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Immiscible fluid flow through nanotubes

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Abstract. We have analyzed the properties that characterize the water/oil interface when flow occurs through a prismatic flexible surface of van der Waals particles at 300 K. Thermodynamics and dynamics properties of the flow as density profiles, interface width and diffusion coefficients were calculated. We have observed a complex mechanism, the back-and-forth movement of the interface when advancing through a nanotube.

Keywords: Interface – Confinement – Flow – Nanotube

The low-Reynolds-numbers flow of continuum Newton fluids has been described by the Stokes equations; however, there remain a number of unresolved questions regarding the fluid interface [1]. Interfaces between coexisting phases are under intense scientific investigation, because of the significant role they play in technological applications. They are critical to the performance of detergents and soaps, to chemical engineering separation processes such as absorption and distillation, to petroleum recovery and the function of biological membranes, to mention just a few examples [2]. An important role for molecular dynamics (MD) simulation is to explore the assumptions used in experimental results. At the molecular level, information about the liquid/liquid interface is contained in the density and orientational profiles, although there is no direct experimental measurement of the orientational profile. In contrast, MD simulation can provide information about the form of these orientational distribution functions [3]. Therefore, the macroscopic flow description must be augmented with the results of the microscopic physics.

In related problems, MD simulations of slow channel flow of a viscous inhomogeneous fluid [1, 4] and water conduction through the hydrophobic channel of a carbon nanotube [5] have been carried out. To this end, we have studied with MD simulation the slow flow of the water/hydrocarbon interface through a rectangular prismatic network (a parallelogram L_x:L_y:L_z = 6.44:3.0:3.0 nm, net constant 0.15 nm), of 3520 single-wall van der Waals particles. We carried out a MD simulation with the aim of characterizing the water/oil interface from its thermodynamic and diffusion properties.

Several MD simulation runs were performed on the water/oil interface using (periodic) boxes. We started with two separate simulations. One of pure SPC/E water [6] (846 molecules) and the other of a mixture of equal numbers of ethane, propane and butane molecules (60 molecules). Later, by joining the two boxes along the x direction a new box was constructed. Then we went to the previously mentioned prismatic surface confining the 860 water molecules (SPC/E, with density 0.928 g/cm^3) and 60 hydrocarbon molecules (butane, propane and ethane, with total density 0.2904 g/cm^3). The x direction is perpendicular to the interfaces. These conditions generated two interfaces, the mutual independence of which requires that the two liquid slabs attain bulk properties.

The criterion for the stability of the interface between two liquids was the equality of the chemical potential in both phases at the interface. For this condition to occur, the pressure components normal to the interface in the two phases must be equal. We therefore performed NPT runs with pressure scaling in the x direction, perpendicular to the interface, by coupling the 1055 Pa (1 atm) hydrostatic bath, and allowing changes in the box length only in that direction. In this way the system was allowed to adjust its bulk pressure by changing the volume of the box. To avoid undesirable effects of long-range Coulomb interactions, we applied a charge group criterion for the interacting atoms within the cutoff (0.9 nm). Consequently, only effective dipole–dipole interactions were present. Then, the box went to the prismatic surface.

Because we considered the NPT simulation sufficient to obtain a stable water/oil interface, we ran a simulation keeping the box volume constant for a period of

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0.5 ns. The criterion for the equilibrium was the stability of the potential energy of the system.

The forces and configuration energies were computed using the modified GROMOS87 package [7]. Only oxygen–oxygen, oxygen–carbon, carbon–carbon, oxygen–van der Waals particle and carbon–van der Waals particle interactions were considered, i.e. Lennard-Jones and electrostatic interactions. The hydrogen atoms interact only through Coulomb forces and the van der Waals particles do not interact with each other through Lennard-Jones forces. Periodic boundary conditions in the flow direction were applied. The boundaries in the other direction were formed with the prismatic surface. The van der Waals particles were attached to a lattice site by a spring force (spring constant $k = 80$) for the thermal roughness control of the prismatic surface [8]; besides with this k value the walls retain their integrity over the duration of the calculation. Deformations of the elastic surface are important factors that produce instability in the complex flux, increasing the probability of wall disintegration at larger Reynolds numbers. The van der Waal particles were particles with mass and the van der Waals parameter of the oxygen atom. Besides, to attach the particles to each lattice site, each van der Waals particle had covalent bonds with the first neighbor. For more details see Ref. [9].

