

Free energy of solvation via the Widom particle insertion method

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Introduction and Purpose

The anomalous properties of water give rise to many interesting natural phenomena such as the Hydrophobic Interaction. In order to study different aspects of the Hydrophobic Interaction, molecular simulation is used. By understanding the mathematical models behind certain physical interactions, one can predict how similar systems may behave in the real world. One of these, the Hydrophobic Interaction, and particularly the Free Energy of solvation, is of interest. In order to find the Helmholtz free energy of solvation ($\Delta A_{\text{solvation}}$) of a methane molecule in water solvent, Monte Carlo simulation in conjunction with the Widom test particle insertion method is employed.

It was found that $U_{\text{system}} = 66$ (nondimensional) at 300K compared to $U_{\text{system}} \sim 66$ as found by A. Chaimovich. This discrepancy may be due to the lack of a tail correction used in the simulations here. It was found that the corresponding $\Delta A_{\text{solvation}} = 66$ kJ/mol at 300K. This point was found to be close to a minimum vs. varying temperature.

Theoretical Models

Two interaction models are used in this simulation – one for water-water interactions, and one for water-methane interactions. Water-water interactions are modeled by the superimposed Lennard-Jones and Gaussian (LJG) interaction potential,

$$U_{LJG} = 4\epsilon \left[\left(\frac{r}{\sigma} \right)^{-12} - \left(\frac{r}{\sigma} \right)^{-6} \right] + B \times \exp \left(\frac{-(r-r_0)^2}{\Delta^2} \right), \quad (1)$$

where ϵ and σ are the Lennard-Jones parameters, and B , r_0 , and Δ are the Gaussian function scales. These parameters, determined by M. S. Shell's relative entropy minimization method, are used to model water as coarse-grained spheres while still retaining water's unique properties [1].

Modeled slightly differently, the methane-water interactions employ just a simple Lennard-Jones (LJ) interaction potential,

$$U_{LJ} = 4\epsilon \left[\left(\frac{r}{\sigma} \right)^{-12} - \left(\frac{r}{\sigma} \right)^{-6} \right], \quad (2)$$

with parameters determined by optimizing the fully-atomic water model in order to be used with coarse-grained water as explained in *The search for the hydrophobic force law* [2]. All the parameters used in simulation are tabulated in Appendix I.

Algorithm

These are canonical NVT simulations in which, 216 water molecules are placed in a cubic box with periodic boundary conditions whose volume is determined by the density of liquid water approximated as $\rho_{H_2O} = 1000$ kg/m³. The maximum Monte Carlo move displacement dr is 0.013L.

Once the potential energy equilibrates, the Widom test particle insertion method is employed in order to calculate the Helmholtz free energy of solvation ($\Delta A_{\text{solvation}}$). This method

consists of randomly inserting a methane particle in the simulation box at equally spaced intervals of moves (time), and calculating the change in potential in order to calculate the excess chemical potential μ_{ex} according to

$$\beta\mu_{ex} = -\ln \langle e^{-\frac{\Delta U}{kT}} \rangle. \quad (3)$$

Then, since

$$\mu_{ex} = \left(\frac{dA}{dN} \right)_{V,T} \approx \left(\frac{\Delta A}{\Delta N} \right)_{V,T}, \quad (4)$$

and $N = 1$, the following equation,

$$\Delta A = \mu_{ex}, \quad (5)$$

is used to calculate $\Delta A_{\text{solvation}}$.

Results and Discussion

As seen in Figure 1, the potential energy of the systems equilibrate by 100,000 Monte Carlo steps. Once equilibrium was reached, Widom test particle insertion commenced.

