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Charge reversal at 0 K

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Abstract
In this contribution we shall explore the conditions under which a charged sphere in contact with a charge reservoir undergoes a charge reversal. The calculations are confined to zero temperature, but some arguments are presented why this system is of particular interest to the physics of highly charged colloidal suspensions containing multivalent counterions.

1. Introduction

Consider a sphere of radius a and charge $-Zq$, uniformly smeared over its surface, in vacuum at zero temperature. Now, suppose that on top of this sphere we put small spherical ions, each of charge q and diameter d. What is the number of counterions necessary to minimize the electrostatic energy?

It has been argued on a number of occasions [1–3] that the ground state always corresponds to an overcharged configuration. Namely, to minimize the electrostatic energy one should put *more* counterions on top of the sphere than is necessary to neutralize its charge. This phenomenon is known as *charge reversal* or *overcharging* and has been observed even at finite temperature in colloidal suspensions containing multivalent counterions. The charge reversal results from the electrostatic correlations between the condensed counterions [4, 3]. To minimize the electrostatic energy, the counterions arrange themselves in such a way as to be as far away as possible from one another. It is precisely the discreteness of the counterion charge that leads to the overcharging phenomenon. If, instead of the discrete counterions a continuous amount of counter-charge was smeared uniformly over the surface of the sphere, the minimum of the electrostatic energy would clearly correspond to a state with no net charge.

In reality, however, one is not free to just ‘put’ counterions on top of the sphere. The counterions do not appear from nowhere, but must be brought to the surface of a sphere from some charge reservoir. Transfer of charge from a reservoir to the sphere costs energy, which has to be taken into account. The question is then: is the charge reversal possible when the transfer energy is properly taken into account? That is: can a charged sphere become overcharged when put in contact with a charge reservoir?

2. Overcharging

Consider the electrostatic energy of a charged sphere with n condensed counterions on its surface. For simplicity we shall suppose that $a \gg d$, so that the condensed counterions can be treated as point particles. The electrostatic energy can then be written as [3]

$$E_n = \frac{Z^2q^2}{2\epsilon a} - \frac{Znq^2}{\epsilon a} + F_n. \tag{1}$$

The first term is the self-energy of a charged sphere, the second term is the electrostatic energy of interaction between the sphere and n condensed counterions and the last term is the electrostatic energy of repulsion between the condensed counterions. To calculate the electrostatic energy of repulsion, it is convenient to express F_n in terms of the free energy of a one-component plasma (OCP). A spherical (OCP) is defined as n ions moving on a surface of a sphere with a uniform (2d) *neutralizing* background. The free energy of the spherical OCP can be written as

$$F_n^{\mathrm{OCP}} = F_n - \frac{n^2q^2}{\epsilon a} + \frac{n^2q^2}{2\epsilon a}. \tag{2}$$

Note that the electrostatic energy of repulsion between n condensed counterions F_n is exactly the same as the one appearing in equation (1). Substituting equation (2) into (1) the electrostatic free energy of the sphere–counterion complex becomes

$$E_n = \frac{(Z-n)^2q^2}{2\epsilon a} + F_n^{\mathrm{OCP}}. \tag{3}$$

At zero temperature the electrostatic energy of the OCP is

$$F_n^{\mathrm{OCP}} = -M_0\frac{q^2n^{3/2}}{2\epsilon a} \tag{4}$$

where M_0 is the Madelung constant. It is found that $M_0 = 1.102$, gives a perfect fit to the energies calculated within the Monte Carlo simulations [5–7]. We note that the Madelung constant for a planar 2d Wigner crystal [8] is $M_0 = 1.106\,103$, so that the topological defects present in the ground state of a spherical OCP are of little practical relevance as far as the electrostatic energy is concerned.

Now the question is: what is the equilibrium net charge of a sphere if it is placed in contact with a charge reservoir? For simplicity we shall take all the ions to be monovalent and symmetric, with diameter d. The overall charge neutrality of the universe requires that the reservoir contains Z more counterions than coions. This excess charge will be expelled to the surface of the reservoir [7].

When the sphere is placed in contact with the reservoir, transfer of charge will take effect. After the sphere's neutralization, the charge transfer can either cease or continue, leading to overcharging. The final number of condensed counterions is determined by the minimum of the grand potential function. Let us define δ as the excess number of condensed counterions. The grand potential is then

$$\Omega(\delta) = \frac{\delta^2q^2}{2\epsilon a} - M_0\frac{q^2(Z+\delta)^{3/2}}{2\epsilon a} - \mu\delta, \tag{5}$$

where μ is the chemical potential of the 'salt' reservoir. Minimization of the grand potential shows that the overcharging, $\delta > 0$, is possible only if

$$\tilde{\mu} > \tilde{\mu}_{\mathrm{c}} \equiv -\tfrac{3}{4}M_0\sqrt{Z}, \tag{6}$$

where the reduced chemical potential is $\tilde{\mu} = \epsilon a \mu / q^2$. If we suppose that the charges in the reservoir at zero temperature are in the form of a sodium chloride crystal, then

$$\mu = -\frac{M_c}{2} \frac{q^2}{\epsilon d}, \tag{7}$$

where $M_c = 1.7476$ is the Madelung constant for the NaCl lattice. Therefore, charge reversal is possible only if

$$Z > Z_c \equiv \left(\frac{2aM_c}{3dM_0} \right)^2. \tag{8}$$

For a sphere of colloidal dimensions $a \approx 1000$ Å, and ions of $d \approx 1$ Å, the critical charge for occurrence of overcharging is $Z_c \approx 10^6$, which is extremely large, corresponding to one elementary charge every 10 Å^2.

3. Conclusion

We have explored a possibility of charge reversal at zero temperature. It is demonstrated that overcharging at zero temperature is possible, but that it can only occur if the object is extremely highly charged. Our results are restricted to zero temperature and might seem to be of only academic interest. This, however, is not the case. The physics of aqueous colloidal suspensions containing multivalent counterions is actually similar to the model presented above. The electrostatic energy of attraction between the multivalent counterions and the monovalent coions is well above the thermal energy. This means that in the bulk most of the counterions are neutralized by the associated coions. Thus, in order for a counterion to condense onto a colloidal particle it must first be re-ionized. The ionization potential of bulk multivalent ions is similar to the chemical potential of the reservoir appearing in the grand potential functional, equation (5). Of course, at finite temperature one should be careful to account for the entropic effects as well. The complete calculation will be presented elsewhere.

Our discussion was restricted to overcharging produced by strong electrostatic correlations. Other forms of overcharging are also possible [9]. For example, hydrophobic interactions between the cationic lipids and the DNA can lead to the formation of lipoplexes in which the bare DNA charge is reversed [10, 11]. This phenomenon occurs even with lipids containing only monovalent cationic head groups. In water the electrostatic interactions between the lipids are quite small. Clearly, in this case, the overcharging is driven not by the electrostatic correlations, but by the hydrophobicly induced attraction between the lipids.

There are also indications that charge reversal is possible in an aqueous colloidal suspension containing only monovalent counterions [12–14]. The simulations find that for microions of sufficiently large diameter there exists a concentric volume centred on a colloidal particle in which the net charge has opposite sign to the bare colloidal charge. This phenomenon seems to be entropic in origin, suggesting that the counterions inside the sheath are bound to the colloidal particle by an electrostatic energy of the order of $k_B T$. Thus, this form of overcharging, should be impossible to detect using electrophoretic mobility measurements [15].

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