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Problem Set 6
Debye–Hückel approximation : Equation of state of an electrolyte or a classical plasma

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Reminder

1 Generalities

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

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

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

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

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

(a) Give an interpretation of the Bjerrum length $l_B = e^2/4\pi\epsilon k_B T$, where T is the temperature. Give a numerical estimate of l_B for monovalent ions in water and in vacuum.

> **Definition :** The Bjerrum length is the separation at which the electrostatic interaction between two elementary charges is comparable to thermal energy scale, $k_B T$.

We want to compare the electrostatic energy $e^2/4\pi\epsilon d$ to the thermal energy $k_B T$. Let d be the distance between two charges,

- if $d \gg l_B$, it means that the thermal energy is greater than the electrostatic energy.
- if $d \ll l_B$, it means that the thermal energy is less than the electrostatic energy.

For water (and monovalent ions),

$$l_B \sim 7 \text{ Å}$$

(b) In what follow, we assume that the density of charges statisfies

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

What does this physically mean ?

It does mean that we have few ions in volume of size l_B^3, in other words it's a regime dominated by thermal energy.

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 $\lim_{r\to\infty} \phi(r) = 0$. 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

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

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

$$\begin{cases} \vec{\nabla} \times \vec{E} = -\dfrac{\partial \vec{B}}{\partial t} = \vec{0} \\ \vec{\nabla} \cdot \vec{E} = \dfrac{rho(\vec{r})}{\epsilon} \end{cases}$$

The first equation gives us that there exist a $\phi(\vec{r})$ such that,

$$\vec{E} = -\vec{\nabla}\phi(\vec{r})$$

And when we put this in the second equation we get,

$$\Delta\phi(\vec{r}) + \frac{\rho(r)}{\epsilon} = 0$$

Which is the *Poisson's equation* and where Δ denote the Laplacian in spherical coordinates,

$$\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}[r\phi(r)] + \frac{\rho(r)}{\epsilon} = 0$$

If we want to go further we need the charge distribution, $\rho(\vec{r})$ is depending on $\phi(r)$, we will use the Boltzmann distribution,

- Positive charges

  $$q = +ze \longrightarrow \mathcal{E}_+ = ze\phi(r)$$

  Meaning that,

  $$n_+(r) = \text{cst} \times e^{-\beta\mathcal{E}_+} = \text{cst}e^{-\beta ze\phi(r)}$$

  > **Remark :** Particles can be either fermions or bosons here, because we are dealing with high enough temperature to neglect such quantum effects.

  If r goes to ∞, $n_+ \to N/2V$ as $\phi(r) \to 0$ meaning,

  $$n_+(r) = \left(\frac{N}{2V}\right) e^{-\beta ze\phi(r)}$$

  We can calculate $\rho_+(r)$,

  $$\rho_+(r) = \frac{zeN}{2V} e^{-\beta ze\phi(r)}$$

- Negative charges
  Exactly the same as the positive charges,

  $$\rho_-(r) = -\frac{zeN}{2V} e^{\beta ze\phi(r)}$$

And now,

$$\rho(r) = \rho_+(r) + \rho_-(r) = -\frac{zeN}{V}\sinh[\beta ze\phi(r)]$$

Meaning we get two equations now,

$$\begin{cases} \dfrac{1}{r}\dfrac{\mathrm{d}^2}{\mathrm{d}r^2}(r\phi(r)) + \dfrac{\rho(r)}{\epsilon} = 0 \\ \rho(r) = -\dfrac{zeN}{V}\sinh[\beta ze\phi(r)] \end{cases}$$

Where the first one comes from electromagnetism and the second one from statistical mechanics.
We can write it,

$$\Delta\phi - \frac{zeN}{\epsilon V}\sinh[\beta ze\phi(r)] = 0$$

Which is known as the Boltzmann equation, it is a non-linear second order differential equation and we can't solve it analytically, so we need to make some assumptions, one can linearization of the sinh or one can make a separation of variable to do so.
The hypothesis we made for this formula was that water is a continuous media and we kind-of did a mean-field approximation.

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

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

where l_D is 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.

We assume a low density, meaning that

$$\beta ze\phi \ll 1$$

Meaning,

$$\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}(r\phi) - \frac{(ze)^2}{\epsilon k_B T}\frac{N}{V}\phi(r) = 0$$

We can rewrite it like

$$\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}(r\phi) - \kappa^2\phi(r) = 0$$

Where $\kappa^{-1} \equiv l_D$ the Debye length.

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}(r\phi) = \kappa^2(r\phi)$$

So,

$$r\phi = Ae^{-\kappa r} + Be^{\kappa r}$$

Meaning,

$$\phi(r) = \frac{A}{R}e^{-\kappa r} + \frac{B}{r}e^{\kappa r}$$

- $r \to +\infty$, $\phi \to 0$ meaning $B = 0$
- $r \to 0$, $\phi \to q/4\pi\epsilon r$ meaning $A = q/4\pi\epsilon_0$

So in the end,

$$\phi(r) = \frac{q}{4\pi\epsilon r} e^{-r/l_D}$$

> **Remark :**
> - It does looks like the yukawa potential from nuclear physics.
> - The Debye length is also called the screening length.

