

Problems - Solutions

Colloids

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 $\epsilon = \epsilon_0 \epsilon_r$. 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:

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

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

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

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

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

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

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:

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

The parameter κ^{-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 $\epsilon = \epsilon_0 \epsilon_r$. 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

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

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, $U_{\pm}(\mathbf{r}) = \pm z e \phi(\mathbf{r})$. In equilibrium, the number density of each species follows the Boltzmann distribution, so the cation and anion densities are

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

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

$$\nabla^2 \phi(\mathbf{r}) = -\frac{1}{\epsilon} [zen_0 e^{-\beta z e \phi} - zen_0 e^{\beta z e \phi} + Q\delta(\mathbf{r})].$$

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

$$\nabla^2 \phi(\mathbf{r}) = \frac{2zen_0}{\varepsilon} \sinh(\beta ze\phi(\mathbf{r})) - \frac{Q}{\varepsilon} \delta(\mathbf{r}).$$

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 $|\beta ze\phi(\mathbf{r})| \ll 1$. In this limit, the hyperbolic sine can be approximated by its argument

$$\sinh(\beta ze\phi) \approx \beta ze\phi.$$

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

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

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** $U_{AO}(r)$:

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

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 $V_{overlap}(r)$ is the overlap volume of the depletion zones, given by

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

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

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 Π .
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 , 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

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

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

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

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, 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.

i Colloids and sedimentation - Problem setting

A particle suspended in a liquid can be defined as *colloidal* if the kinetic energy of its thermally-driven Brownian motion is large enough to prevent it from settling completely to the bottom of the container under the influence of gravity.

A second definition of a colloid is a particle whose gravitational Peclet number Pe is significantly smaller than 1. (The gravitational Peclet number is the ratio of the time taken by a particle to diffuse a distance equal to its radius to the time taken by it to sediment the same distance under gravity.)

Show that these two definitions of a colloid are essentially equivalent.

Solution

To show the equivalence between these two definitions, we need to establish the relationship between thermal energy dominating over gravitational settling and the gravitational Peclet number being much less than 1.

For the first definition, a spherical particle of radius a and density ρ_p in a fluid of density ρ_f , the gravitational force is:

$$F_g = \frac{4\pi a^3}{3}(\rho_p - \rho_f)g$$

The gravitational potential energy difference over a distance equal to the particle radius is:

$$U_g = F_g \cdot a = \frac{4\pi a^4}{3}(\rho_p - \rho_f)g$$

For thermal motion to dominate, we require:

$$k_B T \gg U_g = \frac{4\pi a^4}{3}(\rho_p - \rho_f)g$$

For the second definition, the gravitational Peclet number is defined as:

$$\text{Pe} = \frac{t_{\text{diffusion}}}{t_{\text{sedimentation}}}$$

For diffusion over distance a :

$$t_{\text{diffusion}} = \frac{a^2}{D}$$

where D is the diffusion coefficient given by the Einstein relation: $D = \frac{k_B T}{6\pi\eta a}$.

For sedimentation over distance a under Stokes drag:

$$t_{\text{sedimentation}} = \frac{a}{v_s}$$

where the sedimentation velocity is: $v_s = \frac{F_g}{6\pi\eta a} = \frac{2a^2(\rho_p - \rho_f)g}{9\eta}$.

Therefore:

$$\text{Pe} = \frac{a^2/D}{a/v_s} = \frac{av_s}{D} = \frac{a \cdot \frac{2a^2(\rho_p - \rho_f)g}{9\eta}}{\frac{k_B T}{6\pi\eta a}}$$

Simplifying:

$$\text{Pe} = \frac{2a^3(\rho_p - \rho_f)g \cdot 6\pi\eta a}{9\eta \cdot k_B T} = \frac{4\pi a^4(\rho_p - \rho_f)g}{3k_B T}$$

From the first definition, colloidal behavior requires:

$$k_B T \gg \frac{4\pi a^4}{3}(\rho_p - \rho_f)g$$

This is equivalent to:

$$\frac{4\pi a^4(\rho_p - \rho_f)g}{3k_B T} \ll 1$$

But this is exactly the condition $\text{Pe} \ll 1$ from the second definition.

Therefore, the two definitions are mathematically equivalent: thermal energy dominance over gravitational settling occurs precisely when the gravitational Peclet number is much smaller than unity. Both conditions ensure that Brownian motion prevents complete sedimentation, which is the hallmark of colloidal behavior.

i Hard Rods and Cavity Function - Problem setting

Consider a 1-dimensional (1D) system of **Hard Rods** of length σ . The number density is ρ , and the equation of state is exactly known as (Tonks equation): $Z_{\text{comp}} = \frac{1}{1-\rho\sigma}$.

The potential is:

$$u(x) = \begin{cases} \infty, & x < \sigma \\ 0, & x \geq \sigma \end{cases}$$

The **pair distribution function at contact**, $g(\sigma^+)$, is known to be directly related to the equation of state by the 1D virial theorem (see lecture notes):

$$Z = 1 + \rho\sigma g(\sigma^+)$$

1. Calculate $g(\sigma^+)$ for the 1D hard rod system using the Tonks equation of state and the 1D virial theorem.

2. Determine the value of the Boltzmann factor, $e^{-\beta u(\sigma)}$, at contact.
3. Determine the value of the cavity Function, $y(\sigma) = e^{\beta U(r)} g(r)$, at contact.
4. Explain the physical meaning of $y(\sigma)$. How does it differ from $g(\sigma^+)$ in its interpretation?
5. Derive the full $g(r)$ by maximising the (Shannon) entropy

$$S[p] = - \int_0^\infty p(l) \ln p(l) dl$$

for the probability to find a gap of length l . Assume that the gaps are independent for simplicity and see that the $g(r_0)$ you obtain matches the previous assumptions.

