SOLVENT MEDIATED INTERACTIONS - SOLUTE SIZE EFFECTS 
AND PREDICTIONS OF MEAN FIELD THEORY 

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We investigate the effects of solute/solvent size ratio on the solvent mediated potential of mean force between solutes at infinite dilution. Predictions of Landau-Ginzburg mean field theory are compared with a Percus-Yevick-hypemetted chain 
theory of a mixture of infinitely dilute hard sphere solutes in a solvent of hard spheres with surface adhesion (sticky spheres).

The study of solvent mediated (structural) interactions began with Langmuir [1] and encompasses a host of problems in colloid science and solution theory. The systems of interest, for instance ion-dipole mixtures and hydrophobic solutions, are complex and there is a need for simple theories which capture the essence of solvent effects on solute-solute interactions. Recent progress includes the direct experimental observation of structural forces in aqueous systems [2,3] and the application of simple mean field theory [4-6] and liquid state theories [7] to model systems. Other studies include Monte Carlo calculations with a model water solvent [8] and studies of ion-ion interactions in a dipolar solvent [9-12]. Deutch and co-workers [13] have used the hypemetted chain equation to investigate the interaction of hard sphere solutes in a solvent of equal size hard spheres with a Yukawa potential attraction. They found that the infinite dilution solute-solute potential of mean force changed from an oscillatory to nearly monotonic form as the solvent-solvent attraction was increased. They also observed the solvent depletion near a solute molecule usually associated with monotonic interactions [7] as did Sullivan and Stell [14].

Our previous studies of structural interactions [7] in model solvent systems were for large solute particles (walls) since this simplified the analysis. Here we extend this study to finite size solutes and show that the results are essentially independent of solute size. Further we compare the predictions of liquid state theories directly with the simpler mean field theory.

Consider then an infinitely dilute hard sphere solution of species 2 of diameter $R_2$ in a solvent (species 1) with number density $\rho_1$ and diameter $R_1$. The pair potential is taken to be a surface adhesion ("sticky spheres") [1,2]

$$\exp\left[-\frac{u_{ij}(r)}{kT}\right] - 1 = -1 + \left(\frac{R_{ij}}{12\tau_{ij}}\right) \delta(r - R_{ij}), \quad r \leq R_{ij};$$

$$= 0, \quad r > R_{ij},$$

where $R_{ij} = (R_i + R_j)/2$ and $\tau_{ij}$ measures the strength of the adhesion. The form of eq. (1) ensures that the analysis of this model fluid is simple yet retains the essential physics of the problem; e.g. the model exhibits a realistic liquid-gas phase transition [16]. We seek the solute-solute potential of mean force, $W_{22}$, at infinite dilution from the Ornstein-Zernike equation ($\rho_2 \to 0$):

$$h_{22}(r) = C_{22}(r) + \rho_1 \int dr' h_{12}(r - r') C_{11}(r'),$$

where $h_{ij}$ and $C_{ij}$ are respectively the total and direct correlation functions. Successive use of the Percus-Yevick (PY) and hypemetted chain (HNC) approximations for $C_{22}$ allow the identification [7]
Fig. 1. Potential of mean force \( W_{22} \) between two hard sphere solutes in a sticky sphere solvent at infinite dilution with \( \rho^* = 0.7, T^* = 1.0 \) (low pressure) and solute/solvent size ratio \( R_2/R_1 \): (a) 0.1, (b) 1.0, (c) 5 and (d) \( \infty \). The dotted curve corresponds to the case \( R_2/R_1 = 1 \) in which the solute—solvent adhesion is one quarter of that between solvents.

\[
W_{22}^{\text{HNC}}(r) = -kT \ln \frac{\rho_{22}^{\text{PY}}(r)}{\rho^*},
\]
when \( u_{22}(r) = 0 \).

In this calculation we use the more readily accessible PY solutions [7,15,17] to eqs. (1) and (2) to yield \( W_{22}^{\text{HNC}} \) via eq. (3). Unlike \( W_{22}^{\text{PY}}, W_{22}^{\text{HNC}} \) is well-behaved for all \( R_2/R_1 \), and satisfies the Deryaguin approximation [19]; i.e. \( (R_1/R_2) W_{22}^{\text{HNC}} \) becomes independent of \( R_2 \) as \( R_2/R_1 \to \infty \). We solve eq. (2) using Baxter’s technique [7,15–17,20]. For any specified solvent reduced density, \( \rho^* = \rho R_1^3 \), the solvent—solvent adhesion \( (T_{11}) \) is chosen to yield the same second virial coefficient as a Lennard-Jones fluid with reduced temperature \( T^* = kT/\epsilon \) [7].

