

Solution 12

Debye-Hückel Theory for Electrolytes¹

1. Quite trivially, the charge density due to ion i is given by $ez_i c_i$, so that $\rho(\vec{r}) = \sum_i ez_i c_i(\vec{r})$.
2. By making use of the result of the previous point, eqn (1) can be rewritten as

$$\nabla^2 \phi(\vec{r}) = -\frac{\sum_i ez_i c_i(\vec{r})}{\epsilon \epsilon_0} = -\sum_i \frac{ez_i}{\epsilon \epsilon_0} c_{i,\infty} e^{-\frac{z_i e \phi(\vec{r})}{k_B T}},$$

which is the result reported in eqn (3).

3. By Taylor-expanding the rhs of eqn (3) up to the linear term, we find (we drop the vectorial notation since we are assuming the ions to be distributed isotropically around the origin)

$$\nabla^2 \phi(r) \simeq -\sum_i \frac{ez_i}{\epsilon \epsilon_0} c_{i,\infty} + \left(\sum_i \frac{e^2 z_i^2}{\epsilon \epsilon_0 k_B T} c_{i,\infty} \right) \phi(r).$$

Now, in the first term in the rhs of the previous equation we can recognize the net charge density in bulk, which because of the overall electroneutrality of the solution is equal to zero. As for the second term, dimensional analysis tells us that the whole term in parenthesis is the inverse of a square length. Thus, by defining the *Debye length* l_D as

$$\frac{1}{l_D^2} \equiv \sum_i \frac{e^2 z_i^2}{\epsilon \epsilon_0 k_B T} c_{i,\infty}$$

and using the formula for the Laplacian operator in spherical coordinates, we obtain

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi}{dr} \right) = \frac{1}{l_D^2} \phi(r),$$

which is the equation reported in the main text.

4. Whatever the system we are dealing with, Gauss' law always holds! Thus, the electric field E for $r = a$ can be easily found by computing its flux:

$$4\pi a^2 E(a) = \frac{ze}{\epsilon \epsilon_0} \Rightarrow E(a) = \frac{1}{a^2} \frac{ze}{4\pi \epsilon \epsilon_0}.$$

The hard sphere assumption prevents other ions to enter the volume we considered, so that the result is independent of the other ions.

5. By considering

$$\phi = \frac{u}{r} \Rightarrow \frac{d\phi}{dr} = \frac{1}{r} \frac{du}{dr} - \frac{u}{r^2} \tag{1}$$

and substituting in equation (4), we find

$$\frac{1}{r^2} \frac{d}{dr} \left(r \frac{du}{dr} - u \right) = \frac{1}{l_D^2} \frac{u}{r},$$

¹M. Daune, "Molecular Biophysics" (1999)

from which we easily find

$$\frac{d^2 u}{dr^2} = \frac{1}{l_D^2} u.$$

The general solution of the previous equation is given by

$$u(r) = Ae^{\frac{r}{l_D}} + Be^{-\frac{r}{l_D}},$$

where A and B are determined by the boundary conditions. Substituting for ϕ , we find

$$\phi(r) = \frac{Ae^{\frac{r}{l_D}} + Be^{-\frac{r}{l_D}}}{r}.$$

A boundary condition is given as usual by the fact that the potential is expected to go at zero for $r \rightarrow \infty$, which imposes $A = 0$. On the other hand, if we compute the electric field

$$E(r) = -\frac{d\phi}{dr} = B \frac{e^{-\frac{r}{l_D}}}{r} \left(\frac{1}{r} + \frac{1}{l_D} \right) = Be^{-\frac{r}{l_D}} \frac{1 + \frac{r}{l_D}}{r^2} \quad (2)$$

and we compare the value it takes for $r = a$ with the one we computed in point 4, we obtain

$$E(a) = Be^{-\frac{a}{l_D}} \frac{1 + \frac{a}{l_D}}{a^2} = \frac{1}{a^2} \frac{ze}{4\pi\epsilon\epsilon_0} \Rightarrow B = e^{\frac{a}{l_D}} \frac{ze}{4\pi\epsilon\epsilon_0} \frac{1}{1 + \frac{a}{l_D}}.$$

By substituting the previous result in the formula for ϕ , we then easily obtain the result reported in the main text.