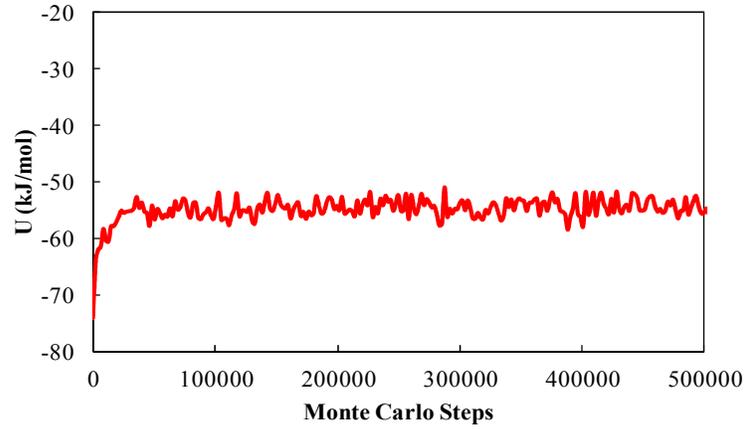


Figure 1. Sample potential energy vs. MC steps at 280K.
The system energy equilibrates by 100,000 MC steps.

In the execution of this experiment, two parameters, temperature and ϵ were varied. Due to the dependence of LJG parameters on temperature, the water-water interaction varies. ϵ was varied so that the methane-water attraction increases to see if a more “hydrophilic” methane solvates more easily in water. As seen in Figure 2, effect does seem to emerge. When ϵ is doubled, the $\Delta A_{\text{solvation}}$ does decrease indicating that it is easier for methane to solvate.

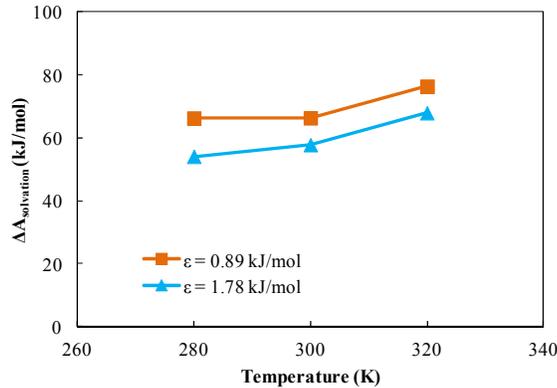


Figure 2. $\Delta A_{\text{solvation}}$ vs. Temperature. The change in free energy of solvation increases as temperature goes up.

As seen in Figure 2, the energy needed for solvation increases as temperature rises. This can be explained by LJ interaction model and how this simulation is designed. As detailed in Appendix I, ϵ_{water} decreases as temperature goes up. Since temperature is in the denominator of equation 3 and ΔU is always positive, as temperature increases the value of the exponential does too. This, in turn increases the values calculated for μ_{ex} and therefore $\Delta A_{\text{solvation}}$. Additionally, since these simulations employ NVT ensembles, inserting particles into a simulated liquid phase without increasing the volume can alter the results. In a future study, the pressure may be tracked to observe the fluctuations in the simulation.

Unfortunately, due to simulation time constraints, statistical precision cannot be confirmed since only a few conditions were run for a relatively small number of MC steps. Expanding the temperature domain as well as probing larger methane-water interaction parameters, may further validate trends seen here. During further study, a longer-running, more statistically absorbent algorithm can be run to produce better averages with appropriate error analysis.

References

- 1. Anomalous waterlike behavior in spherically-symmetric water models optimized with the relative entropy.**
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- 2. The search for the hydrophobic force law**
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- 3. Frenkel, D., & Smit, B. (2002). *Understanding molecular simulation: from algorithms to applications* (2. ed.). San Diego, Calif. [u.a.: Acad. Press.**
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Appendix I: Parameters

Table 1. Lennard-Jones and Gaussian parameters for water-water interactions [1,2].

T(K)	ρ (g/L)	σ (Å)	ϵ (kJ/mol)	ϵ (kJ/mol)	r_0 (Å)	Δ (Å)
240	1000	2.41	24.662	28.424	2.47	1.09
280	1000	2.42	22.572	25.916	2.45	1.1
300	1000	2.43	20.482	23.408	2.46	1.09
320	1000	2.43	19.646	22.99	2.44	1.11
350	1000	2.44	17.556	20.482	2.46	1.09

Table 2. Lennard-Jones parameters for methane-water interactions.

σ (Å)	ϵ (kJ/mol)
3.45	0.89