

Problem Set 4

Debye–Hückel theory: Equation of state of an electrolyte or a classical plasma

We consider a dilute classical system of point-like charges. The system can be either a liquid (*i.e.*, a solvent) in which charged solutes are dissolved (that is, a salt) or a plasma (that is, a mixture of ions and electrons). The charges behave to a first approximation as an ideal gas (to which one must add the contribution of the solvent in the case of an electrolyte). We denote by ϵ the dielectric permittivity of the medium, *i.e.*, the solvent in the case of an electrolyte ($\epsilon = \epsilon_w \simeq 80 \epsilon_0$ for water) or the vacuum permittivity in the case of a plasma ($\epsilon = \epsilon_0$).

We will thus consider a completely ionized gas of volume V formed by $N/2$ positive charges with charge $+ze$ and $N/2$ negative charges with charge $-ze$, with z the valence and where e is the elementary charge.

The interaction energy of the system reads

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N \frac{q_i q_j}{4\pi\epsilon |\mathbf{r}_i - \mathbf{r}_j|}, \quad (1)$$

where \mathbf{r}_i is the position of the i^{th} particle with charge $q_i = \pm ze$. Equation (1) can be conveniently rewritten as

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{2} \sum_{i=1}^N q_i \varphi_i(\mathbf{r}_i) \quad \text{with} \quad \varphi_i(\mathbf{r}_i) = \sum_{\substack{j=1 \\ (j \neq i)}}^N \frac{q_j}{4\pi\epsilon |\mathbf{r}_i - \mathbf{r}_j|}$$

where $\varphi_i(\mathbf{r}_i)$ is the electrostatic potential created at the position \mathbf{r}_i of the ion i by the $N - 1$ other charges.

1 Generalities

- (a) Give an interpretation of the Bjerrum length $\ell_B = e^2/4\pi\epsilon k_B T$, where T is the temperature. Give a numerical estimate of ℓ_B for monovalent ions in water and in vacuum.
- (b) In what follows, we assume that the density of charges satisfies

$$\frac{N}{V} \ll \left(\frac{4\pi\epsilon k_B T}{e^2} \right)^3 \Leftrightarrow \frac{N}{V} \ell_B^3 \ll 1.$$

What does this physically mean?

2 Poisson–Boltzmann equation

We are aiming at calculating the electrostatic contribution to the energy, the free energy, and the pressure of the considered system. The theories developed in the general case (virial expansion, van der Waals mean-field approximation, *etc.*) do not apply here because of the long-range nature of the Coulomb interaction (1). If the solution was homogeneous at all scales, and the electrolyte concentrations were uniform, the total electrostatic energy would be zero and the system would behave like an ideal classical gas. But a given ion changes the charge distribution around it, preferentially attracting charges of opposite sign.

We will therefore describe the cloud created around a given ion of charge q by calculating the electrostatic potential ϕ created by the central ion and the cloud. In what follows, the charge q is placed at the origin, and it is assumed that ϕ depends only on the distance r to the ion (spherical symmetry), with $\lim_{r \rightarrow \infty} \phi(r) = 0$. Moreover, we denote by $\rho(r)$ the charge density of the cloud.

- (a) By writing down the relevant Maxwell equation and assuming that the ionic charge densities follow the Boltzmann distribution, demonstrate the Poisson–Boltzmann equation

$$\Delta\phi(r) = \frac{ze}{\epsilon} \frac{N}{V} \sinh(\beta ze\phi(r)), \quad r > 0, \quad (2)$$

with $\beta = 1/k_B T$. What kind of approximation has been made in writing this equation?

- (b) In the low-density approximation, it is possible to linearize Eq. (2). Demonstrate that in such a case one has

$$\phi(r) = \frac{q}{4\pi\epsilon r} e^{-r/\ell_D}, \quad (3)$$

where ℓ_D is called the Debye length. Give an expression of ℓ_D and discuss the physical meaning of Eq. (3). Estimate ℓ_D for a 1 molar electrolyte of monovalent salt and for a plasma in the same conditions.

- (c) What is the charge density $\rho(r)$ associated to the electrostatic potential $\phi(r)$? Show that

$$\int d^3\mathbf{r} \rho(r) = -q.$$

- (d) We now want to calculate the average electrostatic potential $\langle\varphi_i\rangle$ seen by the ion i ($i = 1, \dots, N$), *i.e.*, created by all the charges of the electrostatic cloud (the contribution of the most distant charges is negligible). Justify the following expression:

$$\langle\varphi_i\rangle = \lim_{r \rightarrow 0} \left\{ \phi_i(r) - \frac{q_i}{4\pi\epsilon r} \right\} = -\frac{q_i}{4\pi\epsilon \ell_D}.$$

- (e) Demonstrate that the total average energy of the charges can be expressed as

$$\langle E \rangle = \frac{3}{2} N k_B T - \frac{V}{8\pi\sqrt{k_B T}} \left[\frac{(ze)^2 N}{\epsilon V} \right]^{3/2}. \quad (4)$$

What are the hypothesis that we have made to derive this result?

3 Free energy and equation of state

- (a) Justify why the average energy (4) is not well-adapted to calculate the equation of state of the electrolyte. (Hint: How does one get the pressure P from $\langle E \rangle$ seen as a thermodynamic potential?)

- (b) We are now trying to calculate the free energy F of the system. First, demonstrate that

$$\langle E \rangle = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right). \quad (5)$$

Then, by integrating Eq. (5), show that

$$F = F_{\text{i.g.}} - \frac{V}{12\pi\sqrt{k_B T}} \left[\frac{(ze)^2 N}{\epsilon V} \right]^{3/2},$$

where $F_{\text{i.g.}}$ corresponds to the free energy of the monatomic ideal gas.

- (c) Demonstrate that the equation of state of the electrolyte can be written as

$$P = k_B T \frac{N}{V} - \frac{1}{24\pi\sqrt{k_B T}} \left[\frac{(ze)^2 N}{\epsilon V} \right]^{3/2}$$

Discuss this result, and especially its relation with the virial expansion.