6. The net charge dq lying in a shell at distance r from the origin is easily found as

$$dq = 4\pi r^2 \rho(r) dr.$$

Remembering that $\rho(r) = \sum_i e z_i c_i$ and making use of eqn (2) in the Debye-Hückel approximation, we easily find that $\rho \propto \phi$, so that

$$dq \propto r^2 \phi(r) \propto r e^{-\frac{r}{l_D}}, \quad (3)$$

where we dropped out all the multiplicative terms independent of r . In the figure below we plot dq as a function of r . As we can see, the net charge in the rest of the solution is maximized at a distance equal to l_D and (as can be seen by having a look at the prefactors in the complete formula for dq) has an opposite sign with respect to the charge of the reference ion. Thus, roughly speaking the reference ion is surrounded by a cloud of thickness $\sim l_D$.

Scaling Arguments for the Fluctuations of Ion Density in Electrolytes²

1. By the very definition of Bjerrum length given in the main text, we easily find

$$\frac{e^2}{4\pi\epsilon\epsilon_0 l_B} = k_B T \Rightarrow l_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T}.$$

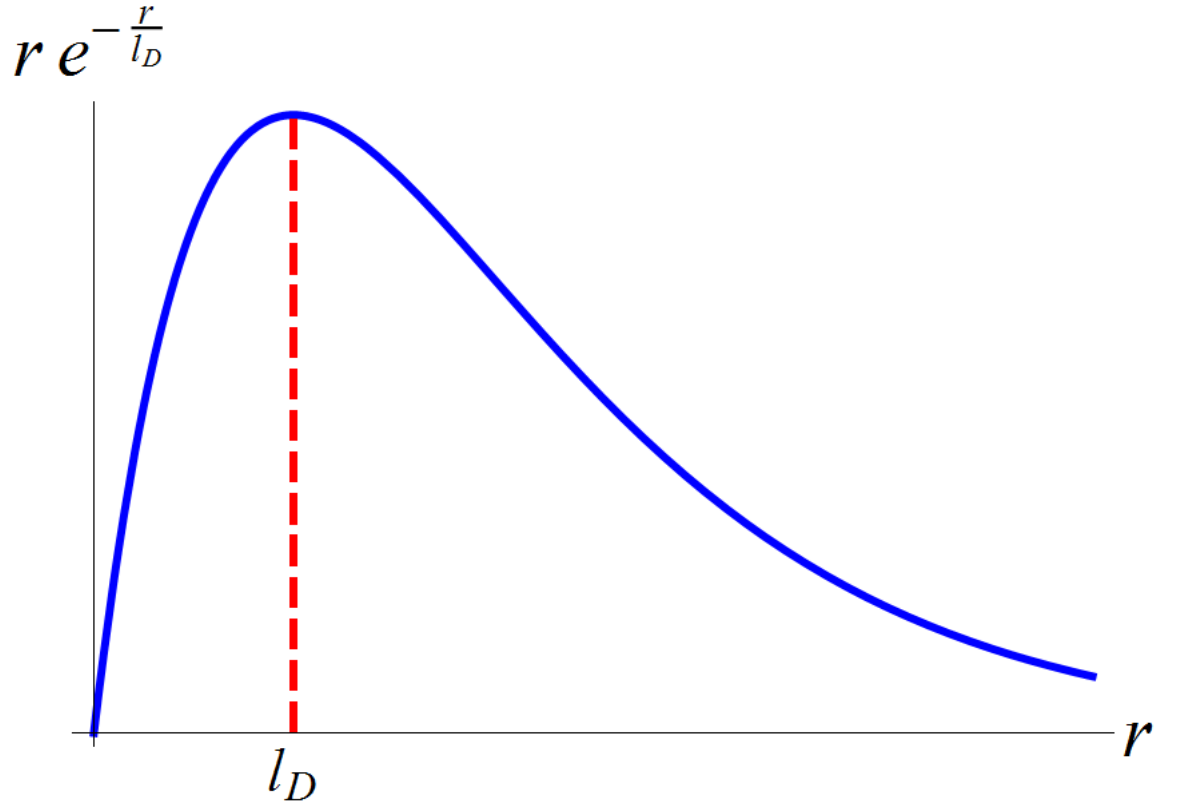
By definition the Debye length is equal to

