Probing the Hydrophobic Interaction Overlap Limit

Katie Weiss[1], Lalitanand Surampudi[2], Hank S. Ashbaugh[3]
[1]Alfred University, Alfred, New York, 14802
[2]Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, LA 70118

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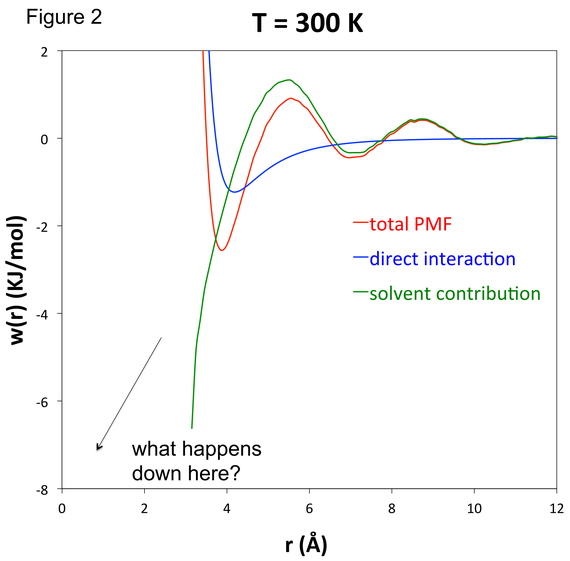
The adage "oil and water don't mix" succinctly captures the phenomenology underlying the hydrophobic effect that drives assembly in aqueous environments, including surfactant micellization, globular protein folding, biomembrane formation, and the environmental fate of pollutants. In this study we have examined the solvent's role in methane/methane interactions in liquid water as an idealized system for teasing apart the thermodynamics of hydrophobic association. We have performed computer simulations over a wide range of temperature (figure 1), from the freezing point to the boiling point of water, to examine the entropic and enthalpic signatures associated with hydrophobic interactions.

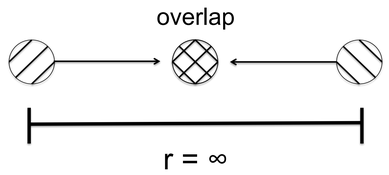
Specifically, we have developed a new approach to extract water's contribution to methane hydrophobic interactions (figure 2) from distant separations probed directly by computer simulations to the overlap limit that simulations do not directly observe (figure 3). This new approach takes an interpolative perspective to examine water mediated interactions in the unobserved overlap limit by obtaining the free energy of two methanes in complete overlap (no separation) and using a polynomial to bridge from the overlap limit to the observed behavior at finite separations. We performed computer simulations of a single methane and methane with twice the interaction strength (figure 4) to evaluate the overlap free energy using thermodynamic integration (figure 5). These calculations are providing new insights into the differences between hydrophobic hydration (solvation of a single methane) and the hydrophobic interaction between two methanes.

Figure 2



$$w(r) = -RT\ell n\, g(r)$$
$$= \varphi_{direct}(r) + \varphi_{solvent\ mediated}(r)$$
$$\varphi_{direct} = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

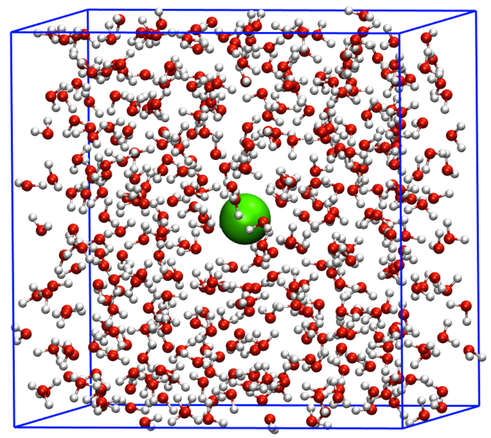
What is the process?