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

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

$$\begin{aligned}
\int \mathrm{d}^3\vec{r}\rho(r) &= -\int \mathrm{d}^3\vec{r}\frac{zeN}{V}\sinh[\beta ze\phi] \\
&\approx -\int \mathrm{d}^3\vec{r}\frac{\beta(ze)^2 q}{4\pi\epsilon r}\frac{N}{V}e^{-\kappa r} \\
&= -\beta\frac{(ze)^2}{\epsilon}q\frac{N}{V}\int_0^{+\infty} \mathrm{d}r r e^{-\kappa r} \\
&= -q\kappa^2\int_0^{+\infty} \mathrm{d}r e^{-\kappa r} \\
&= -q\underbrace{\int_0^{+\infty} \mathrm{d}x x e^{-x}}_{=1} \\
&= -q
\end{aligned}$$

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

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

- $\langle\varphi_i\rangle$ is the potential fest by q_i
- $\lim_{r\to 0}$ because q_i is at 0.
- $\phi_i(r)$ is the total electrostatic potential.
- $\frac{q_i}{4\pi\epsilon r}$ is the electrostatic potential from q_i.

$$\begin{aligned}
\langle\varphi_i\rangle &= \lim_{r\to 0}\left\{\phi_i(r) - \frac{q_i}{4\pi\epsilon r}\right\} = -\frac{q_i}{4\pi\epsilon l_D} \\
&= \lim_{r\to 0}\left\{\frac{q_i}{4\pi\epsilon r}\left[e^{-\kappa r} - 1\right]\right\} \\
&\approx \lim_{r\to 0}\left\{\frac{q_i}{4\pi\epsilon r}\left[1 - \kappa r - 1\right]\right\} \\
&= -\frac{q_i\kappa}{4\pi\epsilon} \\
&= -\frac{q_i}{4\pi\epsilon l_D}
\end{aligned}$$

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

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

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

$$\begin{aligned}
\langle E\rangle &= \langle K(\vec{p}^N) + U(\vec{r}^N)\rangle \\
&= \frac{3}{2}Nk_BT + \langle U(\vec{r}^N)\rangle
\end{aligned}$$

$$\begin{aligned}
\langle U(\vec{r}^N)\rangle &= \left\langle \frac{1}{2}\sum_{i=1}^{N} q_i\varphi_i \right\rangle \\
&= \frac{1}{2}Nq_i\langle\varphi_i\rangle \\
&= -\frac{1}{2}N\frac{q_i^2}{4\pi\epsilon l_D} \\
&= -\frac{Nq_i^2}{8\pi\epsilon}\left(\frac{N}{V}\frac{(ze)^2}{k_BT\epsilon}\right)^{1/2}
\end{aligned}$$

with $q_i = ze$,

$$\langle E\rangle = \frac{3}{2}Nk_BT - \frac{V}{8\pi\sqrt{k_BT}}\left[\frac{(ze)^2}{\epsilon}\frac{N}{V}\right]^{3/2}$$

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 ?)

From thermodynamics, we know that,

$$\langle P \rangle = -\frac{\partial}{\partial V} \langle E \rangle \bigg|_{S,N}$$

It require constant entropy, but, $\langle E \rangle$ is expressed without explicit entropy, we can't calculate like that, so we better use the free energy F,

$$\langle P \rangle = -\frac{\partial F}{\partial V} \bigg|_{T,N}$$

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

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

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

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

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

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \bigg|_{V,N} \qquad\qquad F = -k_B T \ln Z$$

$$= -T^2 \left(\frac{\partial}{\partial T} \frac{F}{T} \right) \bigg|_{V,N}$$

$$\frac{\partial}{\partial T} \left(\frac{F}{T} \right) = -\frac{3}{2} \frac{N k_B}{T} + \frac{V}{8\pi k_B^{1/2}} \left(\frac{(ze)^2 N}{\epsilon V} \right)^{3/2} T^{-5/2}$$

Meaning,

$$\frac{F}{T} = -\frac{3}{2} N k_B ln(\frac{T}{T_0}) - \frac{V}{8\pi k_B^{1/2}} \left(\frac{(ze)^2 N}{\epsilon V} \right)^{3/2} \frac{2/3}{T^{3/2}} + \text{cst}(V)$$

Meaning,

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

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

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

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

$$
\begin{aligned}
\langle P \rangle &= -\left(\frac{\partial F}{\partial V}\right)\bigg|_{T,N} \\
&= k_B T \frac{N}{V} + \frac{1}{12\pi}\left(\frac{1}{k_B T}\right)^{1/2}\left(\frac{(ze)^2}{\epsilon}\right)^{3/2}\left(-\frac{1}{2}\frac{1}{V^3/2}\right) \\
&= \frac{N k_B T}{V} - \frac{1}{23\sqrt{k_B T}}\left(\frac{(ze)^2 N}{\epsilon V}\right)^{3/2}
\end{aligned}
$$

We can write it like,

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