

General View on Solvation in Water and Simple Liquids

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Solubility of hydrophobes in water is very low, but the low solubility itself is not particularly special. There are many pairs of fluids that do not mix. What makes the solvation of nonpolar molecules in water interesting is that the solvation is actually energetically favorable but is entropically so unfavorable that the net solvation free energy is large and positive [1]. This is thermodynamically equivalent to that the solubility becomes even lower as the temperature is raised. This temperature dependence of solubility is well known for noble gases and many hydrocarbons in water at low temperatures.

Microscopic mechanisms of the negative solvation enthalpy of the hydrophobic hydration have long been discussed. Several studies, however, have noted that thermodynamic properties of pure water such as the density maximum at 4°C are the key to understand the hydrophobic hydration [2]. This is consistent with earlier observations that the solvation thermodynamic quantities such as the solvation energy, enthalpy, and entropy are strongly dependent on whether pressure is fixed or volume is fixed in the solvation process [3]. We have demonstrated that under a fixed-volume condition, the solvation of Lennard-Jones (LJ) particles in the LJ solvent is of hydrophobic character in a large region of the solute-solvent interaction parameter space [4]. Here, properties of water as a solvent of nonpolar solutes are compared with those of simple liquids. As shown in Fig. 1, variations of the solvation free energy μ^* of an LJ solute particle in the σ^* , ϵ^* plane for the LJ solvent and water are qualitatively similar to each other. However, the solvation diagrams, which show domains of different types of the solvation, are significantly different as illustrated in Fig. 2. It is shown that this difference comes from smallness of the thermal pressure coefficient of water.

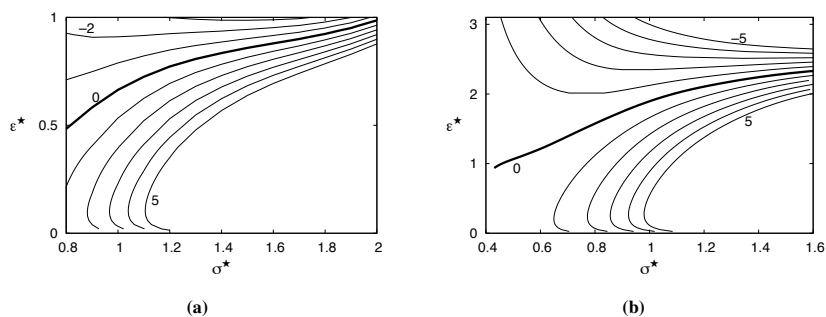


Fig. 1 Contours of μ^*/kT . (a) LJ solute in LJ solvent, (b) LJ solute in water (TIP4P/2005). σ^* , ϵ^* are dimensionless solute-solvent LJ size and energy parameters.

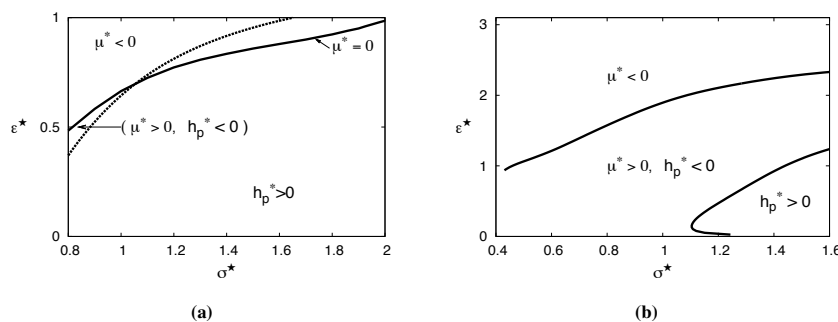


Fig. 2 Solvation diagrams for LJ solutes in (a) LJ solvent and (b) water.

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