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Screening length in concentrated electrolytes

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Abstract

The law of increase of the electrostatic screening length with increasing concentration, recently reported in highly-concentrated electrolytes (ionic liquids, inorganic salts), Refs. [3]-[6], is derived from the dispersive plasmons generated by Coulomb and short-range interactions, the latter arising from screened-charge electrostatic interactions.

Key words: electrolytes; high concentration; screening length

It is well known that an electrostatic potential Q/r, generated by a pointlike charge Q at distance r in vacuum, is screened in an electrolyte according to the law $Qe^{-r/\lambda_D}/r$, where λ_D is the Debye length.[1, 2] For a binary electrolyte consisting of cations/anions with charge $\pm q$ and density $n = 1/a^3$ at temperature T the Debye length is $\lambda_D = a\sqrt{\varepsilon aT/8\pi q^2}$, where ε is the dielectric constant. The screening law holds as long as the screened potential vary slowly over distances much longer than the mean inter-ionic distance. This condition is met in dilute electrolytes, where $\lambda_D \gg a$. In concentrated electrolytes, $\lambda_D < a$ (Bjerrum length $q^2/\varepsilon T \gtrsim a$), the screened potential is, practically, vanishing over long distances. In both cases the region in the immediate vicinity of the ions should be avoided. Recently, it was found experimentally that, at high concentrations, in a wide class of electrolytes, ionic liquids and inorganic salts, there exists a screening length which obeys the law $\Lambda \simeq r_0^3/\lambda_D^2$ (up to a small additive constant), where r_0 is the mean ion diameter[3]-[6] (see also Refs. [7]-[9]). We can see that, for high concentrations, this screening length increases with increasing concentration, in contrast to the Debye length. Scaling arguments have been advanced in Ref. [4] to justify this new law, valid at high concentrations. We show in this Note that this law is a consequence of the dispersive plasmons, arising from Coulomb and short-range interactions. The short-range interactions arise from electrostatic interactions between screened ionic charges.

Let us consider a set of identical particles with mass m and density n, with a pair-wise interaction energy $V(\boldsymbol{r}_1 - \boldsymbol{r}_2)$. A local displacement $\boldsymbol{u}(\boldsymbol{r})$ gives a density variation $\delta n = -n\,div\,\boldsymbol{u}$, such that the interaction energy is

$$U = \frac{1}{2}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 V(\boldsymbol{r}_1 - \boldsymbol{r}_2)\delta n(\boldsymbol{r}_1)\delta n(\boldsymbol{r}_2) = \frac{1}{2}\sum_{\boldsymbol{k}} V(\boldsymbol{k})\delta n(\boldsymbol{k})\delta n(-\boldsymbol{k})\ , \qquad (1)$$

where $V(\boldsymbol{k})$ and $\delta n(\boldsymbol{k}) = -in\boldsymbol{k}\boldsymbol{u}(\boldsymbol{k})$ are the Fourier transforms of the interaction $V(\boldsymbol{r})$ and the density variation $\delta n(\boldsymbol{r})$. We can see that $\delta n(\boldsymbol{k})$ is given by the longitudinal displacement $u(\boldsymbol{k})$ (along the $\boldsymbol{k}$-direction), such that the interaction energy can be written as

$$U = -\frac{1}{2}\sum_{\boldsymbol{k}} n^2 k^2 V(\boldsymbol{k})u(\boldsymbol{k})u(-\boldsymbol{k})\ . \qquad (2)$$

Similarly, the interaction energy with an external source $\phi(\boldsymbol{r})$ is

$$U_e = \int d\boldsymbol{r}\phi(\boldsymbol{r})\delta n(\boldsymbol{r}) = -in\sum_{\boldsymbol{k}} k\phi(\boldsymbol{k})u(-\boldsymbol{k}) \tag{3}$$

and the kinetic energy is

$$T = \frac{1}{2}\int d\boldsymbol{r}nm\left[\dot{u}(\boldsymbol{r})\right]^2 = -\frac{1}{2}nm\sum_{\boldsymbol{k}}\dot{u}(\boldsymbol{k})\dot{u}(-\boldsymbol{k}) \ . \tag{4}$$

