

### 1. Pratt-Chandler theory of the hydrophobic effect

In class we derived the central equations of Pratt and Chandler's theory for small hydrophobic solutes in aqueous solution:

$$h_{AW}(r) = c_{AW}(r) + \bar{\rho}_W \int d\mathbf{r}' h_{WW}(|\mathbf{r} - \mathbf{r}'|) c_{AW}(r') \quad (1)$$

with

$$\begin{aligned} c_{AW}(r) &= 0, & r > R \\ h_{AW}(r) &= -1, & r < R. \end{aligned} \quad (2)$$

$h_{AW}(r) = g_{AW}(r) - 1$  quantifies the average solvent density at a distance  $r$  away from a solute's center. Each solute molecule (denoted A) excludes water molecules (denoted W) from a sphere of radius  $R = (\sigma_W + \sigma_A)/2$ , where  $\sigma_A$  and  $\sigma_W \approx 2.7 \text{ \AA}$  are the van der Waals diameters of solute and solvent molecules, respectively.

We will take the water response function  $h_{WW}(r)$  to be known from experiment, so that Eqs. 1 and 2 determine the direct correlation function  $c_{AW}(r)$ . In this problem you will solve for  $c_{AW}(r)$  numerically.

We begin by writing  $c_{AW}(r)$ ,

$$c_{AW}(r) = \sum_{n=0}^{n_{\max}} c_n \phi_n(r),$$

as a linear combination of  $n_{\max} + 1$  continuous basis functions  $\phi_n(r)$  that each vanish when  $r > R$ :

$$\phi_n(r) = \begin{cases} \left(\frac{r-R}{R}\right)^n, & r < R, \\ 0, & r > R. \end{cases}$$

Representing  $c_{AW}(r)$  exactly would require a complete basis set, i.e.,  $n_{\max} \rightarrow \infty$ . It is more practical of course, to use a small number of basis functions. For our purposes,  $n_{\max} = 3$  provides an accurate solution at very modest computational expense.

(i) Using a computer, solve the set of linear equations that determine  $c_0$ ,  $c_1$ ,  $c_2$ , and  $c_3$ ,

$$\begin{aligned} \int d\mathbf{r}' \phi_n(r') &+ \sum_m c_m \int d\mathbf{r}' \phi_n(r') \phi_m(r') \\ &+ \sum_m c_m \bar{\rho}_W \int d\mathbf{r}' \int d\mathbf{r}'' \phi_n(r') h_{WW}(|\mathbf{r}' - \mathbf{r}''|) \phi_m(r'') = 0, \end{aligned} \quad (3)$$

for solute sizes  $\sigma_A = 2.7 \text{ \AA}, 2.8 \text{ \AA}, \dots, 7.3 \text{ \AA}$ . You will make use of these results in later parts of this problem. For now, just report your expansion coefficients,  $c_n$ , for  $\sigma_A = 3.0 \text{ \AA}, 4.0 \text{ \AA}$  and  $5.0 \text{ \AA}$ .

Narten and Levy's X-ray scattering results for  $\hat{S}_{WW}(k) - 1 = \bar{\rho}_W \hat{h}_{WW}(k)$  at  $T = 25^\circ\text{C}$  and  $\bar{\rho}_W = 0.033 \text{ \AA}^{-3}$  have been provided on the course website as input for your calculations. (The units of wavevector  $k$  in the file "narten\_levy" are  $\text{\AA}^{-1}$ .) Note that the multidimensional integral in Eq. 3 can be evaluated most easily in Fourier space, since

$$\int d\mathbf{r}' \int d\mathbf{r}'' \phi_n(r') h_{WW}(|\mathbf{r}' - \mathbf{r}''|) \phi_m(r'') = \frac{4\pi}{(2\pi)^3} \int_0^\infty dk k^2 \hat{\phi}_n(k) \hat{h}_{WW}(k) \hat{\phi}_m(k). \quad (4)$$

Some analytical results for the suggested basis functions are provided below for your convenience.

$$\begin{aligned}(4\pi)^{-1}\hat{\phi}_0(k) &= \frac{\sin(kR)}{k^3} - \frac{R\cos(kR)}{k^2} \\(4\pi)^{-1}\hat{\phi}_1(k) &= \frac{\sin(kR)}{k^3} + \frac{2(\cos(kR) - 1)}{Rk^4} \\(4\pi)^{-1}\hat{\phi}_2(k) &= -\frac{6\sin(kR)}{R^2k^5} + \frac{2\cos(kR) + 4}{Rk^4} \\(4\pi)^{-1}\hat{\phi}_3(k) &= -\frac{6\sin(kR)}{R^2k^5} + 24\frac{1 - \cos(kR)}{R^3k^6} - \frac{6}{Rk^4}\end{aligned}$$

The Fourier space integrals in Eq. 4 must be evaluated numerically. (A simple procedure like Simpson's rule should be sufficient.) Feel free to use any computational tools you like to solve the matrix equation. If you've grown to like GSL you might find this page useful:

[http://www.gnu.org/software/gsl/manual/html\\_node/Linear-Algebra-Examples.html](http://www.gnu.org/software/gsl/manual/html_node/Linear-Algebra-Examples.html)

The remaining integrals can be worked out analytically; they are not difficult, but they are a little tedious. You are welcome to use symbolic computing software such as Mathematica for this purpose. (If you do so, please submit evidence of your work.)

