Towards an analytical model of hydrophobic hydration

M. Lukšič, B. Hribar-Lee, and T. Urbic

University of Ljubljana, Faculty of chemistry and chemical technology, Aškerčeva c. 5, SI-1000 Ljubljana, Slovenia, E–mail: Miha.Luksic@fkkt.uni-lj.si

A statistical-mechanical model for describing the hydration of a simple hydrophobic solutes is developed. It is founded on an analytical treatment of water [1], residing on a Ben-Naim's image of water molecules [2].

The model is analytical and capable of taking into account the physical harmony between hydrogen bonding and van der Waals interactions. Besides, it considers the orientation-dependent hydrogen bonding of water molecules, which is recognised as crucial in the hydrophobic effect.

Presence of a non-polar solute in water is regarded as a perturbation of the microscopic properties of pure water. In the present model, a water molecule either has no interaction with its neighbour water molecule, or it can form either a hydrogen bond or a van der Waals contact. The solute affects the average energies of these states for water molecules in the first hydration shell, as well as (due to geometric restrictions) it dictates the formation or breakage of hydrogen bonds between the first shell waters.

By writing down the expressions for the partition functions for a water molecule in the bulk and in the first hydration shell of a hydrophobic solute, we were able to calculate the changes in the Gibbs free energy, enthalpy, entropy, and heat capacity as a function of temperature, solute size, and pressure [3]. As validation, we found that the model gives the same trends as Monte Carlo simulations and that it gives agreement with experiments. The advantages of the model are that it allows simple insights into the physics of hydrophobic hydration with the negligible computational time.

1. T. Urbic, K. A. Dill, J. Chem. Phys. 132, 224507 (2010).
2. A. Ben-Naim, J. Chem. Phys. 54, 3682 (1971).
3. M. Lukšič, T. Urbic, B. Hribar-Lee, K. A. Dill, J. Phys. Chem. B, submitted.