$$\Delta G = G(2\times direct) - 2\bullet G(1\times direct)$$

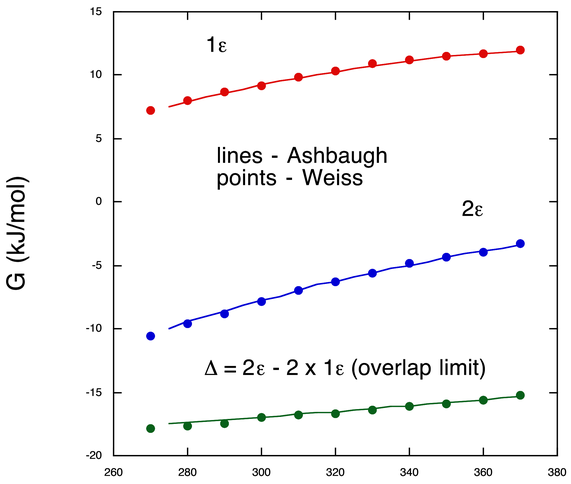
Two methane molecules are brought together for complete overlap with the goal of determining the intercept of $\varphi_{solvent\ mediated}$

Figure 4



Snapshot of simulation with methane (green) in a water box of hydrogen (white) and oxygen (red).

Figure 5



Lennard Jones Potentials of the limit of the solvent contribution as the PMF approaches infinity.

Figure 1

Methane/Methane interaction of methane in a water box shows curious increasing clustering with increasing temperature.

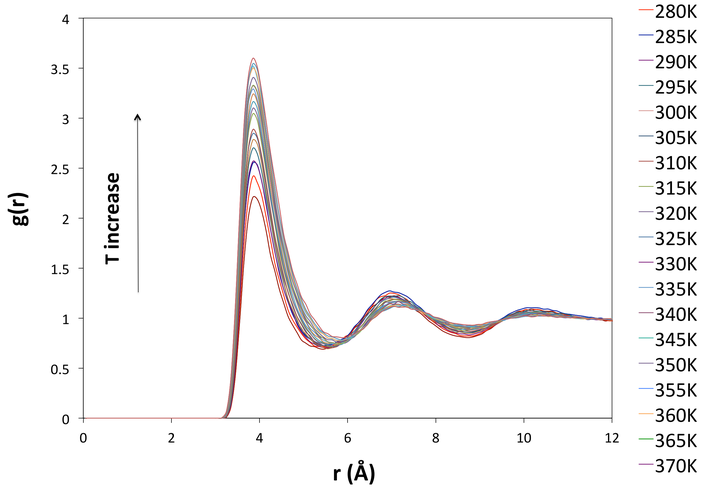
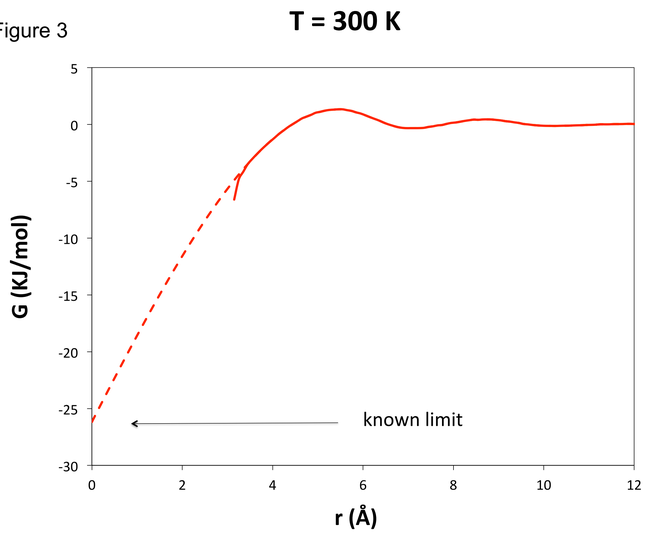


Figure 3



Dotted line is interpolated by knowing the end point.

Conclusions

- Our new polynomial interpolation (figure 3) permits a smooth and accurate description of solvent mediated interactions over all separations
- The success of this interpolation lies with the ability to accurately evaluate the free energy of bringing two methanes from infinitely far away to direct overlap (figure 5)

Acknowledgements

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Tulane University

Alfred University