(ii) Use your solutions for  $c_{\text{AW}}(r)$  to compute the radial distribution function  $g_{\text{AW}}(r)$  characterizing the arrangement of water molecules surrounding a hydrophobic solute. For this purpose, you will need to invert the Fourier transform  $\hat{c}_{\text{AW}}(k)\hat{h}_{\text{WW}}(k)$ . Since this function depends only on the magnitude of  $\mathbf{k}$  (and not the orientation), you may use the relations

$$\begin{aligned}\hat{f}(k) &= \int d\mathbf{r} f(r) e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{4\pi}{k} \int_0^\infty dr r \sin(kr) f(r) \\f(r) &= \int \frac{d\mathbf{k}}{(2\pi)^3} \hat{f}(k) e^{-i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{2\pi^2 r} \int_0^\infty dk k \sin(kr) \hat{f}(k)\end{aligned}$$

Plot your results for the same values of  $\sigma_{\text{A}}$  used in (i). You may find it more convenient to plot  $g_{\text{AW}}(r - R)$  to ease the comparison between the  $g_{\text{AW}}(r)$ 's with different  $\sigma_{\text{A}}$ 's. You can check your results by comparing with Figure 3 in Pratt, L. R. & Chandler, D. (1977) *J. Chem. Phys.* **67**, 3683-3704.

(iii) In lecture we derived an equation for the excess chemical potential,

$$\mu_{\text{ex}}(R) = \mu_{\text{ex}}(\sigma_{\text{W}}/2) + 4\pi\bar{\rho}_{\text{W}}k_{\text{B}}T \int_{\sigma_{\text{W}}/2}^R dR' R'^2 g_{\text{AW}}(R'^+).$$

Use your results from parts (i) and (ii) to calculate  $\Delta\mu(R)$  as a function of  $R$  over the range  $R = 2.7 \text{ \AA}$  to  $R = 5 \text{ \AA}$ . Plot your results.

(iv) Having computed  $c_{\text{AW}}(r)$  and  $h_{\text{AW}}(r)$ , you may now determine the solute-solute distribution function

$$g_{\text{AA}}(r) = 1 + \bar{\rho}_{\text{W}} \int d\mathbf{r}' c_{\text{AW}}(r') h_{\text{AW}}(|\mathbf{r} - \mathbf{r}'|), \quad r > \sigma_{\text{A}}$$

Perform this calculation for a few values of  $\sigma_{\text{A}}$ . Plot your results, which should correspond well with Figure 2 of the Pratt-Chandler paper referenced in part (ii).

## 2. Linear response theory for density fluctuations of two-component systems

Consider a mixture of two molecular species, denoted 1 and 2, whose microscopic density fields,  $\rho_1(\mathbf{r})$  and  $\rho_2(\mathbf{r})$ , obey Gaussian statistics. We thus have in mind an effective energy function

$$\beta U_0 = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' [\delta\rho_1(\mathbf{r})\chi_{11}^{-1}(\mathbf{r}-\mathbf{r}')\delta\rho_1(\mathbf{r}') + \delta\rho_2(\mathbf{r})\chi_{22}^{-1}(\mathbf{r}-\mathbf{r}')\delta\rho_2(\mathbf{r}') + 2\delta\rho_1(\mathbf{r})\chi_{12}^{-1}(\mathbf{r}-\mathbf{r}')\delta\rho_2(\mathbf{r}')] \quad (5)$$

We will specify the couplings  $\chi_{\alpha\nu}^{-1}(r)$  through a set of direct correlation functions  $c_{\alpha\nu}(r)$ ,

$$\chi_{11}^{-1}(r) = \frac{1}{\bar{\rho}_1}\delta(r) - c_{11}(r), \quad \chi_{22}^{-1}(r) = \frac{1}{\bar{\rho}_2}\delta(r) - c_{22}(r), \quad \chi_{12}^{-1}(r) = -c_{12}(r),$$

where  $\bar{\rho}_1$  and  $\bar{\rho}_2$  are the macroscopic number densities of species 1 and 2, respectively. Correlations among the fluctuating density fields are, as usual, related to the inverse of the coupling:

$$\langle \delta\rho_\alpha(\mathbf{r})\delta\rho_\nu(\mathbf{r}') \rangle = \chi_{\alpha\nu}(\mathbf{r}-\mathbf{r}')$$

The presence of multiple species, however, complicates the inverse property a little:

$$\sum_{\mu=1}^2 \int d\mathbf{r}'' \chi_{\alpha\mu}(\mathbf{r}-\mathbf{r}'')\chi_{\mu\nu}^{-1}(\mathbf{r}''-\mathbf{r}') = \delta_{\alpha,\nu} \delta(\mathbf{r}-\mathbf{r}'), \quad (6)$$

where  $\delta_{i,j}$  is the Kronecker delta.

