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Wall–Water Interface. A Molecular Dynamics Study[†]

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This work was aimed at contrasting the properties of water near highly hydrophilic or highly hydrophobic walls. We performed molecular dynamics computer simulations of two systems, both composed of a number of water molecules together with a layer of either purely hydrophilic or purely hydrophobic molecules restrained in mobility so as to form walls. Simulations were done at constant temperature and at constant volume or constant pressure. We found that the hydrophilic wall induces strong ordering near its surface, but such order is present only up to about two molecular diameters away from it. On the other hand, the hydrophobic wall induces a slight ordering, but this ordering remains for several molecular diameters inside the bulk.

Introduction

Among other important characteristics, water has a fundamental role as a solvent. The properties of bulk water are well-known; however, these properties are altered near interfaces, and the resulting properties of water are less well understood. The modifying effects of interfaces are relevant for crystal growth, electrochemistry, and biological processes, to quote only a few. Studies of liquid–solid interfaces by simulation have been done in a large variety of systems, including hard spheres near a hard wall,^{1,2} water–hard wall,³ water–membrane,⁴ crystal–liquid,⁵ and others. In this work we investigate the characteristics of water near either highly hydrophilic or highly hydrophobic walls. Static and dynamic characteristics were obtained by simulation of the molecular dynamics of systems at constant temperature and constant volume or constant pressure. Prior results published for similar systems have omitted the comparison of the contrasting influence of hydrophilic and hydrophobic walls done here. Moreover, prior results have been derived from constant volume simulations, while to reproduce the behavior of water under standard laboratory conditions requires instead constant pressure simulations.

Methods

Molecular dynamics simulations were run using a modified version of the GROMOS package⁶ in which the equation of motion was integrated using a leapfrog algorithm. The simulation box was chosen to be rectangular, the longer side being the *x* axis, and was filled randomly with water molecules. A water layer perpendicular to the *x* axis was then located at about half of the box length in the *x* direction and was given the structure of ice Ih, with oxygen–oxygen distances of 0.27 nm. Hence, it presented

to the neighboring molecules a hydrophilic surface with a regular distribution of hydrogen-bonding sites (the hydrophilic wall). In the hydrophobic wall, the molecules in such a layer were instead given the properties of neutral atoms and were positioned at the same coordinates at which the oxygen atoms were in the hydrophilic wall.

The water or argon molecules were positionally restrained with a harmonic potential. As a consequence, during the simulations the molecules could vibrate around their positions but could not leave their places. Periodic boundary conditions were applied along all box faces; as a consequence, the two regions separated by the membrane are connected through periodicity conditions and thus can be considered contiguous. Figure 1 shows a scheme of the simulated system.

In order to compare our results with previous ones or with relevant experimental conditions, we performed simulations with either constant volume or constant pressure constraints. In GROMOS the pressure is controlled by coupling the system to a hydrostatic bath. The positions of the walls of the box and the atomic coordinates were therefore adjusted during the run to preserve the internal pressure close to the reference pressure selected. A relaxation parameter was imposed to avoid instability. In our case, we did not want to change the wall lattice dimensions, so changes were made only in directions perpendicular to the *x* axis. This anisotropic adjustment of the pressure may produce some undesired pressure effect; however, this will disappear when the system reaches equilibrium. The reference pressure was selected as 1 001 325 Pa (1 atm). The temperature was controlled by coupling the system to a thermal bath. In the case of constant volume, it remained fixed for the complete run. Water was modeled with a SPC/E model,⁷ and neutral atoms of hydrophobic wall have the same parameters as 12-6 Lennard-Jones interactions of SPC/E water oxygens. To avoid undesirable effects of long range Coulombic interactions, the interacting atoms within the cutoff (half minor box length) were always selected including full water molecules. Therefore only effective dipole–dipole interactions were present.

