a molecular level, above the detection limits of the system simulated. It seems to exist in a separation gap between the two liquids with a typical size of a van der Waals radius. So, the two liquids are in close contact but without mutual solvation (excluding the equilibrium solubility of each liquid in the other). Interpenetration exists, but in such a small extension that the mean width of the interface remains negative. The interface is not planar, in part due to the thermal motion of the interfacial molecules of both liquids.

The interfacial dynamics is dominated by oscillations with a small relaxation period, but these oscillations are strongly correlated in time, indicating some structured regular general dynamic behaviour. This work will be followed by investigation into the extent

to which the interfacial dynamics affects the ion-transfer kinetics across interfaces.

Acknowledgements

Financial support from the Fundação para a Ciência e a Tecnologia (Lisbon) and project PRAXIS/2/2.1/QUI/474/94 is acknowledged. P.A.F. thanks PRAXIS XXI for a doctoral scholarship.

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