At high concentrations both the Coulomb interaction and a short-range interaction are present. We apply these results to a binary electrolyte consisting of cations with charge q, mass m_1 and density n and anions with charge $-q$, mass m_2 and density n, with a Coulomb interaction $\varphi(k) = \pm 4\pi q^2/k^2$ and short-range interactions $\chi_{1,2}(k)$ (cation-cation, anion-anion) and $\chi(k)$ (cation-anion) (with spherical symmetry); in the above formulae $V(\boldsymbol{k}) = \varphi(k) + \chi_1(k)$ for cations, $V(\boldsymbol{k}) = \varphi(k) + \chi_2(k)$ for anions and $V(\boldsymbol{k}) = -\varphi(k) + \chi(k)$ for the cation-anion interaction. A dielectric constant can be included in the Coulomb potential. The equations of motion for the two displacements $u_{1,2}(\boldsymbol{k})$ are

$$m_1\ddot{u}_1 + nk^2\left(\varphi + \chi_1\right)u_1 - nk^2\left(\varphi - \chi\right)u_2 = -ik\phi \ ,$$

$$m_2\ddot{u}_2 + nk^2\left(\varphi + \chi_2\right)u_2 - nk^2\left(\varphi - \chi\right)u_1 = ik\phi \ , \tag{5}$$

where we dropped out the argument $\boldsymbol{k}$. It is convenient to introduce the centre-of-mass displacement u and the relative displacement v,

$$u = \frac{m_1 u_1 + m_2 u_2}{M} \ , \ v = u_1 - u_2 \ ,$$

$$u_1 = u + \frac{m_2}{M}v \ , \ u_2 = u - \frac{m_1}{M}v \ , \tag{6}$$

where $M = m_1 + m_2$; equations (5) become

$$M\ddot{u} + nk^2\left(\chi_1 + \chi_2 + 2\chi\right)u - \frac{nk^2}{M}\left(m_1\chi_2 - m_2\chi_1 + \Delta m\chi\right)v = 0 \ ,$$

$$\Delta m\ddot{u} + nk^2\left(\chi_1 - \chi_2\right)u + 2m\ddot{v} + nk^2\left(2\varphi - \chi + \frac{m_2\chi_1 + m_1\chi_2}{M}\right)v + = -2ik\phi \ , \tag{7}$$

where $\Delta m = m_1 - m_2$ and $m = m_1 m_2/M$ is the reduced mass. By making use of $u, v \sim e^{-i\omega t}$, we get the solutions

$$u = -ik\phi\frac{nk^2(m_1\chi_2 - m_2\chi_1 + \Delta m\chi)}{mM^2\left(\omega^2 - \omega_1^2\right)\left(\omega^2 - \omega_2^2\right)} \ ,$$

$$v = ik\phi\frac{1}{m\left(\omega^2 - \omega_1^2\right)} \ , \tag{8}$$

where

$$\omega_1^2 = \omega_p^2 + \frac{nk^2}{2m_1 m_2}\overline{m\chi} \ , \ \omega_p^2 = \frac{nk^2\varphi}{m} = \frac{4\pi nq^2}{m} \ ,$$

$$\overline{m\chi} = \frac{2}{M}\left(m_1^2\chi_2 + m_2^2\chi_1 - 2m_1 m_2\chi\right) \tag{9}$$

and

$$\omega_2^2 = \frac{nk^2}{M}\left(\chi_1 + \chi_2 + 2\chi\right) \tag{10}$$

in the long-wavelength limit $k \to 0$ (see also Ref. [10]). We can see that ω_2 is the frequency of a sound wave, associated with the motion of the centre of mass. In the limit of long wavelengths this motion mode may be neglected, since $u \sim k^3$, equation (8). The frequency ω_1 corresponds

to dispersive plasmons, associated with the motion of the relative coordinate. Its square can be written as $\omega_1^2 = \omega_p^2 + v_s^2 k^2$, where ω_p is the plasma frequency and $v_s = (n\overline{m\chi}/2m_1 m_2)^{1/2}$.

If the external interaction arises from an electric potential φ_0, *i.e.* $\phi = q\varphi_0$, the internal electric field is $E_i = -4\pi n q v = -ik\frac{\omega_p^2}{\omega^2 - \omega_1^2}\varphi_0$ and the total electric field is

$$E_t = -ik\varphi_0 \left(1 + \frac{\omega_p^2}{\omega^2 - \omega_1^2} \right) = -ik\varphi_t \tag{11}$$

in the long-wavelength limit, where φ_t is the total potential. It follows the dielectric function

$$\varepsilon_i = \frac{\omega^2 - \omega_1^2}{\omega^2 - \omega_1^2 + \omega_p^2} = 1 - \frac{\omega_p^2}{\omega^2 - v_s^2 k^2} \ . \tag{12}$$

This is a dielectric function with spatial dispersion (compare with the excitonic dielectric function with spatial dispersion in Refs. [11]-[13]). In the static limit $\omega = 0$ this dielectric function tends to infinity (a perfect screening, $k \to 0$). In this case the total dielectric constant tends to the dielectric function of the medium.