A total number of 576 water molecules were included in a box of initial dimensions of 4.674 nm × 1.799 nm × 2.196 nm. At the desired temperature, 300 K, the system was allowed to equilibrate for 10 ps, which is far more than necessary to reach equilibrium. By use of a constant-temperature, constant-pressure algorithm, total energy is not conserved unless the system is in equilibrium. Therefore, it was possible to monitor for equilibrium by ascertaining the constancy of both the total energy and the box volume. Thermal coupling constant was

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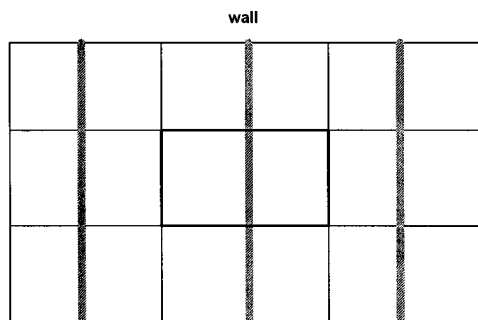


Figure 1. Schematic representation of the simulation box and their images. The wall is at the center in both the hydrophilic and hydrophobic cases.

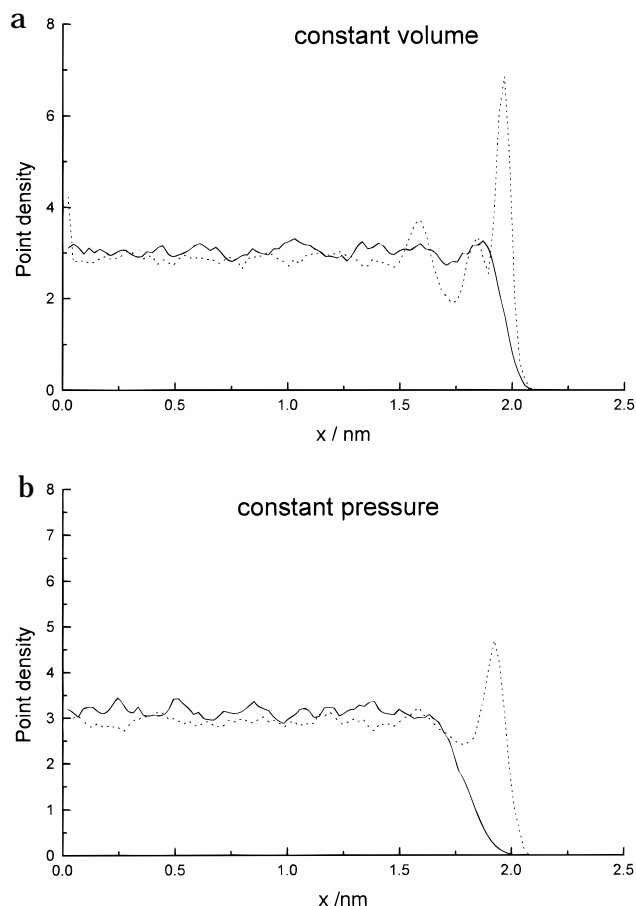


Figure 2. Density of water molecules as a function of the x coordinate, perpendicular to the wall: (a) hydrophilic (---) and hydrophobic (—) at constant volume; (b) hydrophilic (---) and hydrophobic (—) at constant pressure.

selected as 50 ps^{-1} and the pressure coupling constant as 5 ps^{-1} times the water compressibility.

At each condition selected (constant volume or pressure) the system was run for 40 ps after the equilibration period, using a time step of 0.002 ps. Trajectories were collected every ten time steps for further analysis.

