

Concentration dependence of the Flory-Huggins interaction parameter in aqueous solutions of capped PEO chains

Lawrence R. Pratt

Department of Chemical & Biomolecular Engineering



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Molecular Stat-Mech from La Nouvelle-Orléans

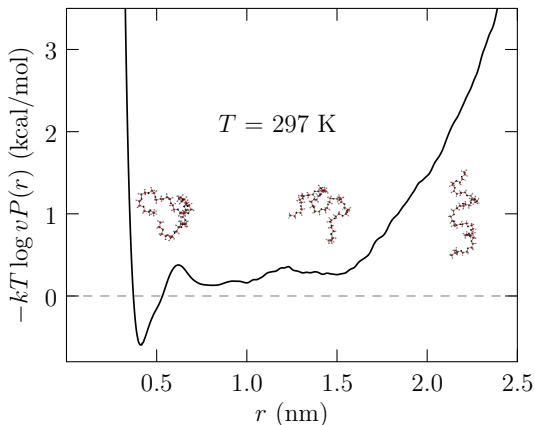


FH $\chi(\varphi)$ in aqueous solutions

Abstract

- 1 For aqueous solutions, the FH interaction 'constant' $\chi(\varphi)$ is a strong function of composition φ , thus the FH theory is not naively correct.
- 2 A principal reason for this is that a vdW picture fails for typical aqueous conditions.
- 3 For aqueous solutions, a focus on the small molecule solvent (the water) can be effective, avoids direct polymer stat-mech, and connects to osmotic stress experiments.

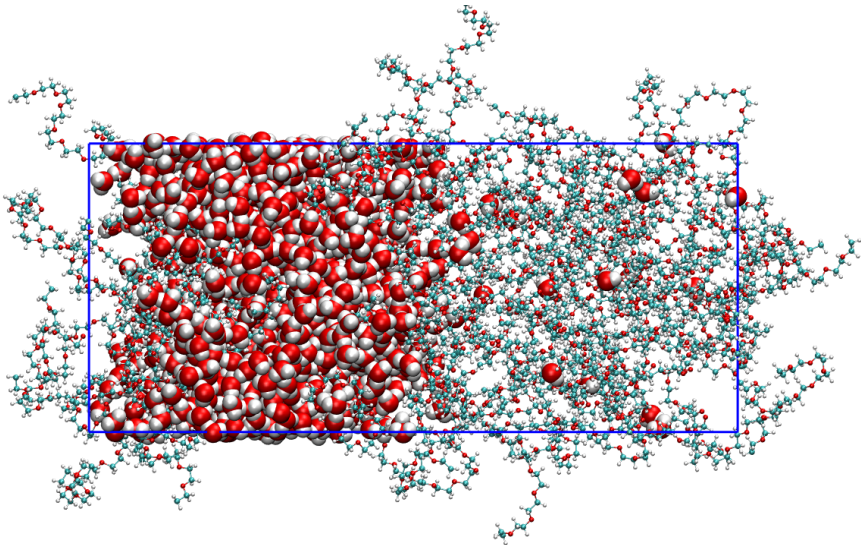
Capped PEO (aq): classic hydrophobic bond



¹M. I. Chaudhari and L. R. Pratt, OIL SPILL REMEDIATION: COLLOID CHEMISTRY-BASED PRINCIPLES AND SOLUTIONS, pp. 247-257, editors P. Somasundaran, R. S. Farinato, P. Patra, and K. Papadopoulos (John Wiley & Sons, Hoboken New Jersey, 2014): "Microstructures of capped ethylene oxide oligomers in water and n-hexane."

[See: <http://arxiv.org/abs/1303.6597> and <https://dx.doi.org/10.6084/m9.figshare.3123898.v1>]

High concentrations (here $m=11$, $M = 27.6$)



Flory-Huggins $\chi_{wp}(\varphi)$

1 FH theory

$$\frac{\beta \Delta G_{\text{mix}}}{n_w + Mn_p} = \varphi \ln \varphi + \frac{(1 - \varphi)}{M} \ln (1 - \varphi) + \varphi (1 - \varphi) \chi_{wp}$$

2 'w' = solvent (water), 'p' = polymer (internally complicated)

3 p = PEG, $\chi_{wp}(\varphi)$ dependence on φ .

- strong for water
- substantial for methanol (but different from water)
- weak for ethanol. Of course, PEG =
 $\text{H} - (\text{CH}_2 - \text{CH}_2 - \text{O})_M \text{H}$

Solution: follow the water

- The water reports on the polymer as in osmotic stress approaches:

$$\beta \Delta \mu_{\text{w}}^{(\text{ex})} = -\ln \varphi - \beta \pi \bar{v}_{\text{w}}$$

- Retain the concentration dependence of $\chi_{\text{wp}}(\varphi)$:

$$\beta \Delta \mu_{\text{w}}^{(\text{ex})} = \left(1 - \frac{1}{M}\right) (1 - \varphi) + \frac{\partial (\varphi \chi_{\text{wp}})}{\partial \varphi} (1 - \varphi)^2$$

- In the low p-concentration limit ($p_{\text{solution}} = \text{constant}$)

$$\frac{\beta \pi V}{n_{\text{p}}} \sim 1 + \left(\frac{n_{\text{p}}}{V}\right) \bar{v}_{\text{w}} M^2 \left(\frac{1}{2} - \frac{\partial (\varphi \chi_{\text{wp}})}{\partial \varphi}\right)$$

Liquid water is an easy case by now.