We started several NVT MD simulations. The temperature was controlled by coupling the system to a thermal bath at 300 K with a time constant of 0.3 ps. A twin-range cutoff for nonbonded forces of 0.9/0.9 nm was used. The covalent bond lengths for water and hydrocarbon molecules, as the van der Waals particles of the prismatic network, were constrained by the SHAKE procedure (tolerance 0.0001 nm). The system was run using a time step of 2 fs. Trajectories were collected every ten time steps for further analysis. Both dynamics simulations were run on a Pentium computer.

We simulated the flow, of low Reynolds numbers of order of less than 0.1, through a nanotube by introducing an equivalent procedure to the gravity force applied to each atom [1, 4, 10]. This flow is generated by applying different uniform acceleration to each fluid in the direction of the nanotube. Because, we are dealing with small systems and short times, many trial-and-error runs were carried out in order to extract an average velocity, V_a, from important thermal noise.

In order to obtain a large V_a spectrum, a series of simulations – about ten simulations – were done. From the atom trajectory analysis, relations between V_a and different properties that characterize the interface flow were obtained.

One important thermodynamics interface property is the density profile of fluids along the flow. To this end, the density profile was calculated using 64 slabs parallel to the yz plane along the x direction by averaging the time frames over the last 60 ps of the NVT simulation. Using the center-of-mass of water as a reference frame, the densities were calculated.

We comment that the two profiles have suitable normalization: the water profile with oxygen bulk density and the hydrocarbon profile with the corresponding bulk density of the molecular center of mass.

In the static situation both interfaces are symmetric, but in our case the symmetry is broken. However, with the object to improve the statistics we symmetrized the data from the two interfaces. The profile density at $V_a = 0.09$ nm/ps is displayed in Fig. 1. Similar profiles were observed for different mean velocities.

The simulation shows that the water density profile exhibits a pronounced layering effect as in the free simulation, and from this data, we can observe a well-defined interface. The density profile is rather different from that reported by others authors [11, 12, 13] in nonconfined systems. The interface is placed at 4.18 nm; it corresponds to the middle point of the distance over which the water density profile drops from 90 to 10%. The water density dropped more slowly to zero than the densities of the hydrocarbons did. The peak of the hydrocarbon mixture density profile in the interfacial region is markedly much lower and wider than the similar one in a nonconfined system.

The interface width obtained in our simulations was about 0.39 ± 0.02 nm (Fig. 2) and was much narrower than the interface of the confined equilibrium system

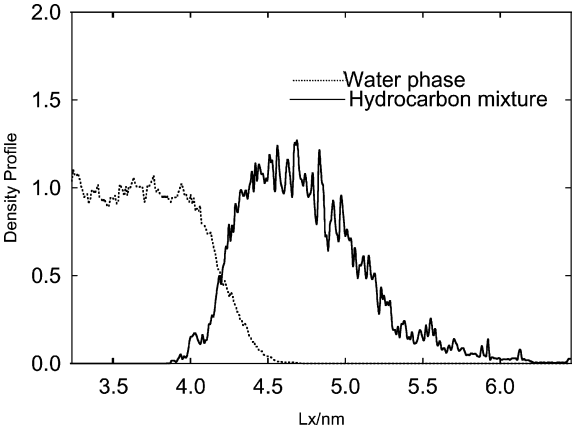

Fig. 1. Density profiles of water/oil interface in the x direction. The *dotted line* is the water density; the *solid line* is the hydrocarbon mixture