Results and Discussion

Figure 2 shows the density profiles along the x axis (perpendicular to the wall) for the hydrophilic and hydrophobic walls at constant volume (Figure 2a) and constant pressure (Figure 2b). At constant volume, the hydrophilic wall results in a high density peak near the wall and two minor peaks after that. The hydrophobic wall instead “repels” water from the wall. At constant pressure, which is the condition really relevant to standard laboratory conditions, the hydrophilic wall only induces

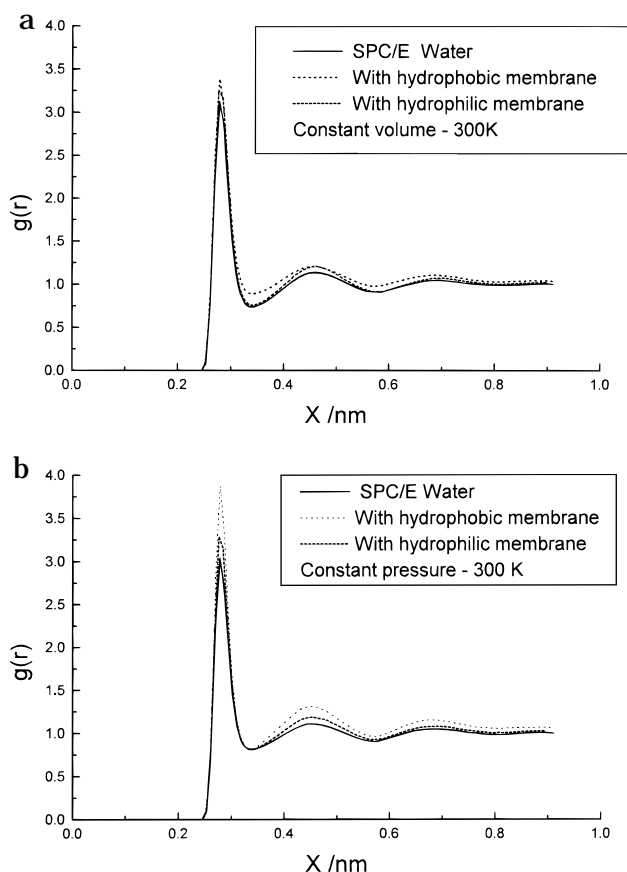


Figure 3. Radial distribution function of water molecules: (a) hydrophilic (---), hydrophobic (···), and pure water (—) at constant volume; (b) hydrophilic (---), hydrophobic (···), and pure water (—) at constant pressure.

one major peak. The water in contact with the hydrophobic wall does not change qualitatively. In both cases it is observed that after the first peaks the density profile of the water in the presence of the hydrophilic wall is somewhat flatter than the one in contact with the hydrophobic wall. Some ripples can be observed in the latter case, although observation of the density only along x -axis cannot be considered as a proof of higher structure.

The high and well-defined peaks of water near to the hydrophilic wall may induce one to consider that the volume density of water near the wall is higher than in the bulk. This is not the case for the global simulation; the bulk density is 3.317×10^{22} oxygens/cm³, and the density for a layer near the wall is 3.195×10^{22} oxygens/cm³. This difference may be due to statistical errors, since the number of water molecules in the layer is relatively low. The result rules out the intuitive idea that there is much higher volume density near the wall. In a somewhat comparable experimental situation, data were interpreted⁸ as if the wall induced higher volume density. Earlier Monte Carlo¹ and molecular dynamics² simulations of hard spheres near a hard wall show the same effects of higher peaks and lower volume density near the wall than in the bulk.

If some long range effect is present, it should be observed in some bulk property, as the radial distribution functions. Figure 3 shows the oxygen–oxygen radial distribution functions for pure water, water with the hydrophilic wall interposed, and water with the hydrophobic membrane

