

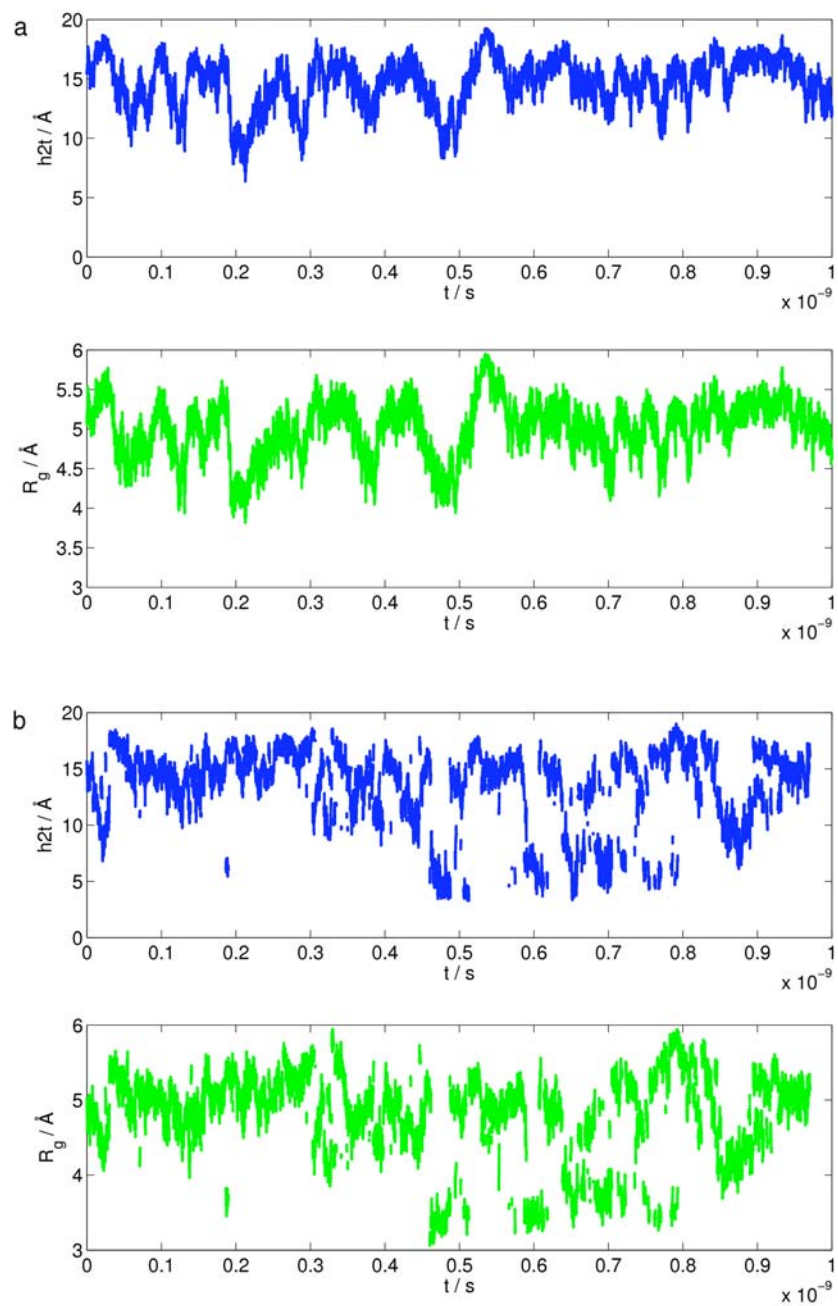
# Supplementary Information

## Solubility and Molecular Conformations of $n$ -Alkane Chains in Water