We are interested in the total electric potential in the static limit (equation (11)), given by

$$\varphi_t = \varphi_0 \left(1 - \frac{\omega_p^2}{\omega_1^2} \right) = \varphi_0 \frac{k^2}{k^2 + k_0^2} \ , \tag{13}$$

where $k_0^2 = \omega_p^2/v_s^2 = 8\pi M q^2/\overline{m\chi}$. We can see that an external Coulomb potential $\varphi_0 = Q/r$ generated by a pointlike charge Q in vacuum is screened as

$$\varphi_t = \frac{Q}{r} e^{-k_0 r} \ , \tag{14}$$

the screening length being

$$\Lambda = \frac{1}{k_0} = \left(\frac{\overline{m\chi}}{8\pi M q^2} \right)^{1/2} = v_s/\omega_p \ . \tag{15}$$

The screening is due to plasmons, which, at short wavelengths ($k \gtrsim k_0$), are disrupted by the individual motion of the ions (Landau damping, see Ref. [14]).

For long distances, *i.e.* in the limit $k \to 0$, the Coulomb interaction $\varphi(k) = \pm 4\pi q^2/k^2$ dominates; for short distances ($k \to \infty$) it is replaced by the short-range interaction. We assume that a short-range interaction $\chi(k)$ is the Fourier transform of a hard-core interaction energy χ_0 extending over a volume v with a radius r, such that, in the long-range limit $rk \ll 1$ it is given by $\chi(k) = \chi_0 v$. Within the hard-core approximation two like ions in contact can be viewed as a rigid solid with an orientation given by a vector $\boldsymbol{r}$, whose magnitude is twice the ion diameter. For various orientations this vector describes a sphere. Therefore, the short-range interaction appears in a sphere with radius twice the ion diameter. We note that such a sphere involves two pairs of ions.

The ionic charge is screened locally within a Debye length λ_D. At high concentrations λ_D may be shorter than $r/2$. For short Debye lengths a screened potential $qe^{-\kappa r}/r$, $\kappa = 1/\lambda_D$, can be approximated by a Coulomb potential q/r in a volume v_l with radius l. For short distances the screened potential can be written as $qe^{-\kappa r}/r = q/r - q\kappa....$ The term $-q\kappa$ is the contribution of the other ions. Therefore the interaction energy with an ion with charge q is $\frac{1}{2}q^2\kappa$. On the other hand, the interaction energy due to a Coulomb potential at distance l is q^2/l; therefore, $\kappa l = 2$, *i.e.* $l = 2\lambda_D$. A charge density q/v_l generates a Coulomb interaction at the distance l. The charge in an infinitesimal volume Δv is $q\Delta v/v_l$, so the interaction energy with a pointlike charge q is
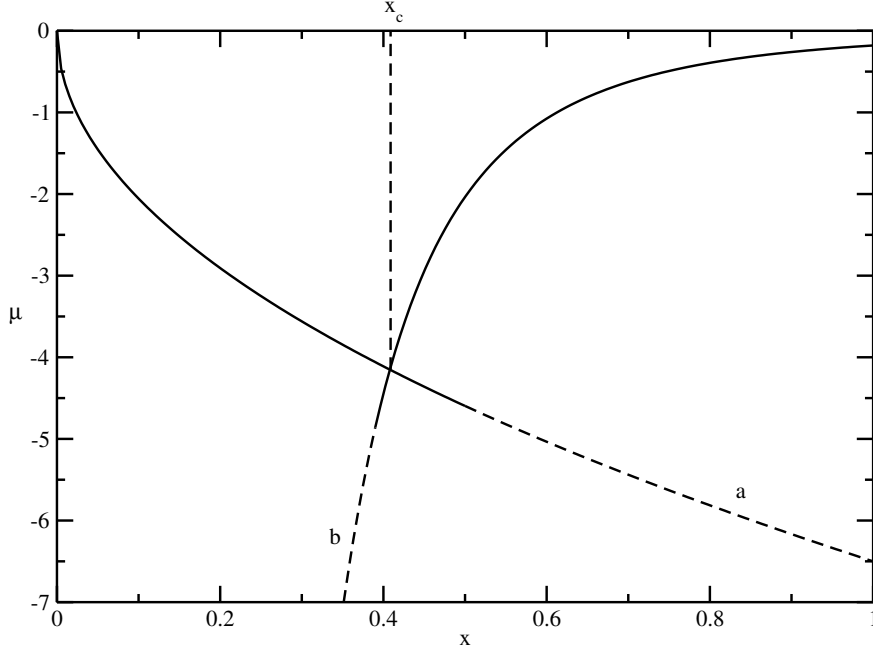
Figure 1: The chemical potentials $10^{12}\mu_d$ for a dilute gas of charges ($\mu_d \simeq -\frac{2}{3}q^2\kappa$, curve a) and $10^{12}\mu_c$ for highly-concentrated charges (μ_c, equation (20)), in ergs, *vs* concentration $x = 10^4 r_0^3 n$ ($r_0 = 2\text{Å}$, $m = 35$, $T = 300K$, $\varepsilon = 1$, see the text). The critical concentration is $x_c = 0.41$.

