

# Problems - Solutions

## Colloids

### **i** Interaction of two charged colloidal spheres - Problem setting

Consider a colloidal particle of total charge  $Q$  located at the origin, immersed in a solvent of permittivity  $\varepsilon = \varepsilon_0 \varepsilon_r$ . The solvent contains a symmetric electrolyte with two mobile ionic species:

- Cations of charge  $+ze$  and bulk concentration  $n_0$ ,
- Anions of charge  $-ze$  and bulk concentration  $n_0$ .

1. Show that The mean electrostatic potential  $\phi(\mathbf{r})$  satisfies Poisson's equation:

$$\nabla^2 \phi(\mathbf{r}) = -\frac{1}{\varepsilon} [ze n_+(\mathbf{r}) - ze n_-(\mathbf{r}) + Q\delta(\mathbf{r})].$$

Assuming the ions form an ideal gas in thermal equilibrium, their local densities follow Boltzmann distributions:

$$n_+(\mathbf{r}) = n_0 \exp[-\beta ze \phi(\mathbf{r})], \quad n_-(\mathbf{r}) = n_0 \exp[+\beta ze \phi(\mathbf{r})],$$

where  $\beta = 1/(k_B T)$ .

2. Use these expressions to obtain the (simplified) *nonlinear Poisson-Boltzmann equation* :

$$\nabla^2 \phi(\mathbf{r}) = \frac{2ze n_0}{\varepsilon} \sinh(\beta ze \phi(\mathbf{r})) - \frac{Q}{\varepsilon} \delta(\mathbf{r}).$$

3. Find physical conditions to linearise the equation.
4. Solve the resulting linear equation for spherical symmetry to obtain the screened Coulomb (Debye-Hückel) potential:

$$\phi(r) = \frac{Q}{4\pi\varepsilon} \frac{e^{-\kappa r}}{r}, \quad \kappa^2 = \frac{2n_0 z^2 e^2}{\varepsilon k_B T}.$$

The parameter  $\kappa^{-1}$  is the Debye screening length, and the solution shows that ionic screening converts the long-range Coulomb potential into a short-range Yukawa potential. The following real to Fourier space mappings may be useful

Real space	Fourier space
$f(\mathbf{r})$	$f(\mathbf{k})$
$\nabla^2 f(\mathbf{r})$	$-k^2 f(\mathbf{k})$
$\delta(\mathbf{r})$	1
$\frac{e^{-\kappa r}}{4\pi r}$	$\frac{1}{k^2 + \kappa^2}$

## Solution

We start by considering a single colloidal particle of total charge  $Q$  located at the origin, immersed in a solvent characterized by a permittivity  $\varepsilon = \varepsilon_0 \varepsilon_r$ . The solvent contains a symmetric electrolyte composed of two mobile ionic species: cations of charge  $+ze$  and bulk concentration  $n_0$ , and anions of charge  $-ze$  with the same bulk concentration  $n_0$ . The overall system is globally electroneutral in the bulk, so the net ionic charge far from the colloid is zero. The presence of the charged colloid generates an electrostatic potential  $\phi(\mathbf{r})$  in the surrounding medium.

The mean electrostatic potential satisfies Poisson's equation, which relates the divergence of the electric field to the local charge density. In this system, the total charge density consists of the fixed colloidal charge, represented by  $Q\delta(\mathbf{r})$ , and the contribution from the mobile ions, which depends on their local concentrations. This gives

$$\nabla^2 \phi(\mathbf{r}) = -\frac{1}{\varepsilon} [ze n_+(\mathbf{r}) - ze n_-(\mathbf{r}) + Q\delta(\mathbf{r})].$$

To relate the ionic densities to the electrostatic potential, we assume the ions behave as an ideal gas in thermal equilibrium. Each ion experiences a potential energy proportional to its charge times the local potential,  $U_{\pm}(\mathbf{r}) = \pm ze\phi(\mathbf{r})$ . In equilibrium, the number density of each species follows the Boltzmann distribution, so the cation and anion densities are

$$n_+(\mathbf{r}) = n_0 \exp[-\beta ze \phi(\mathbf{r})], \quad n_-(\mathbf{r}) = n_0 \exp[+\beta ze \phi(\mathbf{r})],$$

where  $\beta = 1/(k_B T)$  is the inverse thermal energy. This captures the intuitive fact that cations are repelled by positive potentials and attracted to negative potentials, while anions behave oppositely.

Substituting these expressions for  $n_+$  and  $n_-$  into Poisson's equation yields

$$\nabla^2 \phi(\mathbf{r}) = -\frac{1}{\varepsilon} [ze n_0 e^{-\beta ze \phi} - ze n_0 e^{+\beta ze \phi} + Q\delta(\mathbf{r})].$$

The difference of exponentials can be written as twice a hyperbolic sine, leading to the nonlinear Poisson–Boltzmann equation

$$\nabla^2 \phi(\mathbf{r}) = \frac{2ze n_0}{\varepsilon} \sinh(\beta z e \phi(\mathbf{r})) - \frac{Q}{\varepsilon} \delta(\mathbf{r}).$$

This equation describes how the potential generated by the colloid is screened by the surrounding ions. The nonlinearity arises because the ionic response depends exponentially on the potential itself.