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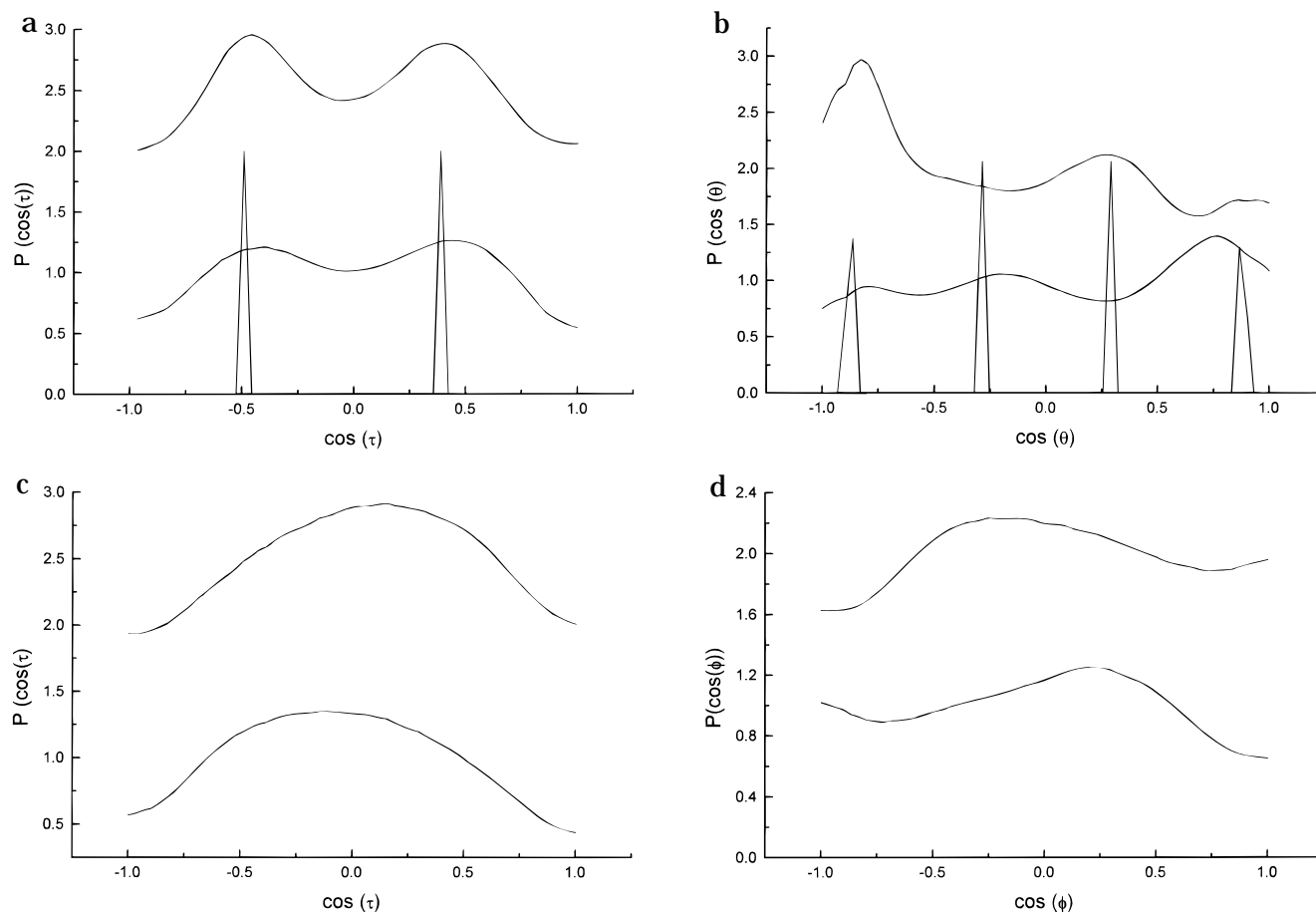


Figure 4. Angular distribution of the water molecules nearest to the wall. At bottom is the left layer and at the top the right one (a and b, hydrophilic case). The narrow peaks correspond to the angular distribution functions for ice and the scale has been reduced (c and d, hydrophobic case). The angle τ is the angle formed by the bisector of HOH and the vector perpendicular to the wall and θ the angle formed by the vector HH and the vector perpendicular to the wall.

interposed, at constant volume (Figure 3a) and at constant pressure (Figure 3b). The radial distribution function for pure water was obtained with a box of the same size, cutoff, and all other conditions used for the other simulations, including the pressure control for the case of constant pressure, to avoid any possible difference due to effects created by the geometry.