$q^2\Delta v/v_l l$ (for a purely Coulomb potential the charge is pointlike). The total interaction energy with the nearest neighbours is obtained by summing up all these contributions over the volume v, such that we get $\chi_0 = q^2 v/v_l l$ and $\chi(k) = q^2 v^2/v_l l$. Therefore, we have $\chi_{1,2}(k) = q^2 v_{1,2}^2/v_l l$. As said above, this interaction involves two pairs of ions. The cation-anion interaction involves two cation-anion pairs, which amounts to a cation pair and an anion pair; consequently, we have $\chi(k) = -q^2 v_1 v_2/v_l l$. These are short-range interactions arising from screened ionic charges. We note that these interactions are thermal-equilibrium effective interactions, through the temperature dependence of the Debye length. By making use of $\chi_{1,2}(k)$ and $\chi(k)$ in equation (9), we get

$$\overline{m\chi} = \frac{2q^2}{Mv_l l}\left(m_1 v_1 + m_2 v_2\right)^2 \quad , \tag{16}$$

such that the screening length given by equation (15) becomes

$$\Lambda = \frac{1}{\sqrt{4\pi v_l l}}\frac{m_1 v_1 + m_2 v_2}{M} = \frac{1}{\sqrt{3}}\frac{m_1 r_1^3 + m_2 r_2^3}{Ml^2} \quad , \tag{17}$$

where $r_{1,2}$ are the radii of the volumes $v_{1,2}$. According to our assumption of a hard-core interaction, $r_{1,2}$ should be replaced by twice the ion diameters $2r_{01,2}$; also, we replace the radius l by twice the Debye length, $l = 2\lambda_D$. It follows that in equation (17) we get an additional factor 2; equation (17) becomes

$$\Lambda = 1.15\frac{m_1 r_{01}^3 + m_2 r_{02}^3}{M\lambda_D^2} \tag{18}$$

($2/\sqrt{3} = 1.15$). For ionic diameters close to each other, $r_{01} \simeq r_{02} \simeq r_0$, we may approximate the fraction in equation (18) by r_0^3/λ_D^2. Equation (18) gets the form $\Lambda \simeq 1.15 r_0^3/\lambda_D^2$, which is the scaling law derived in Ref. [4] (where the numerical coefficient is 1.12, see Ref. [4], Supplemental Material). The dielectric constant enters this formula through the Debye length.

Also, we note that under these conditions the frequency of the sound mode given by equation (10), $\omega_2^2 \sim \chi_1 + \chi_2 + 2\chi \sim (v_1 - v_2)^2 \simeq 0$, is vanishing ($v_1 \simeq v_2$). The interplay between the Coulomb interaction q^2/d at distance d and the short-range interaction $\chi_0 = q^2 v/v_l l$ gives $d = v_l l/v$, or, from equation (17), $d \simeq 8r_0^3/3\Lambda^2 \simeq 2\lambda_D^4/r_0^3$, which, at high concentrations may be smaller than $2r_0$. In the range from d to $2r_0$ we have a superposition of Coulomb interaction and short-range interaction.

