

Problems - Solutions

Colloids

Interactions of two charged spheres - 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 κ 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 κ^{-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).

Second virial coefficient for depletion interactions - 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, $U(r) = U_{\text{AO}}(r)$ 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:

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

which is just the hard-sphere contribution.

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

The overlap is written as (lecture notes)

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

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 , Π

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

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

dropping subleading contributions leads to

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

Then, by applying the same expansion to the integral, the integral becomes

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

which should lead 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, Π 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 Π .

4. Physical interpretation

- B_2 **decreases** with increasing polymer concentration (via Π) 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.