The curves at constant volume do not show any significant differences. If anything, we might say that water in the presence of the hydrophobic wall has less defined differences between the first and the second peak. On the other hand, at constant pressure, the curves obtained show a very different behavior. In the presence of the hydrophobic membrane, the water reveals higher first, second, and third peaks.

From the above results we must conclude that the presence of the hydrophobic wall induces a slight but extensive change in the surrounding water. The hydrophilic membrane, on the other hand, induces a remarkable modification near the interface but only weakly alters the water properties a few molecular diameters away from the wall.

We can derive further information on the structure of water from the angular distribution function. The angular distribution function is defined here as the distribution probability of the cosine of the angle formed by the bisector of the HOH angle or the HH vector of water molecules and a vector perpendicular to the wall, *i.e.*, the x axis, plotted against the cosine of the angle. For a random orientation of two vectors, such distribution is a constant,⁹

and such is the result obtained for the bulk. We divided the simulation box in ten layers parallel to the wall, layers 5 and 6 being the ones flanking the wall on its left and right sides, respectively. This gives a layer thick of about 0.4 nm which is comparable to the thickness used by other works, as the one of Karim and Haymet¹⁰ and seems enough to describe the properties at this level. We computed the radial distribution function for the molecules belonging to each layer. For the outermost layers, no particular orientation is observed. However, as the layers become closer to the wall, a particular distribution appears in each case. Figure 4 shows only the angular distribution functions corresponding to layers 5 and 6.

The positions of the peaks of the angular distribution functions correspond to those arising from ice, showing that the wall (an icelike structure) induces the same structure on the interfacial liquid layer. The broader lines observed indicate that the structure is less defined, as expected. This behavior is similar to the one observed by other works done for water–ice interfaces.¹¹

As we see in Figure 4c,d, the angular distribution functions corresponding to the water near the hydrophobic wall show only one peak for each case. For the HOH–wall angle the peaks are near to but not exactly zero. The curves for layer 5, to the left of the wall, and layer 6, to the right of the wall, have the peak at negative and positive values, respectively. This shows that the hydrophobic wall, through the effect of repulsion, directs the water molecules so as to break the reorientation symmetry through

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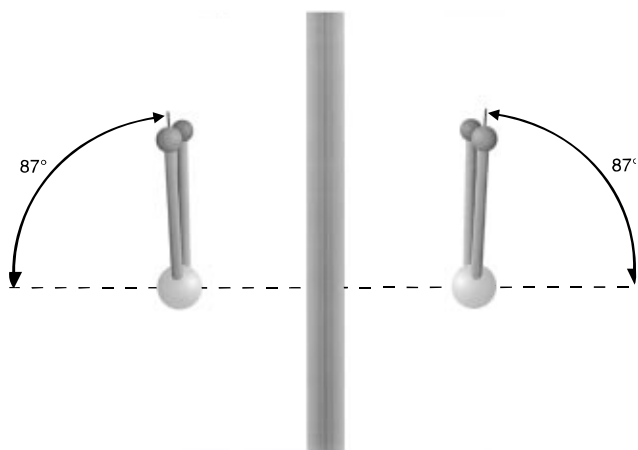


Figure 5. Orientation of the water molecules nearest to the hydrophobic wall, as could be deduced from the peaks observed in Figure 4c,d.

