Journal Club for Condensed Matter Physics
https://www.condmatjclub.org
DOI:10.36471/JCCM_November_2020_03

The pressure in ionic solutions

Osmotic pressure between arbitrarily charged planar surfaces: A revisited approach
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Eur. Phys. J. E. (2018) **41**: 11

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Understanding the interaction between charged macromolecules in an ionic solution is of paramount importance. For measuring these interactions in concentrated solutions, some experiments consist in controlling the osmotic pressure of a reservoir of water in which the biomolecules solution is in equilibrium. It allows to concentrate biomolecules such as DNA upon increasing the osmotic pressure of the reservoir. For describing these interactions, Adar and Andelman, the authors of the paper discussed here, consider two planar surfaces immersed in an ionic solution. The boundary conditions correspond either to imposed potentials on the plates or imposed charged surfaces. The aim is to describe the thermodynamic state of the solution in between the two plates and to calculate the interaction between the plates, either attractive or repulsive.

This problem is complex because many different regimes exit, depending on the distance between the plates, the strength of the potential, the ionic strength of the solution, and the valence of the ions. As a consequence, many different regimes exist and a comprehensive description of the problem allowing to clearly relate these different regimes was lacking. The authors propose such a description in the context of the mean field Poisson-Boltzmann model. The starting point of the authors is the following equation :

$$\frac{\epsilon}{4\pi}\Delta\Psi = 2n_b \sinh\left(\frac{e\Psi}{k_B T}\right) \tag{1}$$

where Ψ is the electrostatic potential, ϵ the dielectric constant of the solution, n_b the bulk concentration of ions, e the elementary charge and $k_B T$ is the thermal energy. Upon integration, the authors obtain

$$\frac{-\epsilon}{8\pi}\Psi'^2 + 2n_b k_B T \cosh\left(\frac{e\Psi}{k_B T}\right) = P \tag{2}$$

where P is the pressure in the solution and is a constant of the problem. When the plates are far apart, the pressure P is equal to the van't Hoff term $P_b = 2n_b k_B T$ [1]. I will come back to this point later. In dimensionless units, it yields

$$\Pi = p - 1 = -\frac{1}{2}E^2 + 2\sinh^2\frac{\psi}{2} \tag{3}$$

where p is the pressure and Π the osmotic pressure. The osmotic pressure is given by the pressure minus the bulk van't Hoff term $P_b = 2n_b k_B T$ of the ideal ionic solution. Π corresponds to the interaction between the two plates. When Π is negative, the interaction is attractive and it is repulsive when Π is positive.

The important points are that when Π is negative, the electrostatic potential is monotonous between the two plates. The previous equation can then be integrated between the potentials ψ_1 and ψ_2 according to the variable $d\psi$ to yield an analytic relation between the osmotic pressure Π and the distance d between the plates. When Π is positive (repulsive plates), the electric field is monotonous between the two plates. The previous equation can also be integrated between the two electric fields on the plates (corresponding to two imposed surface charges) E_1 and E_2 according to the variable dE, which yields an analytical relation between the positive osmotic pressure and the distance d between the plates. In both cases, these relations can be inverted numerically which allows to plot the osmotic pressure as a function of the distance between two plates, either in the attractive regime or repulsive regime.

These results allow to plot a phase diagram with regions corresponding either to attractive forces or repulsive forces between the plates in the (Ψ, E) plane. These regions are separated by two lines of zero osmotic pressure. The formalism introduced in this article allows also to determine the crossover between the attractive and repulsive regimes for two plates with imposed potential. If one starts from the attractive regime ($\Pi < 0$) the crossover is reached by taking the limit where Π_- tends to zero. At small distance plates which were attractive at large distances become repulsive. A similar crossover can be described for two plates with imposed charges. The interaction which was repulsive at large distances may become attractive at short distances.

Finally, the formalism allows to recover the standard descriptions corresponding to various limiting cases classically described in the literature: the ideal gas regime for which the repulsive force corresponds to the osmotic pressure of an ideal solution of ions; the Gouy-Chapman regime for large surface charges regime and the Debye-Hckel regime at small osmotic pressure and electric fields. By clarifying how all these regimes are connected and by establishing general analytical results, this article contributes to clarify the physics at play and should be very useful for people interested by these issues.

An important point to note is that the pressure P between the two plates is uniform and appears as an integration constant of equation (1). The pressure in the solution when the plates are far apart or when there is only one plate is then equal $P_b = 2n_b k_B T$. This result has been obtained by Ben-Yaakov et al [1] and deserves some comments. The derivation stems from the relation

$$F - \Sigma_i \mu_i n_i = -PV \tag{4}$$

where μ_i is the chemical potential of specy i and n_i the volume fraction of specy i. However, the bulk pressure of the solution cannot be $P_b = 2n_b k_B T$ [2] but is the atmospheric pressure under which the system is equilibrated. What the formalism of reference [1] and the considered article show is that the pressure is uniform between the two plates and is equal to the bulk pressure when they are far apart. The pressure cannot be obtained directly from the Poisson-Boltzmann incompressible model, which considers only degrees of freedom at fixed density. When using relation (6) below, Ben-Yaakov et al have varied the ions concentration, but not that of water. The free energy contains indeed a term like

$$f_m = n_1(\ln n_1 - 1) + n_2(\ln n_2 - 1) + n_3(\ln n_3 - 1) \tag{5}$$

where n_1, n_2, n_3 are the volume fraction of constituents 1, 2 and 3. Note that these volume fractions here are not constrained by a relation of the type $n_1 + n_2 + n_3 = 1$, but are free to vary independently. The quantity $f_m - \Sigma n_i \frac{\partial}{\partial n_i} f_m = -PV$ [1] now reads

$$f_m - \Sigma n_i \frac{\partial}{\partial n_i} f_m = -(n_1 + n_2 + n_3) \tag{6}$$

instead of the van't Hoff term. This last term adds to a density dependent term that one may add to the free energy such as $1/2K(n_1+n_2+n_3-1)^2$ where $K \gg 1$. One needs then to consider the mechanical equilibrium with the atmosphere so that the total pressure is equal to the atmospheric pressure. The presence of the van't Hoff term in the pressure is thus an artifact of the incompressibility of the model and of not considering the water volume fraction as an independent variable. It is indeed not possible to obtain directly an equation of state from an incompressible model. One needs to introduce the density as a degree of freedom to do so, *e.g.* as did Prigogine regarding simple liquids [3].

The integration constant of equation (1) when the plates are far apart should be $P - P_{atm} + 2n_b k_B T$ to yield

$$\frac{-\epsilon}{8\pi}\Psi'^2 + 2n_b k_B T \cosh\left(\frac{e\Psi}{k_B T}\right) = P - P_{atm} + 2n_b k_B T \tag{7}$$

In dimensionless units, the osmotic pressure should then be given by

$$\Pi = p - \frac{P_{atm}}{2n_b k_B T} = -\frac{1}{2}E^2 + 2\sinh^2\frac{\psi}{2} \tag{8}$$

and the physics described in the article by Adar and Andelman would be unchanged. Among the perpectives are the issues regarding the pressure in the vicinity of charged cylinders or more complex geometries.

References

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