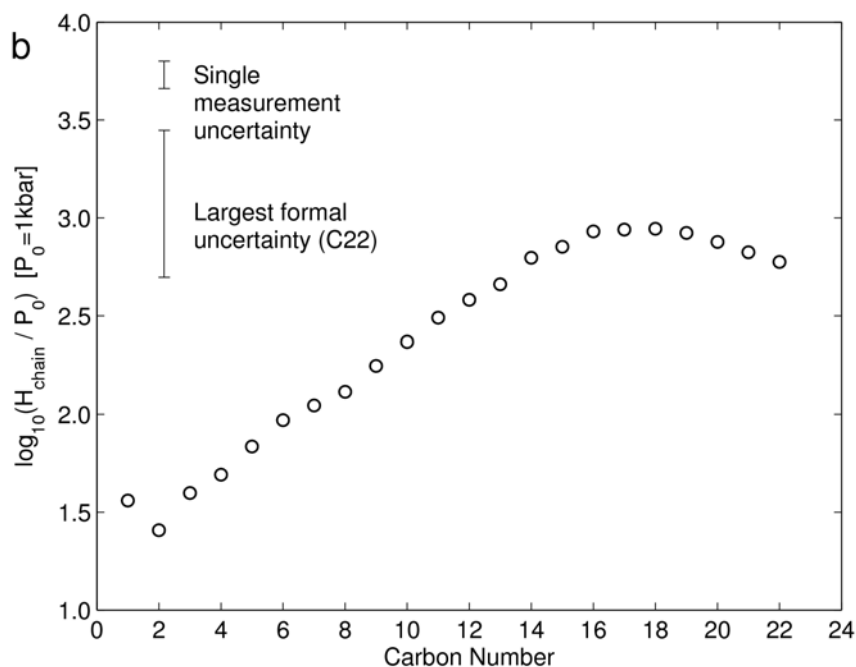
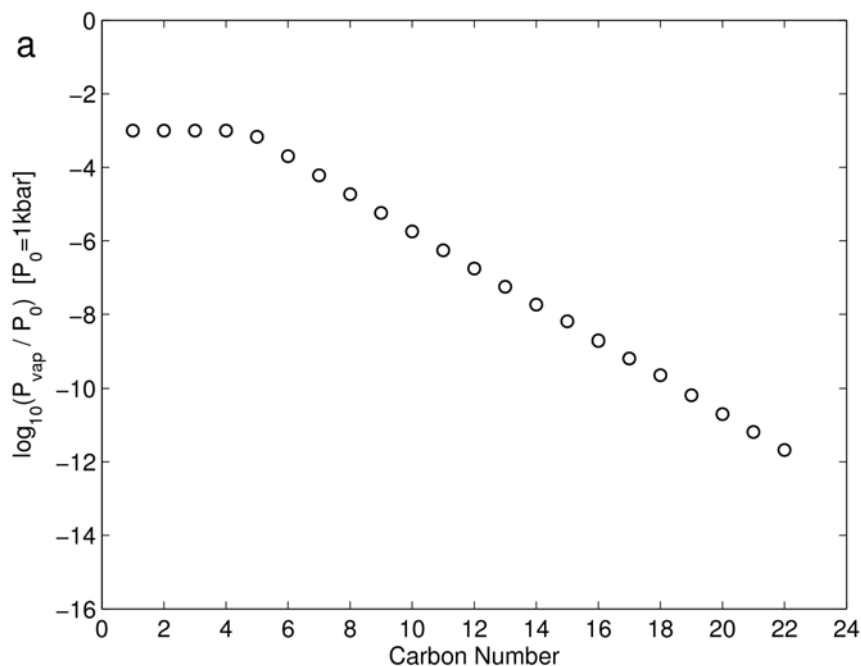
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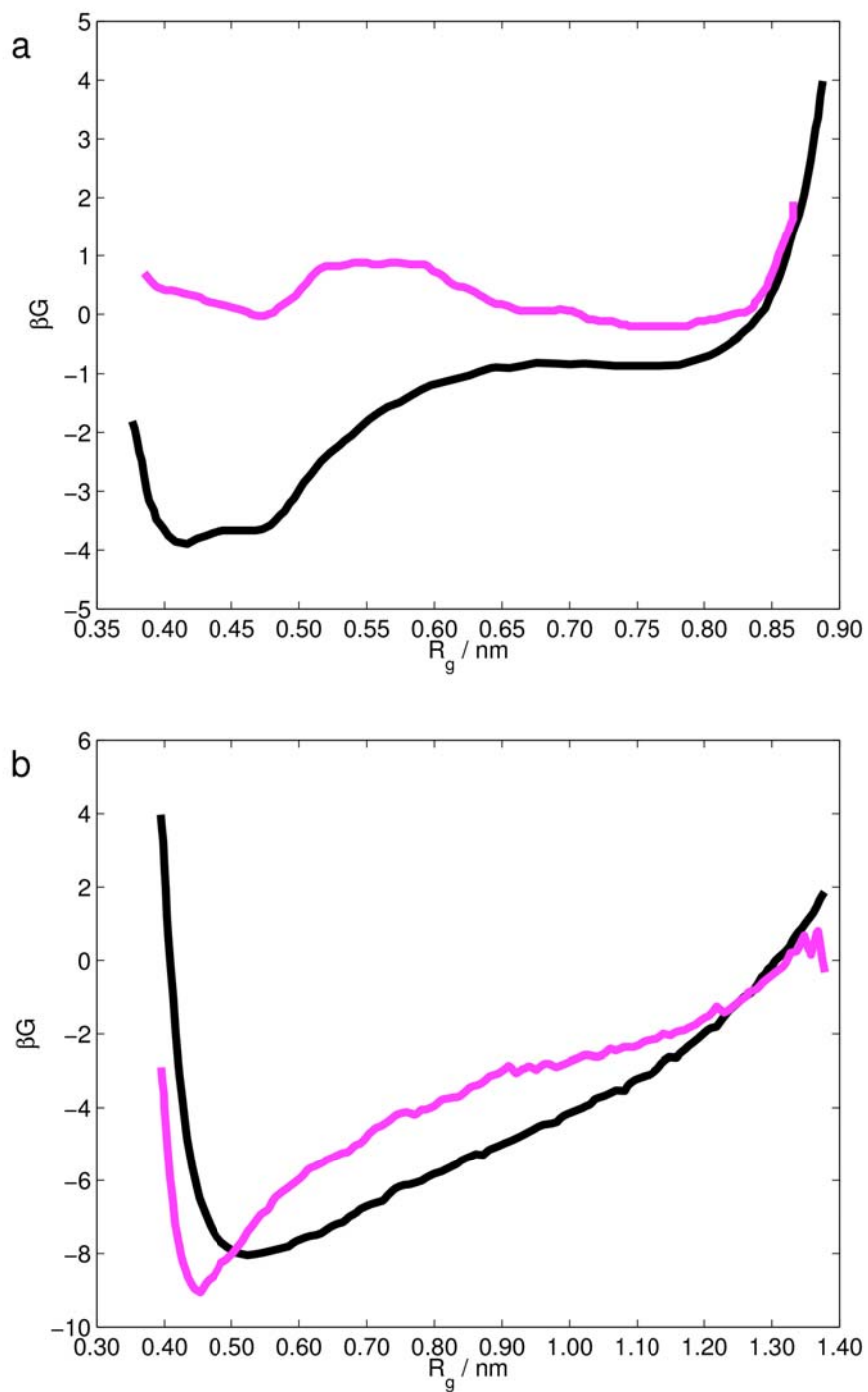