(i) Let  $\hat{\chi}_{\alpha\nu}^{-1}(k)$  and  $\hat{\chi}_{\alpha\nu}(k)$  be the Fourier transforms of  $\chi_{\alpha\nu}^{-1}(r)$  and  $\chi_{\alpha\nu}(r)$ :

$$\hat{\chi}_{\alpha\nu}^{-1}(k) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \chi_{\alpha\nu}^{-1}(r), \quad \hat{\chi}_{\alpha\nu}(k) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \chi_{\alpha\nu}(r).$$

Write an equation relating  $\hat{\chi}(k)$  and  $\hat{\chi}^{-1}(k)$ . Bold symbols here denote matrices, e.g., the  $(\alpha, \nu)$  element of  $\hat{\chi}(k)$  is the function  $\hat{\chi}_{\alpha\nu}(k)$ :

$$\hat{\chi}(k) = \begin{pmatrix} \hat{\chi}_{11}(k) & \hat{\chi}_{12}(k) \\ \hat{\chi}_{12}(k) & \hat{\chi}_{22}(k) \end{pmatrix}, \quad \hat{\chi}^{-1}(k) = \begin{pmatrix} \hat{\chi}_{11}^{-1}(k) & \hat{\chi}_{12}^{-1}(k) \\ \hat{\chi}_{12}^{-1}(k) & \hat{\chi}_{22}^{-1}(k) \end{pmatrix}.$$

(ii) Show that

$$\hat{\chi}_{12}(k) = \hat{c}_{12}(k) \left[ \left( \frac{1}{\bar{\rho}_1} - \hat{c}_{11}(k) \right) \left( \frac{1}{\bar{\rho}_2} - \hat{c}_{22}(k) \right) - \hat{c}_{12}^2(k) \right]^{-1}$$

(iii) In class we argued that setting  $c(r) = -\beta u(r)$ , where  $u(r)$  is the interaction potential between a pair of molecules, is generally a bad idea. In particular, this way of using linear response theory would not do justice to the effects of excluded volume. For interactions with a large spatial range, however, this approach might be expected to capture density correlations over length scales much larger than a molecule's size. One such long-ranged potential is the Coulomb interaction energy between point charges,  $u(r) \propto r^{-1}$ , which decays much more slowly with distance than most intermolecular interactions.

For our Gaussian field theory of mixtures, let us therefore imagine the two species to be ions of different charge ( $q_1$  and  $q_2$ ) and employ the naïve closure

$$c_{11}(r) = -\beta \frac{q_1^2}{r}, \quad c_{22}(r) = -\beta \frac{q_2^2}{r}, \quad c_{12}(r) = -\beta \frac{q_1 q_2}{r}.$$

Combining these equations with your results from previous parts of this problem, and using the Fourier transform

$$\int d\mathbf{r} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{r} = \frac{4\pi}{k^2},$$

show that

$$\hat{\chi}_{12}(k) \propto \frac{1}{k^2 + \lambda^{-2}}.$$

Identify the proportionality constant and the length scale  $\lambda$  in terms of parameters  $\bar{\rho}_1$ ,  $\bar{\rho}_2$ ,  $q_1$ ,  $q_2$ , and temperature.

(iv) Using the definition of microscopic density fields, e.g.,  $\rho_1(r) = \sum_{j_1=1}^{N_1} \delta(\mathbf{r} - \mathbf{r}_{j_1})$ , write an exact relationship between  $\chi_{12}(r)$  and the radial distribution function  $g_{12}(r)$  describing the average density of type-2 ions surrounding a tagged type-1 ion.

(v) Combining all of your results, calculate  $g_{12}(r)$ . When performing the inverse Fourier transform of  $\hat{\chi}_{12}(k)$ , you might find it useful to recall the following identities:

$$\frac{1}{k^2 + a^2} = \frac{1}{(k + ia)(k - ia)} = (2k)^{-1} \left[ \frac{1}{(k + ia)} + \frac{1}{(k - ia)} \right], \quad \sin kr = \text{Im } e^{ikr}$$

$$\int_{-\infty}^{\infty} dk \frac{e^{ikr}}{k - ia} = 2\pi i e^{-ar}, \quad \int_{-\infty}^{\infty} dk \frac{e^{ikr}}{k + ia} = 0,$$

(vi) With your result for  $g_{12}(r)$  in hand, comment on the physical significance of the length scale  $\lambda$ .