

COMMENTS

Comment on “Molecular Thermodynamics of Hydrophobic Hydration”

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Recently, Besseling and Lyklema¹ have performed a theoretical study of the thermodynamics of hydrophobic hydration. They concluded that the negative hydration enthalpy of apolar molecules is due to a decrease in the number of repulsive non-hydrogen-bonding interactions between neighboring molecules. Moreover, they argued there is a decreased H bonding for hydrophobic surfaces.

Our simulation data, on the contrary, reveal that the presence of a wall composed by nonpolar atoms leads to an increase in the number of four-hydrogen-bonded water molecules. Molecular dynamics simulation of water close to purely hydrophilic and purely hydrophobic walls indicates that the hydrophobic surface has a larger effect on the properties of surrounding water than the hydrophilic surface.² This conclusion also has experimental support.³ To further investigate hydrophobic interactions, we have extended our prior study² by simulating the behavior of water near a purely hydrophobic wall at different temperatures.

Molecular dynamics simulations were run using a modified version of the GROMOS package.⁴ The simulation box was rectangular with the longer axis along the *x* direction. It was randomly filled with water molecules, except that a layer of argon-like atoms perpendicular to the *x* axis was placed at about half of the box length in the *x* direction. These argon-like atoms were positional restrained with a harmonic potential to the fixed spacing of the oxygen in ice Ih. Given our periodic boundary conditions, this layer appears to the water molecules as an infinite wall of nonpolar atoms.

Coupling the system to a hydrostatic bath controlled the pressure. The positions of the walls of the box and the atomic coordinates were adjusted during the run to preserve the internal pressure close to the reference (1 001 325 Pa = 1 atm). To avoid changes in the wall lattice dimensions, corrections were only made in directions perpendicular to the *x* axis. Weak

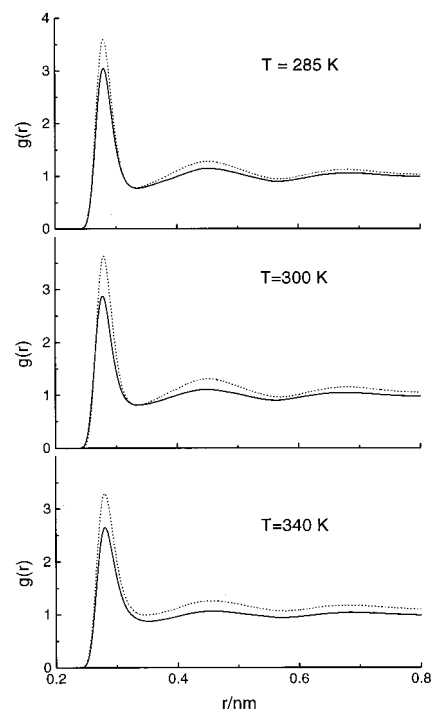


Figure 1. Radial distribution function of water molecules in the presence of a hydrophobic wall at constant pressure and different temperatures: (—) “pure” SPC/E water; (···) water in the presence of the hydrophobic wall.

coupling of the system to a thermal bath controlled the temperature. We used the SPC/E model⁵ for water.

A total number of 576 water molecules were included in a box of initial dimensions of $4.674 \times 1.799 \times 2.196$ nm³. At each temperature, the system was allowed to equilibrate for 10 ps, which is far more than necessary to reach equilibrium; constancy of total energy and box volume served as controls for equilibrium. After equilibrium, the system was run for 40 ps using a time step of 0.002 ps; trajectories were collected every 10 steps.

Figure 1 shows the oxygen–oxygen radial distribution functions for pure water and water with the hydrophobic membrane plotted at different temperatures. The radial distribution function for pure water was obtained with a box of the same size and cutoff and under the same conditions used for the other simulations to avoid any possible difference due to geometry. For each temperature, the presence of the hydrophobic wall produces clear increases in the first, second, and third peaks compared with the case of pure water. At higher temperatures, as expected, the heights of the peaks decrease, but in all cases the presence of the hydrophobic wall makes the peaks better defined. From these results we must conclude that the presence of the hydrophobic wall induces a slight but definite change in the surrounding water.

The network of hydrogen bonds (H bonds) reveals further characteristics of this effect. We have reported² that the presence of a hydrophobic wall displaces the distribution of the

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TABLE 1: Ratio of Frequency of HB of Water in the Presence of the Hydrophobic Membrane over the Frequency in Pure Water

	temp/K		
	285	300	340
1 HB	0.74	0.72	0.59
2 HB	0.82	0.83	0.82
3 HB	0.93	0.93	1.05
4 HB	1.15	1.19	1.41

number of H bonds toward the formation of four H bonds, when compared with the case of pure water. Table 1 shows that this is also the case at different temperatures. Increasing the temperature decreases the absolute number of four-H-bonded water molecules (not shown); however, Table 1 shows that the *relative* number of four-H-bonded molecules increases in each case in the presence of the hydrophobic surface. This shifting of the hydrogen bond distribution to the four-bonded state will be at least one of the causes of the negative entropy of hydrophobic hydration.

The present simulation results do not agree with the predictions of Besseling and Lyklema.¹ The main discrepancy is our finding of a larger hydrogen-bond network in the presence of

the hydrophobic wall. One reason might be that our “wall” is actually a collection of apolar centers, which is closer to reality; the microscopic irregularity of this wall may generate effects different than those arising from an ideal flat surface.

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References and Notes

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