The equation can be linearized under the condition that the potential is small compared to the thermal voltage, specifically when  $|\beta z e \phi(\mathbf{r})| \ll 1$ . In this limit, the hyperbolic sine can be approximated by its argument

$$\sinh(\beta z e \phi) \approx \beta z e \phi.$$

The Poisson–Boltzmann equation then reduces to a **linear** differential equation

$$\nabla^2 \phi(\mathbf{r}) - \kappa^2 \phi(\mathbf{r}) = -\frac{Q}{\varepsilon} \delta(\mathbf{r}),$$

where the inverse Debye length  $\kappa$  is defined by

$$\kappa^2 = \frac{2n_0 z^2 e^2}{\varepsilon k_B T}.$$

This linearized equation is known as the Debye–Hückel equation and describes the potential around a point charge in a screening medium.

This can be solved in Fourier space using the relations:

Real space	Fourier space
$f(\mathbf{r})$	$f(\mathbf{k})$
$\nabla^2 f(\mathbf{r})$	$-k^2 f(\mathbf{k})$
$\delta(\mathbf{r})$	1
$\frac{e^{-\kappa r}}{4\pi r}$	$\frac{1}{k^2 + \kappa^2}$

This gives

$$\phi(r) = \frac{Q}{4\pi\varepsilon} \frac{e^{-\kappa r}}{r}.$$

At short distances ( $r \ll \kappa^{-1}$ ), the potential reduces to the familiar Coulomb form, while at larger distances it decays exponentially due to ionic screening. The characteristic decay length  $\kappa^{-1}$  is the Debye screening length, which increases with decreasing ionic strength and temperature. This solution illustrates how the electrolyte effectively screens the electrostatic interactions between colloidal particles, converting the long-range Coulomb potential into a short-range interaction that governs the stability and dynamics of colloidal suspensions.

**Note.** In the linearised regime, the Poisson-Boltzmann equation reads

$$\nabla^2 \phi - \kappa^2 \phi = -\frac{Q}{\varepsilon} \delta(\mathbf{r})$$

A similar equation exists in field theory for a massive scalar field  $\Phi(\mathbf{r})$ : it is the Klein-Gordon equation in Euclidean space

$$(-\nabla^2 + m^2) \Phi(\mathbf{r}) = J(\mathbf{r})$$

It is easy to identify the field the mass and the source with the respective static potential field, the Debye screening parameter and the point charge. The Yukawa potential is then simply the **propagator** (the Green's function).

### **i** Second virial coefficient for depletion interactions - Problem setting

Consider a dilute suspension of spherical colloidal particles of radius  $R_c$  in a solution of small ideal polymer coils of radius  $R_p \ll R_c$ . The polymers are non-adsorbing and behave as an ideal gas outside the colloids. The colloids interact via the **Asakura–Oosawa depletion potential**  $U_{AO}(r)$ :

$$U_{AO}(r) = \begin{cases} \infty, & r < 2R_c \\ -\Pi V_{\text{overlap}}(r), & 2R_c \leq r \leq 2R_c + 2R_p \\ 0, & r > 2R_c + 2R_p \end{cases}$$

where  $r$  is the center-to-center distance,  $\Pi = n_p k_B T$  is the so called *osmotic pressure* of the polymer solution, and  $V_{\text{overlap}}(r)$  is the overlap volume of the depletion zones, given by

$$V_{\text{overlap}}(r) = \frac{\pi (4R_{\text{eff}} + r) (2R_{\text{eff}} - r)^2}{12},$$

with  $R_{\text{eff}} = R_c + R_p$ .

1. Write the expression for the *second virial coefficient*  $B_2$  in terms of the interaction potential:

$$B_2 = -2\pi \int_0^\infty (e^{-\beta U_{AO}(r)} - 1) r^2 dr$$

2. Assuming the polymer-induced attraction is *weak* ( $\beta|U_{AO}(r)| \ll 1$ ) and that the polymers are much smaller than the colloids, expand the exponential to first order and simplify the integral.
3. Express the resulting  $B_2$  in terms of  $R_c$ ,  $R_p$ , and the polymer osmotic pressure  $\Pi$ .
4. Discuss qualitatively how  $B_2$  depends on polymer concentration and size, and explain what a **negative**  $B_2$  implies for colloidal aggregation.

### Solution

The second virial coefficient  $B_2$  measures the effective two-body contribution to the pressure of a dilute colloidal suspension, following the virial expansion. It is defined for a pairwise potential  $U(r)$  as:

$$B_2 = -2\pi \int_0^\infty (e^{-\beta U(r)} - 1) r^2 dr.$$

Here,  $U(r) = U_{AO}(r)$  is the Asakura–Oosawa depletion potential.

1. Rewrite  $B_2$

The AO potential has three regions:

- Hard-core region ( $r < 2R_c$ ), where  $U = \infty \rightarrow e^{-\beta U} = 0$ . The integrand becomes  $-1$ , giving contribution:

$$B_2^{HC} = -2\pi \int_0^{2R_c} (-1) r^2 dr = 2\pi \int_0^{2R_c} r^2 dr = \frac{16\pi}{3} R_c^3,$$

which is just the hard-sphere contribution.

