

Suspensions and polymer solutions

Solution of Exercise 1

1. We assume again that the local concentration $c_i(\mathbf{r})$ of each ion species i is related to a local electrostatic potential $\psi(\mathbf{r})$ via the Boltzmann distribution,

$$c_i(\mathbf{r}) = c_{bi} e^{-\beta z_i e \psi(\mathbf{r})}. \quad (1)$$

We define $y(\mathbf{r}) \equiv \beta e \psi(\mathbf{r})$ and assume that y is sufficiently small (smaller than $1/z_{\max}$, where z_{\max} is the absolute valence of the most highly charged ion). We can then linearize Eq. (1),

$$c_i(\mathbf{r}) \simeq c_{bi} [1 - z_i y(\mathbf{r})]. \quad (2)$$

The local charge density is $\rho(\mathbf{r}) = \sum_i z_i e c_i(\mathbf{r})$. When we substitute Eq. (2) in this expression, we get two terms. The first, $\sum_i z_i e c_{bi}$, is equal to zero because of the overall neutrality of the solution. The second term gives

$$\rho(\mathbf{r}) = -e \left(\sum_i z_i^2 c_{bi} \right) y(\mathbf{r}). \quad (3)$$

Substituting this charge density in the Poisson equation, $\nabla^2 \psi = -(4\pi/\epsilon)\rho$, we get

$$\nabla^2 y = \kappa^2 y, \quad (4)$$

with the following screening length:

$$\kappa^{-1} = \left[\frac{4\pi e^2}{\epsilon k_B T} \left(\sum_i z_i^2 c_{bi} \right) \right]^{-1/2}. \quad (5)$$

2. (a) Assume that the positive plate is at $x = -d/2$ and the negative one at $x = d/2$. We need to solve the DH equation for the dimensionless electrostatic potential,

$$y''(x) = \kappa^2 y(x), \quad (6)$$

subject to the boundary conditions,

$$y'(x = \mp d/2) = \mp \frac{4\pi\sigma e}{\epsilon k_B T}. \quad (7)$$

The symmetry of the problem is such that the solution must be antisymmetric, $y(x) = C_1 \sinh(\kappa x)$, with C_1 a constant. Imposing the boundary condition (7), we find $C_1 = -4\pi\sigma e / [\epsilon k_B T \kappa \cosh(\kappa d/2)]$. This yields the solution for the electrostatic potential,

$$\psi(x) = -\frac{4\pi\sigma}{\epsilon\kappa} \frac{\sinh(\kappa x)}{\cosh(\kappa d/2)}. \quad (8)$$

The surface potentials of the left-hand and right-hand plates are, therefore,

$$\psi_{\text{L,R}} = \psi(x = \mp d/2) = \pm \frac{4\pi\sigma}{\epsilon\kappa} \tanh(\kappa d/2). \quad (9)$$

The free energy per unit area of the system is

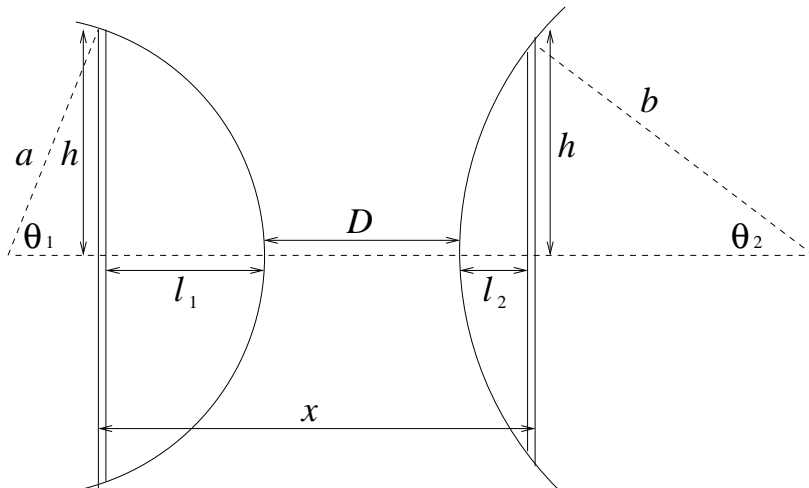
$$\frac{F(d)}{S} = \int_0^\sigma d\sigma' \psi_{\text{L}}(\sigma') + \int_0^{-\sigma} d\sigma' \psi_{\text{R}}(\sigma') = \frac{4\pi\sigma^2}{\epsilon\kappa} \tanh(\kappa d/2). \quad (10)$$

This free energy includes the self-energies of the two individual plates, $F_{\text{self}}/S = F(d \rightarrow \infty)/S = 4\pi\sigma^2/(\epsilon\kappa)$. Subtracting the self-energy, we obtain the free energy of interaction per unit area,

$$\frac{F_{\text{int}}(d)}{S} = \frac{4\pi\sigma^2}{\epsilon\kappa} [\tanh(\kappa d/2) - 1]. \quad (11)$$

- (b) For similarly charged plates we got a similar expression for F_{int}/S , with the tanh replaced by a coth. For large arguments $\tanh(x) - 1 \simeq -2e^{-2x}$ and $\coth(x) - 1 \simeq 2e^{-2x}$. Thus, at large distances the two cases behave as expected — both interactions decay as $e^{-\kappa d}$, with repulsion between the similarly charged plates and attraction between the oppositely charged ones. However, at short distances the behavior is drastically different! For $d \rightarrow 0$ the tanh vanishes, leaving an attraction between the oppositely charged plates of $-4\pi\sigma^2/(\epsilon\kappa)$, as in a Coulomb (salt-free) system. In sharp contrast, the coth term in the interaction of the similarly charged plates *diverges* as $d \rightarrow 0$.
- (c) The difference between the two cases stems from the behavior of the ions in the solution. In the oppositely charged case the total charge of the two plates is zero. Hence, as the two plates get closer, there can be less and less ions in-between while the system remains overall neutral. However, in the similarly charged case, ions are always necessary to neutralize the system. As the plates get closer, the ionic cloud gets squeezed, leading to an increased repulsion.

3.



- (a) In the figure (the curvatures are exaggerated!) we see $h = a \sin \theta_1 \simeq a\theta_1$, and also $h = b \sin \theta_2 \simeq b\theta_2$. In addition, $l_1 = a - a \cos \theta_1 \simeq a\theta_1^2/2$, and $l_2 = b - b \cos \theta_2 \simeq b\theta_2^2/2$. From these relations we get

$$x = D + l_1 + l_2 \simeq D + \frac{a+b}{2ab} h^2. \quad (12)$$

The area of a ring element is, therefore,

$$dS = 2\pi h dh = \pi d(h^2) \simeq \frac{2\pi ab}{a+b} dx, \quad (13)$$

and the total force between the spheres is

$$f_{\text{sph}}(D) = \int dSp \simeq \frac{2\pi ab}{a+b} \int_D^\infty dx p(x) = \frac{2\pi ab}{a+b} \frac{F_{\text{pl}}(D)}{S}. \quad (14)$$

If we set $a = b$ we get the result for equal spheres derived in the class, $f_{\text{sph}} \simeq \pi a F_{\text{pl}}/S$.

- (b) The result for a sphere and a planar surface is obtained by setting $b \rightarrow \infty$: $f_{\text{sph}} \simeq 2\pi a F_{\text{pl}}/S$. Thus, the force between a sphere and a surface is, within the Derjaguin approximation, twice the force between two identical spheres at the same separation.