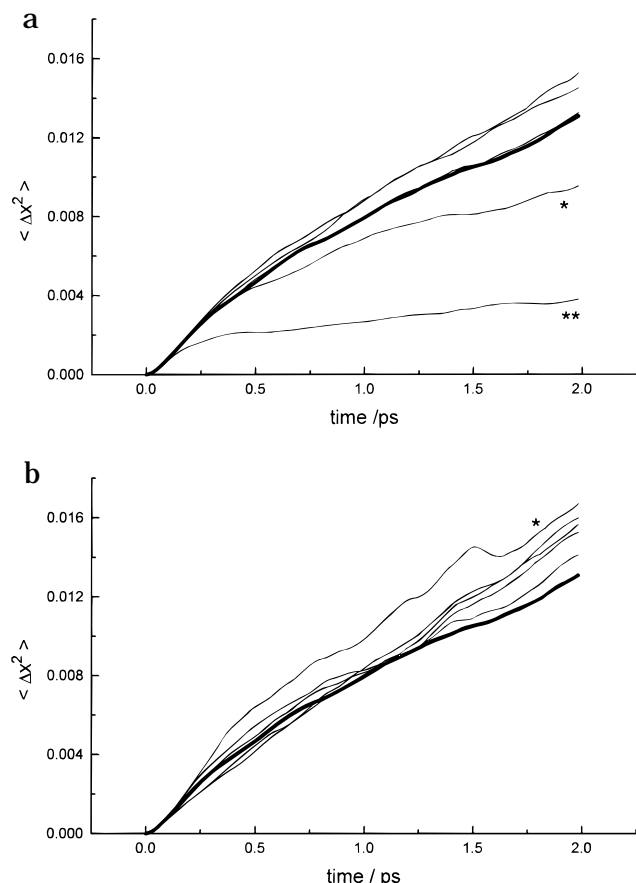


Figure 6. $\langle (x(t) - x(0))^2 \rangle$ versus time: (a) hydrophilic layers, * and ** are the closest layers, in that order; (b) hydrophobic layers, * is the closest layer. Five curves are presented, corresponding to the averages of the symmetric layers on both sides of the wall, in addition to those for pure water.

the wall which exists for the hydrophilic wall. From the curves observed for the HH, orientation we can fix the water position. Figure 5 shows the orientation of water molecules on both sides of the wall.

The membrane might also modify the dynamic behavior of the water molecules in the surroundings of the interface and influence the diffusion coefficient. We therefore computed the diffusional behavior of water in the different layers described above. Since we want to restrict our analysis to molecules that remain completely within each layer, we have restricted such analysis to short times. This means a limitation: For such short times, the

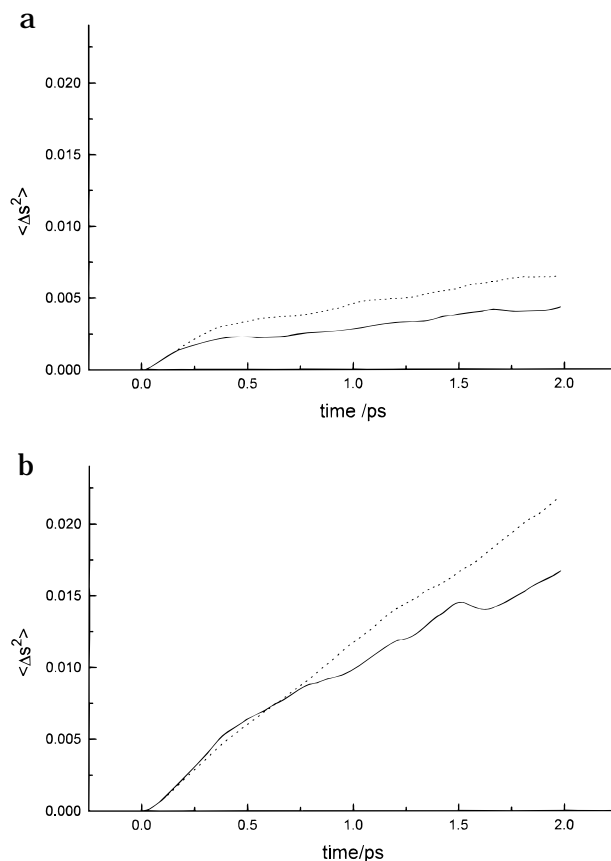


Figure 7. Same as Figure 6 comparing the movement parallel (—) and perpendicular (···) to the wall: (a) hydrophilic, (b) hydrophobic.

movement of the molecules is highly correlated, so we cannot compute proper diffusion coefficients. However, we can record the behavior of $[x(0) - x(t)]^2$ as a function of time. To improve the statistics, we have calculated averages for all the molecules belonging to each layer during 2 ps, subsequently averaging over 40 ps of simulation time.