**Figure S1.** Trajectories of head to tail distance,  $h_{2t}$ , and radius of gyration,  $R_g$ , for  $n$ -hexadecane ( $C_{16}$ ) in water at 298K and 1 bar throughout 1ns (a) MD and (b) REMD simulations.



**Figure S2.** Variation of vapor pressure and Henry's constant in aqueous solution for  $n$ -alkanes at 298K and 1 bar. (a) Logarithm of the dimensionless  $n$ -alkane vapor pressure,  $P_{\text{vap}}/P_0$ , at 298K and 1 bar as a function of carbon number, where  $P_0=1\text{kbar}$  is an arbitrary constant which serves to non-dimensionalize the argument of the logarithm. Vapor pressures are calculated from standard literature expressions, as described in the main text. Methane ( $C_1$ ) through  $n$ -butane ( $C_4$ ) are gases at 298K<sup>1,2</sup> while  $n$ -pentane

(C<sub>5</sub>) through *n*-heptadecane (C<sub>17</sub>) are liquids under these conditions<sup>1, 2</sup>. For *n*-octadecane (C<sub>18</sub>) and heavier chains, the stable phase is a solid<sup>1,2</sup>, but we have treated them as supercooled liquids so as not to introduce a discontinuity in the vapor pressure trend due to a phase change. (b) Logarithm of the dimensionless Henry's constant,  $H_{chain}/P_0$ , for *n*-alkanes in water at 298K and 1 bar as a function of carbon number, where  $P_0=1\text{kbar}$  is the same arbitrary constant described above. Henry's constants were calculated using the methods described in the main text. The uncertainty associated with each point on the plot – the single measurement uncertainty – was estimated from the standard deviation of the results of five independent simulations for *n*-tetradecane (C<sub>14</sub>). The error bar associated with the *n*-docosane (C<sub>22</sub>) result represents the largest formal uncertainty associated with any single result, computed from the propagation of uncertainties through the incremental Widom insertion calculation.



**Figure S3.** Free energy landscapes for 25mer hydrophobic polymers in the ideal gas at 298K (black curves) and in aqueous solution at 298K and 1 bar (pink curves) at infinite dilution determined by Athawale et al.<sup>3</sup>. Since these simulations were conducted under conditions of constant temperature and pressure, the pertinent free energy is the Gibbs free energy,  $G$ ,  $\beta = 1/(k_B T)$  and  $R_g$  is the radius of gyration. Comparison between the constant pressure simulations of Athawale et al. and the constant

volume simulations of the current study are valid since the simulation boxes considered in the current work were sufficiently large that conformational changes in the alkane chain had negligible impact on the pressure, and the  $pV$  contribution behaves, to an excellent approximation, as an additive constant for comparative purposes. (a) Free energy landscapes for a 25mer composed of methane-like monomers with a harmonic bond stretching potential, a harmonic bond bending potential and dispersion interactions between non-bonded monomers. (b) Free energy landscapes for a 25mer composed of ethane-like monomers with a harmonic bond stretching potential and dispersion interactions between non-bonded monomers.

## References

- (1) Perry, R. H.; Green, D. W. *Perry's Chemical Engineers' Handbook*; McGraw-Hill: New York, 1997.
- (2) Thermodynamics Research Center, NIST Boulder Laboratories, M. Frenkel director (2005) "Thermodynamics Source Database" in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, eds Linstrom PJ, Mallard WG (National Institute of Standards and Technology, Gaithersburg MD, 20899 (<http://webbook.nist.gov>))
- (3) Athawale, M. V.; Goel, G.; Ghosh, T.; Truskett, T. M.; Garde, S. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 733-738.