- Depletion region ( $2R_c \leq r \leq 2R_c + 2R_p$ ), where  $U(r) = -\Pi V_{overlap}(r)$ .
- No interaction ( $r > 2R_c + 2R_p$ ), where  $U = 0 \rightarrow e^{-\beta U} - 1 = 0$ .

The overlap is written as (lecture notes)

$$V_{\text{overlap}}(r) = \frac{4\pi}{3} R_d^3 \left[ 1 - \frac{3}{4} \frac{r}{R_d} + \frac{1}{16} \left( \frac{r}{R_d} \right)^3 \right], \quad r \leq R_d = 2R_c + 2R_p$$

and can be shown to be equivalent to

$$V_{\text{overlap}}(r) = \frac{\pi (4R_{\text{eff}} + r) (2R_{\text{eff}} - r)^2}{12}$$

So the integral reduces to contributions from  $r < 2R_c$  (hard core) and  $2R_c \leq r \leq 2R_c + 2R_p$  (depletion).

2. Linearize the exponential. For weak polymer-induced attraction,  $\beta|U| = \beta\Pi V_{\text{overlap}} \ll 1$ , we can expand:

$$e^{-\beta U(r)} \approx 1 - \beta U(r) = 1 + \beta \Pi V_{\text{overlap}}(r).$$

Then the integrand in the depletion region becomes:

$$-(e^{-\beta U} - 1) \approx -\beta \Pi V_{\text{overlap}}(r).$$

So the contribution to  $B_2$  from the depletion region is:

$$B_2^{\text{dep}} = -2\pi \int_{2R_c}^{2R_c+2R_p} (e^{-\beta U} - 1) r^2 dr \approx -2\pi \beta \Pi \int_{2R_c}^{2R_c+2R_p} V_{\text{overlap}}(r) r^2 dr.$$

3. Express  $B_2$  in terms of  $R_c$ ,  $R_p$ ,  $\Pi$

Combining the hard-core and depletion contributions, the second virial coefficient is

$$B_2 = \frac{16\pi}{3} R_c^3 - 2\pi \beta \Pi \int_{2R_c}^{2R_c+2R_p} V_{\text{overlap}}(r) r^2 dr$$

We then calculate the second integral we just need to choose how to represent the overlap. We use the second expression above and leverage the fact that  $R_p \ll R_c$  and that then the integral runs over  $r = 2R_c + x$  with  $x \in [0, 2R_p]$ , so with  $x$  clearly subleading

So, then

$$4R_{\text{eff}} + r = 6R_c + 4R_p + x$$

and

$$2R_{\text{eff}} - r = 2R_c + 2R_p - 2R_c - x = 2R_p - x$$

So together

$$V_{\text{overlap}}(x) = \frac{\pi(6R_c + 4R_p + x)(2R_p - x)^2}{12}$$

dropping subleading contributions leads to

$$V_{\text{overlap}}(x) \approx \frac{6\pi R_c(2R_p - x)^2}{12}$$

Then, we rewrite

$$\int_{2R_c}^{2R_c+2R_p} V_{\text{overlap}}(r) r^2 dr$$

as

$$\int_{2R_c}^{2R_c+2R_p} V_{\text{overlap}}(x) (2R_c + x)^2 dx$$

and approximate as

$$\approx (2R_c)^2 \int_0^{2R_p} V_{\text{overlap}}(x) dx$$

and then

$$B_2 \approx \frac{16\pi}{3} R_c^3 - 2\pi\beta\Pi (2R_c)^2 \int_0^{2R_p} \frac{\pi}{2} R_c (2R_p - x)^2 dx$$

So we finally integrate

$$\int_0^{2R_p} (2R_p - x)^2 dx$$

via a change of variable  $y = 2R_p - x$

$$\int_0^{2R_p} (2R_p - x)^2 dx = \int_{2R_p}^0 y^2 (-dy) = \int_0^{2R_p} y^2 dy = \frac{(2R_p)^3}{3} = \frac{8R_p^3}{3}$$

which leads to

$$B_2 \approx \frac{16\pi}{3}R_c^3 - \frac{32\pi^2}{3}\beta\Pi R_c^3 R_p^3$$

where  $R_c$  is the colloid radius,  $R_p$  is the polymer radius,  $\Pi$  is the osmotic pressure of the polymer solution, and  $V_{\text{overlap}}(r)$  is the overlap volume between two colloids at separation  $r$ . This formula shows how  $B_2$  depends explicitly on  $R_c$ ,  $R_p$ , and  $\Pi$ .

#### 4. Physical interpretation

- $B_2$  **decreases** with increasing polymer concentration (via  $\Pi$ ) and polymer size ( $R_p$ ).
- When the depletion attraction is strong enough,  $B_2$  can become **negative**, which signals that attractive interactions dominate over repulsion.
- Negative  $B_2$  implies a tendency for **colloidal aggregation** or even phase separation, because the effective interaction favours close approach of colloids.