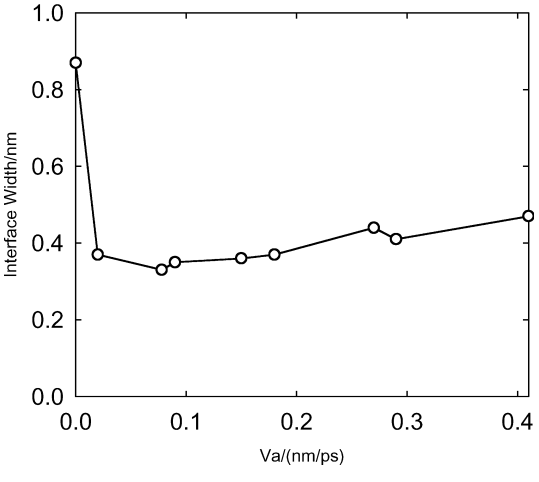

Fig. 2. Interface width versus water average velocity, V_a

(0.87 nm). Besides, the molecular water/hydrocarbon ratio (W/H), that characterizes the hydrophobicity of the interface, W/H = 8 ± 1, is larger than in confined equilibrium systems, W/H = 5.

As a consequence of this behavior, fewer water and hydrocarbon molecules are involved in the interface owing to driven flux forces increasing the hydrophobicity of the interface. Further complementary information is given in Fig. 3a and b concerning to the cross-sectional densities of the water and hydrocarbon mixture for the flux with $V_a = 0.09$ nm/ps. These profiles are not different with respect to each flux and also for zero-flux profiles. The water profile exhibits a pronounced layering effect as in the free simulation. The first-layer minimum is 0.5 nm closes to the wall than the zero flux. The hydrocarbon cross-sectional density shows that the molecules remain close to the wall over all the simulation.

We report some dynamics properties of this complex flow at $V_a = 0.09$ nm/ps. A profile velocity of the water phase is displayed in Fig. 4. We can see that it is not Bernoulli flow. The profile represents a typical turbulent flow of the "plug" type.

Continuing our analysis of the dynamics properties of the flow, starting from the atom trajectories, we

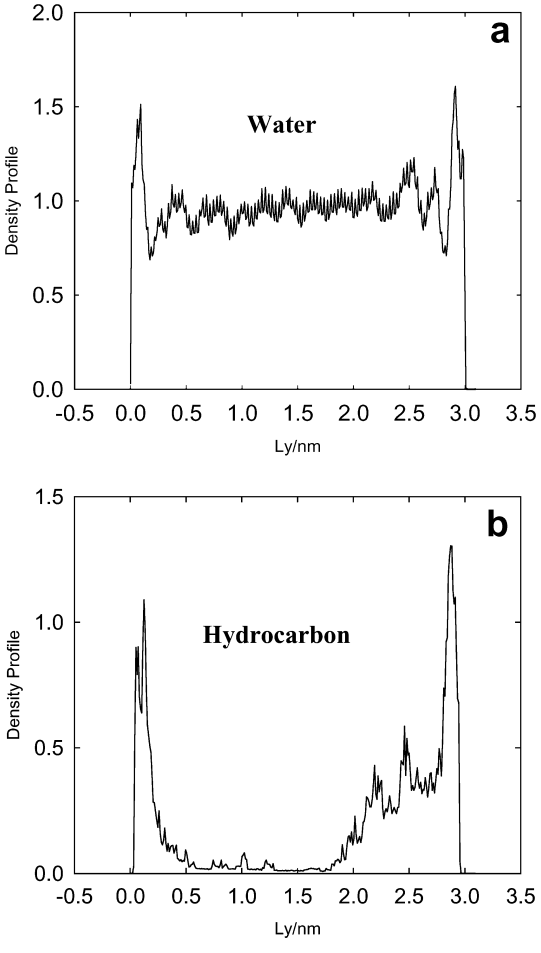

Fig. 3. a Cross-sectional density of the water phase. **b** Cross-sectional density of the hydrocarbon phase

