Problem Set
Stability of a colloidal system

Colloids are solid or liquid particles, with a size of the order of a few μm, dispersed in a liquid medium. Such particles are surface charged, and their electrostatic repulsion ensures the stability of the colloidal suspension. However, in the case where the solvent is ionized, ions with opposite charges can screen the repulsive electrostatic interaction between the colloids, so that the attractive van der Waals forces may dominate. In this Problem Set, we aim at understanding under which conditions such a colloidal suspension can be stable and does not form an aggregate.

1 The double layer phenomenon

Let us consider a simple one-dimensional model. The surface of the colloid is modelled as an infinite flat surface (in the plane yz) carrying a uniform charge density σ. The colloid, assumed to be a perfect conductor, occupies the half-space $x < 0$, while the electrolyte occupies the other half-space ($x > 0$). Let us assume that the electrostatic potential $V(x)$ and the volume charge density $\rho(x)$ of the solvent only depends on x. Finally, we assume that the permittivity of the solvent is equal to the vacuum one, ϵ_0.

(a) Give an equation linking $V(x)$ and $\rho(x)$ for $x > 0$. Which relation relates the surface charge density σ and the electric field $\mathbf{E}(0)$ at the surface of the colloid?

(b) The solvent consists of a solution of positive and negative ions of equal valence z. In the following, let us set $V(+\infty) = 0$. At thermal equilibrium, show that $\rho(x) = -2ze\nu \sinh(\beta zeV(x))$ for $x \geqslant 0$. What is ν? Deduce from your answer above that $V(x)$ satisfies the following differential equation:

$$\frac{\mathrm{d}^2V}{\mathrm{d}x^2} = \frac{2ze\nu}{\epsilon_0} \sinh(\beta zeV(x)). \tag{1}$$

What kind of approximation did you employ?

(c) Assuming that the electrostatic potential V_0 at the surface of the colloid is weak (with respect to what?), linearize and solve Eq. (1). What is the relation between V_0 and σ? Show that we recover the case of a parallel-plate capacitor of thickness $\xi = (\epsilon_0 k_\mathrm{B}T/2\nu z^2e^2)^{1/2}$, where ξ corresponds to the Debye length.

(d) Evaluate ξ for $T = 300\,\mathrm{K}$ in the case of a solution of monovalent ions at the concentration of $10^{-2}\,\mathrm{mol.l^{-1}}$, for $V_0 = 200\,\mathrm{mV}$.[1] Comment on the assumptions of the model, given that the colloid is made of gold and has a radius of $0.5\,\mu\mathrm{m}$. Discuss the approximation of question (c) above.

(e) Let us now solve Eq. (1) without any approximation. By integrating Eq. (1) once, show that

$$E(x) = \sqrt{\frac{8\nu k_\mathrm{B}T}{\epsilon_0}} \sinh\left(\frac{\beta zeV(x)}{2}\right).$$

Give an expression of σ as a function of V_0.

(f) Let us set $y(x) = \tanh(\beta zeV(x)/4)$. Show that $y(x)$ is a solution of the first-order differential equation

$$\frac{\mathrm{d}y}{\mathrm{d}x} = -\frac{y(x)}{\xi}.$$

Deduce from the equation above an exact expression for $V(x)$. Plot V as a function of x.

[1] We recall that $k_\mathrm{B} = 1.38 \times 10^{-23}\,\mathrm{JK^{-1}}$, $\epsilon_0 = 8.85 \times 10^{-12}\,\mathrm{Fm^{-1}}$ and $e = 1.60 \times 10^{-19}\,\mathrm{C}$.

(g) The system (colloid+solvent) can be considered as an electrostatic system characterized by the temperature T and either the potential V_0 or the charge q of the surface, these two parameters being related. Give an expression of the electrostatic work to be performed when bringing a charge from infinity to its position in the solvent. Deduce the differential of the internal energy E, the free energy F, and the "Gibbs energy" defined by $G = F - qV_0$. What is the purpose of this function?

(h) Justify the use of the following formula to calculate the Gibbs energy of the system (colloid+solvent) per unit of the surface $\mathcal{A}$ of the colloid, $g = G/\mathcal{A}$:

$$g = -\int_0^{V_0} \mathrm{d}V \, \sigma(T, V).$$

Deduce that

$$g = -16\nu k_\mathrm{B} T \xi \sinh^2\left(\frac{\beta z e V_0}{4}\right).$$

2 Interactions between colloids and aggregation conditions

We now intend to calculate the interaction energy between two spherical colloids ① and ②, with radius a and center-to-center distance r. We consider the limiting case where the two colloids are very close to one another. We hence generalize the preceding model to two parallel planar surfaces, with equal surface charge density σ and equal electrostatic potential V_0 with respect to infinity. The colloid ① occupies the space $x < 0$, while the colloid ② occupies the space $x > \ell$, with $\ell = r - 2a$.

(a) What is the differential equation verified by $V(x)$ for $0 \le x \le \ell$? Show that

$$E(x) = E_1 \sqrt{\cosh\left(\beta z e V(x)\right) - \cosh\left(\beta z e V_\mathrm{m}\right)}, \quad 0 \leqslant x \leqslant \frac{\ell}{2},$$

where $V_\mathrm{m} = V(\ell/2)$ and where E_1 is a constant to be specified. Deduce from your answer above an expression between σ, V_0, and V_m.

(b) At fixed temperature, we now aim at calculating the electrostatic interaction energy per surface unit between the two colloids. Justify that the work to be done in order to bring the two colloids close to one another is given by

$$W = -2\int_0^{V_0} \mathrm{d}V \left[\sigma(V) - \sigma_\infty(V)\right].$$

What is the physical meaning of $\sigma_\infty(V_0)$ and what is its expression?

(c) Let us assume that ℓ/ξ is sufficiently large so that $zeV_\mathrm{m} \ll k_\mathrm{B}T$. Calculate $\sigma - \sigma_\infty$ to lowest nonvanishing order in $\beta z e V_\mathrm{m}$. Let us further assume that V_m can be approximated by twice the potential created by a single colloid at the distance $x = \ell/2$ from its surface (which has a potential V_0). Calculate then $\sigma(V) - \sigma_\infty(V)$, and show that

$$W = \frac{B}{\xi^2}\,\mathrm{e}^{-\ell/\xi}, \quad \text{with} \quad B = 64\nu k_\mathrm{B} T \xi^3 \tanh^2\left(\frac{\beta z e V_0}{4}\right).$$

(d) One can show that the van der Waals interaction energy between two infinite planar surfaces takes the form $U_\mathrm{vdW} = -A/\ell^2$, where A is a positive constant.[2] Sketch the interaction energy $U_\mathrm{tot} = W + U_\mathrm{vdW}$ as a function of ℓ and for various values of the ratio $\alpha = A/B$. In particular, show that for $\alpha < \alpha_\mathrm{c}$ (where α_c shall be specified), U_tot presents a maximum and a minimum. For which value of α does this maximum vanish? With the help of your results above, discuss the stability of the colloidal suspension.

[2] One can demonstrate this result using the attractive interaction between two atoms, $u(r) = -a/r^6$, and by starting with the calculation of the interaction energy between a semi-infinite medium and one atom. Then, one can consider a cylinder of section $\mathrm{d}S$ and thickness $\mathrm{d}x$, and finally the interaction between two semi-infinite media.