Figure 6 shows the mean square displacement in the direction perpendicular to the wall for the hydrophilic (Figure 6a) and hydrophobic (Figure 6b) cases. We show averages for symmetrical layers, compared with the same magnitudes for pure water. In the presence of the hydrophilic wall, water differs in behavior depending on whether it is far from the wall or near it. The rate of displacement is reduced in the layers close to the wall; for the other layers, its behavior is close to that of pure water. That is not the case for the hydrophobic wall, in which we see that the mean square displacement is, in all cases, slightly *higher* than that for pure water. The hydrophobic wall therefore seems to produce a type of order that facilitates diffusional movements, while highly hydrophilic interactions rather restrict them.

For hard spheres near a hard wall it was observed² that the diffusion parallel to the wall was faster than that perpendicular to it.

We verify that in our present system there are not differences in the diffusion along different directions when we are far from the wall. Close to the wall, in both hydrophilic and hydrophobic surfaces, molecules have higher mobility when they move parallel to the surface than when they move perpendicular to it (Figure 7).

Further information on the structural behavior can be obtained from the study of the hydrogen bonds network. Figure 8 shows the distribution of hydrogen bonds in water

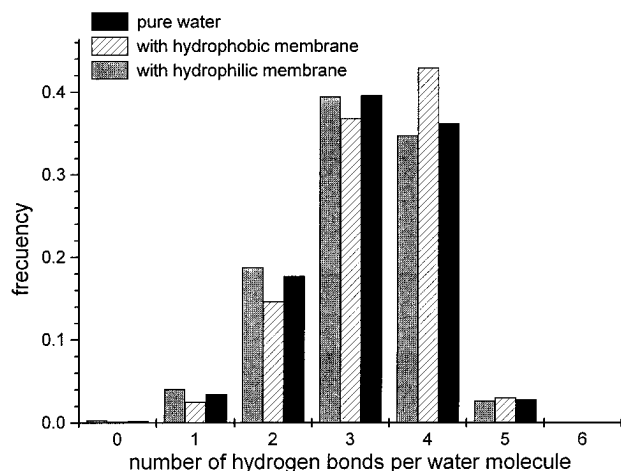


Figure 8. Hydrogen bond distribution per water molecule for the pure water, water in the presence of the hydrophobic wall, and water in the presence of the hydrophilic wall.

for the case of pure water, water in the presence of a hydrophilic wall, and water in the presence of a hydrophobic wall. We see that the distribution of H-bonds of water when in the presence of the hydrophilic wall is almost the same as the distribution for pure water. The small shift to the lower number of H-bonds is due to the water-wall bonding that are not computed in the result shown in the picture. For the case of the water in the presence of the hydrophobic wall, we observe a clear shift to higher number of H-bonds per molecule. This is in good agreement to the previous results of the radial distribution functions and density and with the current view of the hydrophobic hydration, that give rise to the hydrophobic interaction.¹²

Conclusions

It appears that the hydrophilic wall induces strong order on the water near to it, forcing the liquid into an icelike structure. This order, however, only extends for a few molecular diameters. In the case of the hydrophobic wall, the ordering effect is milder but extends for several molecular diameters. Such behavior is not surprising considering prior experimental data on the dielectric relaxation of water near hydrophobic compounds.¹³ In such experiments the observed shift in the dielectric relaxation time of water might mean either that the restriction in the rotational correlation time of water is very high, which is unlikely, or that a small change is extended to a relatively large volume, which appears more likely and agrees with the present results.

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