1. Calculate $g(\sigma^+)$

We use the Tonks equation and the virial theorem:

$$Z_{comp} = \frac{1}{1 - \rho\sigma}$$

$$Z_{comp} = 1 + \rho\sigma g(\sigma^+)$$

Setting the two expressions for Z equal:

$$1 + \rho\sigma g(\sigma^+) = \frac{1}{1 - \rho\sigma}$$

Isolating $g(\sigma^+)$:

$$\rho\sigma g(\sigma^+) = \frac{1}{1 - \rho\sigma} - 1$$

Combine the right side using a common denominator:

$$\rho\sigma g(\sigma^+) = \frac{1 - (1 - \rho\sigma)}{1 - \rho\sigma} = \frac{\rho\sigma}{1 - \rho\sigma}$$

Dividing by $\rho\sigma$:

$$g(\sigma^+) = \frac{1}{1 - \rho\sigma}$$

This is the exact, analytic expression for the contact value for 1D hard rods.

2. Determine $e^{-\beta u(\sigma)}$

The Boltzmann factor $e^{-\beta u(x)}$ at contact $x = \sigma$ is determined by the potential $u(x)$:

$$e^{-\beta u(\sigma)} = e^{-\beta(0)} = 1$$

Since the potential is zero for $x \geq \sigma$, the particles are not interacting via the direct core repulsion precisely at σ^+ .

3. Determine $y(\sigma)$

The cavity function $y(x)$ is related to $g(x)$ and the Boltzmann factor:

$$g(x) = e^{-\beta u(x)} y(x)$$

At contact, $x = \sigma$:

$$g(\sigma^+) = e^{-\beta u(\sigma)} y(\sigma)$$

Substituting the results from (1) and (2):

$$\frac{1}{1 - \rho\sigma} = (1) \cdot y(\sigma)$$

Therefore, the cavity function at contact is:

$$y(\sigma) = \frac{1}{1 - \rho\sigma}$$

In this 1D case, $g(\sigma^+)$ and $y(\sigma)$ are equal.

4. Explain the meaning of $y(\sigma)$

Let's think of the direct correlation function

It is useful to think about the Percus-Yevick approximation for the direct correlation function

$$c(r) = (1 - e^{+\beta u(r)}) (h(r) + 1)$$

(see lecture notes).

This can be rewritten as

$$c(r) = (1 - e^{+\beta u(r)}) g(r) = (1 - e^{+\beta u(r)}) y(r) e^{-\beta u(r)}$$

and then

$$c(r) = (e - \beta u(r) - 1) y(r) = f(r) y(r)$$

where we used the Mayer f-function. Both $f(r)$ and $y(r)$ are continuous and differentiable, making solving the Ornstein Zernicke problem a tractable problem. In particular, $y(r)$ allows us to remove the discontinuities caused by the potential at short distances and focus on the correlations produced outside of the core.

The $g(r)$ is the **total probability** of finding a particle exactly one rod length (σ) away from another particle, given the direct physical repulsion (σ^- region) *and* the indirect correlations (the rest of the fluid). It is an **experimental, measurable** quantity directly linked to pressure via the virial theorem.

The cavity function $y(r)$ is the probability of finding a particle at distance σ **if the direct, instantaneous repulsive interaction $u(x)$ were suddenly removed** (i.e., if $u(\sigma)$ was momentarily zero). It represents the correlation due **only to the structure induced by the surrounding fluid**.

We can reread the PY appoximation in this light

$$c(r) = g_{\text{total}} - g_{\text{indirect}}$$

We assume that there is a potential of mean force $w(r)$ generating the correlations, such that

$$g(r) = g_{\text{total}}(r) = e^{-\beta \epsilon w(r)}$$

and then we decide to **approximate** the indirect but by **removing** the inetrparticle potential from the potential of mean force

$$g_{\text{indirect}} = e^{-\beta(w(r)=u(r))}$$

Then the PY approximation with the $c(r) = f(r)y(r)$ comes about.

5. Derivation

Hard rods **cannot overlap**, so:

$$g(r) = 0 \quad (r < \sigma).$$

Let the free gap between rods be

$$l = r - \sigma \geq 0$$

We use the maximum entropy principle to find $p(l)$.

We want to maximise

$$S[p] = - \int_0^\infty p(l) \ln p(l) dl$$

subject to

$$\int_0^\infty p(l) dl = 1, \quad \int_0^\infty l p(l) dl = \lambda$$

where the mean free gap is

$$\lambda = \frac{1 - \rho\sigma}{\rho}$$

Via Lagrange multipliers

$$\delta \left[- \int p \ln p dl + \alpha \left(\int pdl - 1 \right) + \gamma \left(\int lp dl - \lambda \right) \right] = 0$$

and then

$$p(l) = \frac{1}{\lambda} e^{-l/\lambda}$$

and

$$\gamma = -\frac{1}{\lambda}, \quad \alpha = 1 - \ln \lambda$$

We then convert from gap probability to pair correlation.

The pair correlation is the probability to find the particle at some position r scaled by the density:

$$g(r) = \frac{p(r - \sigma)}{\rho}.$$

Substitute $p(l)$ and λ :

$$g(r) = \frac{1}{(1 - \rho\sigma)} \exp \left[-\frac{\rho(r - \sigma)}{1 - \rho\sigma} \right].$$

Checks:

$$g(\sigma^+) = \frac{1}{1 - \rho\sigma}.$$

Matches the 1D hard-rod equation of state:

$$P = \frac{\rho k_B T}{1 - \rho\sigma}.$$