It is worth giving a numerical estimation of typical values of the quantities discussed above. We take $a = 3$Å, $r_0 = 2$Å and m corresponding to the atomic mass number 35; we get the plasma frequency $\omega_p \simeq 4.4 \times 10^{12} s^{-1}$ (electron charge $q = -4.8 \times 10^{-17} esu$), the Debye length $\lambda_D \simeq 0.4$Å at room temperature ($\varepsilon = 80$) and the screening length $\Lambda \simeq 62$Å. The velocity $v_s = \omega_p \Lambda$ is $v_s \simeq 2.7 \times 10^6 cm/s$. Also, the thermal velocity of the ions is $v_t = \sqrt{T/m} \simeq 2.4 \times 10^4 cm/s$, such that we may estimate a collision frequency $\tau^{-1} \simeq 10^{12} s^{-1}$. We can see that $\omega_p \tau > 1$, *i.e.* the plasmon is relatively well defined, in a collisionless regime, which means that the screening described above is effective. We expect a much smaller dielectric constant for small distances a, such that the plasma frequency is higher.

The plasma excitations derived above govern the thermodynamic properties at high concentrations. According to the hamiltonian given by equations (2)-(4) and the second equation of motion (7), we may restrict ourselves to the motion of the relative coordinate v in the long-wavelength limit. This is the motion of $V k_0^3/6\pi^2$ independent harmonic oscillators with frequency ω_p, where V denotes the volume. The corresponding free energy is

$$F = -\frac{V k_0^3 T}{6\pi^2}\left[\frac{\hbar\omega_p}{2T} - \ln\left(e^{\hbar\omega_p/T} - 1\right)\right] \; ; \tag{19}$$

this formula is valid at thigh concentrations; it leads to a chemical potential

$$\mu_c \simeq -\frac{7k_0^3\hbar\omega_p}{48\pi^2 n} \; . \tag{20}$$

The high-concentration is defined by $q^2/T \gtrsim a$ (or $q^2/\varepsilon T \gtrsim a$) , *i.e.* $\hbar\omega_p/T \gg \sqrt{4\pi\hbar^2/ma^2 T}$, where the quantum-mechanical localization energy $\hbar^2/ma^2$ is much smaller than the temperature T. The chemical potential given by equation (20) increases with concentration like $\mu_c \sim -1/n^{1/2}\Lambda^3 \sim -1/n^{7/2}$, which is faster than the dependence $\mu_c \sim -1/n$ suggested in Ref. [4]. It is worth noting that the thermodynamics of these oscillators is in the quantum-mechanical regime ($\hbar\omega_p/T > \ln 2$).

The chemical potential given by equation (20) can be compared to the well-known chemical potential of the dilute gas of charges $\mu_d \simeq -q^2\kappa$, $\kappa = 1/\lambda_D$ (the logaritmic term may be neglected) in order to get a (very approximate) estimate of the critical temperature T_c and the critical density $n_c = 1/a_c^3$ of the transition to a liquid (at constant volume); the resulting relationship between these two quantities is, approximately, $T_c^{7/2}(a_c/r_0)^{12} \simeq 2.3 \times 10^6 \sqrt{mr_0^2/\hbar^2}(q^2/\varepsilon r_0)^4$ (at constant pressure the chemical potential of the dilute gas is $\mu_d \simeq -\frac{2}{3}q^2\kappa$, which produces a very minor difference). Making use of the numerical data given above ($r_0 = 2$Å, $m = 35$) we get $a_c/r_0 \simeq 29/\varepsilon^{1/3}$ at $T = 300K$ and $\lambda_{D,c} \simeq 3.3$Å, such that $r_0/\lambda_{D,c} \simeq 0.6$. A direct comparison of these formulae with the experimental data would imply the little known concentration dependence of the dielectric constant.[15] The quantities $10^{12}\mu_d \simeq -\frac{2}{3}q^2\kappa$ (curve a) and $10^{12}\mu_c$ given by equation (20) (curve b) are shown *vs* concentration $x = 10^4(r_0/a)^3$ for $r_0 = 2$Å, $m = 35$, $T = 300K$ and $\varepsilon = 1$ in Fig. ...; the critical concentration is $x_c = 0.41$. We can see that the curves (a) and (b) in Fig. ... agree qualitatively with the experimental data and the theoretical curve given in Ref. [4] (for aqueous $NaCl$ solutions).

In conclusion, the long screening length appearing in highly-concentrated electrolytes is due to the screening produced by dispersive plasmons, arising from the Coulomb interaction and the short-range interaction of the screened ionic charges, the latter being effective at high concentrations. By using this short-range interations, the scaling law of the long screening length reported in Ref. [4] is derived.

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