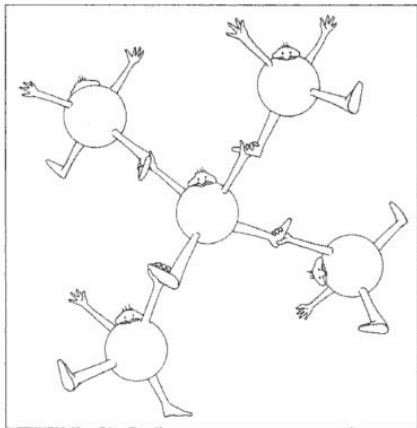
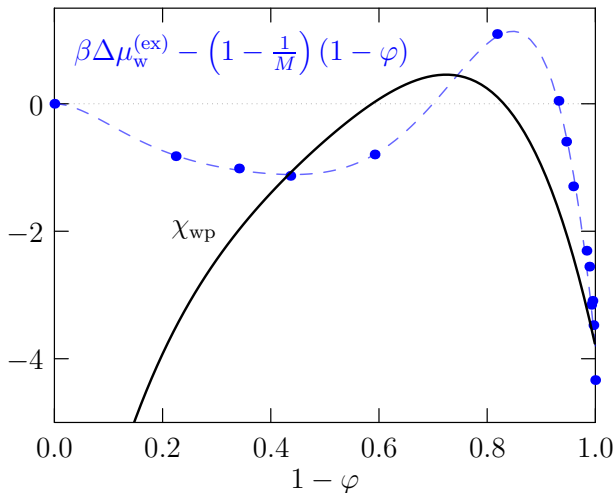


Figure 6.5 Water molecules—with hands representing hydrogens and feet representing lone pairs of electrons—perform a dance that involves grabbing neighbors by the ankles. These clasps, due to hydrogen bonding, lead to a tetrahedral arrangement of neighbors around each molecule. This is the central motif of the structure of water, and the key to all its anomalous properties.

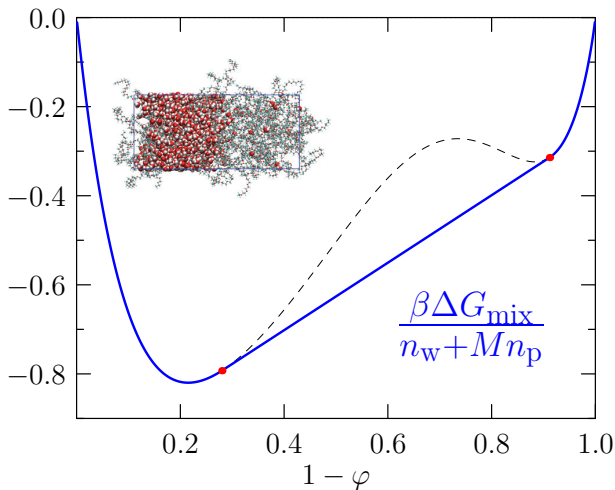
- P Ball, LIFE'S MATRIX: A BIOGRAPHY OF WATER (University of California Press, 2001)

Results

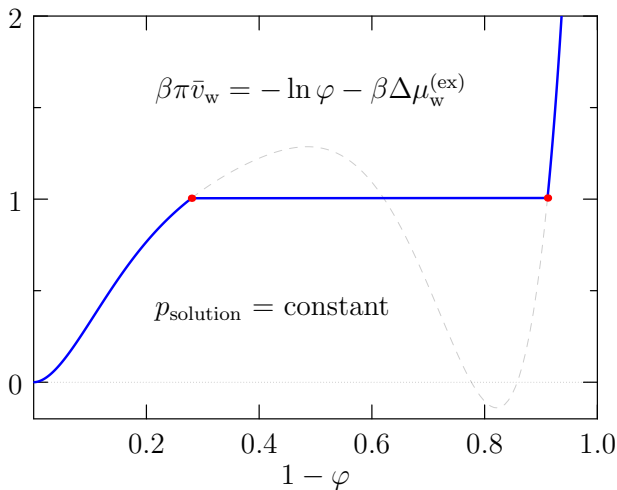


¹MI Chaudhari, LR Pratt, and ME Paulaitis, "Concentration dependence of the Flory-Huggins interaction parameter in aqueous solutions of capped PEO chains," *J. Chem. Phys.* **141**, 244908 (2014).

Predicted/confirmed water-PEO phase separation



Osmotic pressure ($p_{\text{solution}} = \text{constant}$)



Conclusions

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