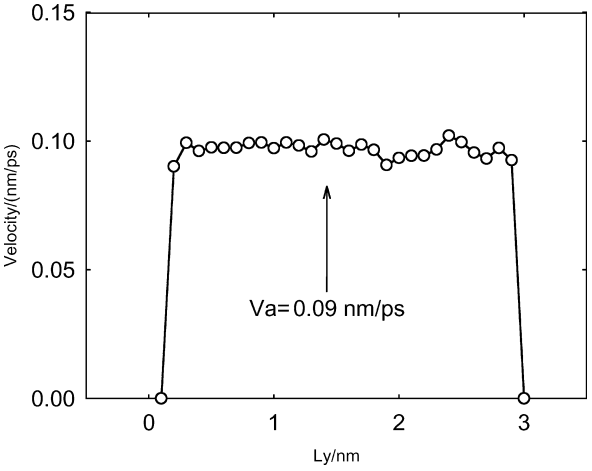

Fig. 4. Velocity profile of the water phase at $V_a = 0.09$ nm/ps

calculated the dynamics diffusion coefficients, D_f, of water versus V_a for different flows. Figure 5 shows that this relation is rather linear in V_a. We can study quantitatively the effect of V_a on diffusion in the flow. Consider the diffusivity of water in the flow direction:

$$D_f = D_e + CV_a, \tag{1}$$

where $D_e = 2 \times 10^{-5}$ is the diffusion coefficient of water at equilibrium ($V_a = 0.0$) and $C = 149.5$ ps/nm. This relation differs from the quadratic dependence of V_a of Tayor–Aris theory which was obtained by simulation with van der Waals particles of Poiseuille flow [1].

An enlightening question emerges when a complex mechanism during the advance of the interface through a nanotube is observed. This mechanism can be explained by Fig. 6, where the center of mass of the water phase evolves in the flow direction with the simulation time.

This quasi-periodic movement of the center of mass, the back-and-forth motion, has a positive V_a for each cycle. Therefore, the mechanism produces a real advance of the fluids. We also observe that from the constant value of the interface width for all V_a (Fig, 2) and, in addition, the profile velocity of the plug flow (Fig. 4), the

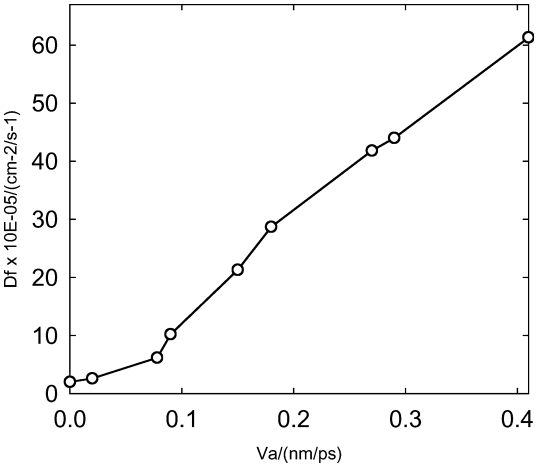

Fig. 5. D_f versus V_a of the water phase

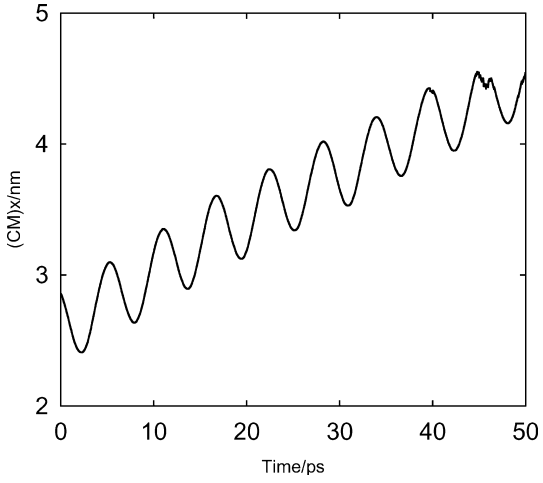

Fig. 6. Center-of-mass (CM_x) evolution of the water phase with simulation time

oil phase takes care of all displacements of the water phase. All this behavior could be seen by means of the molecular animation program GOPENMOL. We think that the atomic roughness and the elastical nature of the prismatic surface are possibly responsible for this movement.

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