$$\frac{1}{l_D^2} \equiv \sum_i \frac{e^2 z_i^2}{\epsilon\epsilon_0 k_B T} c_i,$$

which, for a monovalent solution, reads

$$\frac{1}{l_D^2} \equiv \frac{2e^2}{\epsilon\epsilon_0 k_B T} c = 8\pi l_B c \Rightarrow l_D = \frac{1}{\sqrt{8\pi l_B c}}.$$

²We acknowledge Prof. M. Rubinstein for this physical argument.



2. i) If we assume the ions to be non-interacting, if we assume the region to be much larger than the size of the ions, the average concentration of ions is the one in bulk, i.e. $\langle c_+ \rangle = \langle c_- \rangle = c$ (we are denoting by c_+ and c_- the concentration of positive and negative ions respectively). Let us denote the number of ions in the region as n_+, n_- . If the size of the region is R , we have $\langle n_+ \rangle \sim \langle c_+ \rangle R^3$ and $\langle n_- \rangle \sim \langle c_- \rangle R^3$. Thus, on average the total charge within this region is $\langle Q \rangle = \langle n_+ - n_- \rangle e = 0$. ii) In an ideal gas, the typical fluctuations scale as the square root of the number of particles: $\langle \Delta n^2 \rangle \sim \langle n \rangle$. Thus, if we consider the charge fluctuations, we obtain $\langle Q^2 \rangle = \langle (n_+ - n_-)^2 \rangle e^2 \sim \langle n_+ \rangle e^2 \sim c e^2 R^3$. iii) Even if we are considering non-interacting ions, we now want to calculate what is the electrostatic energy $U(R)$ of such a collection of charges. Some easy computations show that (we drop out numerical prefactors)

$$U \sim \frac{\langle Q^2 \rangle}{\epsilon \epsilon_0 R} \sim \frac{c e^2 R^3}{\epsilon \epsilon_0 R} \sim c k_B T l_B R^2,$$

thus showing that the electrostatic energy increases with the size of the region.

3. When $R \sim l_D$ the previous formula reads

$$U \sim k_B T c l_B l_D^2 \sim k_B T,$$

where we have substituted the result found in point 1. Thus, this simple argument leads to a very important conclusion on the Debye length, namely the fact that it is the length scale at which electrostatic energy overcomes thermal fluctuations. In other words, the picture of ideal gas is not far from reality when we consider regions of small size, since entropy completely annihilates the electrostatic interaction. On the other hand, at length scales larger than l_D the system can be seen as an ensemble of blobs which are strongly correlated with respect to each other.

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4. A nice picture of such a strong correlation is given by the analysis of fluctuations. As we have seen in point 2, for $R < l_D$ we basically have $\langle \Delta n^2 \rangle \propto R^3$. On the other hand, for length scales larger than l_D the interaction energy overcomes entropy, so that thermal fluctuations cannot completely mix up the ions. The best they can do is to pump in or out energy of the order of $k_B T$, so that the fluctuations will be such that

$$\frac{\langle \Delta n^2 \rangle e^2}{\epsilon \epsilon_0 R} \sim k_B T \Rightarrow \langle \Delta n^2 \rangle \sim \frac{\epsilon \epsilon_0 k_B T}{e^2} R \sim \frac{R}{l_B} \propto R,$$

which is a very slow increase with R when compared to the pure entropic one. This can be seen by computing the decay of relative fluctuations with size: while below the Debye length we have the typical ideal gas behaviour $\Delta n/n \sim 1/n^{1/2}$, at larger length scales the strong correlation results in a much faster decay, i.e. $\Delta n/n \sim 1/n^{5/6}$ (remember that $n \propto R^3$ and look at the formula above).