In figs. 1 and 2 the effect of solute/solvent size ratio on \( (R_1/R_2)W_{22} \) is shown for low and high pressures, respectively. For hard sphere solutes \( (T_{12}, T_{22} \to \infty) \) \( W_{22} \) is monotonic and becomes oscillatory as the solute—solvent interaction becomes attractive although this effect is less pronounced as \( R_2/R_1 \) increases. It is clear that \( W_{22}/R_2 \) is not strongly dependent on \( R_2 \).

As the solvent—solvent attraction increases (smaller \( \tau_{11} \)) the solute—solute attraction also increases. These results indicate that our earlier studies [7] of the interaction of large solutes (walls) do bear upon finite size solutes. However, for more strongly correlated solvents, such as water, the different clathrate cages formed about small solutes [21] and near interfaces require more detailed study.

So far our results have provided some insight into the conditions under which we can expect to find oscillatory or monotonic forms of \( W_{22} \), but calculations for more realistic potentials rapidly become impossible. It is therefore desirable to have a simple analytic theory of solute—solute interactions due to solvent structure. This possibility has been foreshadowed in a recent mean field theory based on the Landau—Ginzburg formalism [4–6]. When solute induced perturbations of solvent structure in an infinitely dilute solution are small and slowly varying, mean field theory predicts an essentially exponential form for \( W_{22} \) with a decay length \( \xi \) given by [6]

\[
\xi^2 = \frac{\rho_1}{\rho_1 + 1} \int h_{11}(r) r^2 dr,
\]

which depends only on the properties of the pure solvent. The predictions of eq. (4) are compared in table 1 with decay length for exponential interaction energies for large solutes (hard walls) separated by sticky sphere and Lennard-Jones fluids [7]. For the sticky sphere fluid \( \xi \) was calculated using PY \( h_{11} \) while for the Lennard-Jones case Monte Carlo calculations of \( h_{11} \) were used. The agreement is good even though \( \xi \) is only of the order of a molecular diameter. This is remarkable since, strictly speaking, mean field theory should only be valid when the correlation length is of the order of many molecular diameters [6].

A direct test of the mean field theory prediction of \( W_{22} \) for large solutes is presented in fig. 3 for the most favourable case; i.e. for low pressures when \( \xi = O(2R_1) \). Taking the order parameter (a concept invoked in the mean field theory) as the local solvent density about a solute, \( \delta \rho/\rho = h_{12}(r) \), mean field theory predicts [6]...
Table 1
Comparison at decay lengths predicted by eq. (4) and determined from exponential interaction energies for large hard sphere solutes interacting across model solvents

| ρ* | T* | ε/|R_1| | mean field theory | numerical |
|-----|-----|----------------|-----------------|-------------------|-----------|
| 0.5 | 1.3 | 1.79           | 1.81            |
| 0.7 | 1.3 | 0.77           | 0.81            |
| 0.7 | 1.0 | 1.40           | 1.43            |
| 0.75| 1.05| 0.92           | 0.95            |
| 0.85| 1.3 | 0.44           | 0.54            |

Lennard-Jones fluid

| 0.75 | 1.07 | 1.8 | 1.5 |

The interaction energy per unit area between two planar surfaces to be

\[ E = \frac{2\epsilon h^{2}_{12}(0)}{\kappa} \frac{e^{-\eta/\xi}}{1 + e^{-\eta/\xi}}, \]

where \( \xi \) is given by eq. (4) and \( \kappa \) is the bulk solvent isothermal compressibility. Use of the Deryaguin relation [19] then yields the potential of mean force between two large solutes (\( R_2 \to \infty \))

\[ W_{22}/R_2 = -\frac{2\pi h^{2}_{12}(0)}{\kappa} \eta^2 \ln(1 + e^{-\eta/\xi}). \]  

The quantities \( h^{2}_{12}(0) \), \( \xi \) and \( \kappa \) are calculated using the PY equations for a sticky sphere fluid [7] against a hard wall. The comparison in fig. 3 indicates that the mean field theory underestimates the \( W_{22}^{\text{HNC}} \) by about 30% consistent with uncertainties usually found with the PY and HNC theories. It appears that a major difficulty with the mean field theory here, and with small solutes, is in specifying the boundary value of the order parameter, here taken as \( h^{2}_{12}(0) \). For the case of a solvent near a hard wall we have the exact result \( h^{2}_{12}(0) = (\rho P/\rho - 1) \) where \( P \) is the pressure of the solvent. In addition the assumption of a constant boundary condition, independent of solute separation, may be too restrictive [6]. None the less the comparison in fig. 3 is an honest test of the mean field theory.

We have investigated the effects of solute/solvent size ratio on the solute—solute potential of mean force at infinite dilution using a PY—HNC approximation for a system of sticky spheres. The scaled potential of mean force \( (R_1/R_2)W_{22} \) is not strongly dependent on the size ratio. We have also shown that a very simple mean field theory is capable of giving a reasonable description of the solute—solute potential of mean force. This encourages the search for a simple analytic description of solvent mediated solute—solute interaction that does not require extensive numerical computations.

References
