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ABSTRACT

The screening, the configurational correlations and the interaction correlations in the theory of binary electrolytes are examined, by exploiting the charge conservation and the properties of the equilibrium state. Validity conditions for the linearised Debye–Huckel screened potential are provided. A non-zero ionic radius is employed in order to account for solvation effects, and limitations on the contribution of the ionic radius are derived. A possible stabilisation of the ions in equilibrium positions, arising from counterion configurational correlations, is analysed for associated electrolytes, and the corresponding correlation energy is derived. A van der Waals-type equation is presented for strong electrolytes. Some well-known technical difficulties of the theory of electrolytes are revisited, with emphasis on statistical-dynamical correlations, excluded volume and multiple-boundary conditions.

1 Introduction

The Debye–Huckel classical theory of electrolytes [1] enjoyed many discussions throughout the years. The attempts of improving, or extending, this theory highlight its central concept of screening the electrical charges (see, for instance, Refs. [2,3]). In electron plasmas (like ionised gases or electrons in metals) the electrons, which are much more mobile than the ions, screen the ion interaction [4]. A similar situation occurs in colloids, where the electrolyte charges are more mobile than the colloid particles [5], or in electrolytes with a high mass asymmetry. In these cases, an asymmetry occurs in treating the screening, in the sense that one kind of charges is screened by the other kind. Extended studies on colloidal particles with various shapes, placed in various environments, are included in Refs. [6–12], where interesting phenomena are reported, like charge inversion and amplification, capacitive compactness, estimation of the double-layer extension, etc. In electrolyte solutions, with comparable dynamical properties of the ions, the screening is due to both kinds of ions. Difficulties raised by an inadvertent ionic asymmetry in electrolytes have been discussed long time ago, in connection with the electrolyte conductance [13,14].

We analyse in this paper the screening, the configurational correlations and the interaction correlations in binary electrolytes, with the aim of providing a consistent treatment of the Debye-screened potential. In order to account for solvation effects a non-zero ionic radius is explicitly employed, and the corrections brought by this radius to the interaction energy and the limiting law of ion mobility (electrical conductance) are re-derived. Limitations imposed upon the contribution of the excluded volume are presented. A possible stabilisation of the ions in equilibrium positions (counterion configurational correlations) is discussed in associated electrolytes. Well-known

technical difficulties of the theory of electrolytes are revisited [15,16], with emphasis on statistical-dynamical correlations, excluded volume of the particles and multiple-boundary conditions in a space with multiple voids (ionic volume).

2 Excluded volume and ionic density

To begin with, as a general remark, the density of an ensemble of N pointlike particles with determined (distinct) positions r_i is

$$n(r) = \sum_i \delta(r - r_i) . \tag{1}$$

For any fixed position r all the functions $\delta(r - r_i)$ are zero, except the function with r_i close to r, inside a mean volume per particle v_0. In a continuum model, we can write $n(r) = 1/v_0$ and $n(r) = 1/v_0 = \Delta N/\Delta V$, where ΔN is the number of particles within an infinitesimal volume ΔV constructed around the point r (the volume ΔV is large at the microscopic scale of the particles and infinitesimally small at the macroscopic scale). The positions of the particles are statistical variables in this case, and the probability of localising ΔN particles in the volume ΔV is given by the Boltzmann distribution

$$\frac{\Delta N}{N} = \frac{e^{-\beta U(\mathbf{r})}}{\int dr e^{-\beta U(\mathbf{r})}} \Delta V , \tag{2}$$

where $\beta = 1/T$ is the inverse of the temperature T, V denotes the volume and $U(\mathbf{r})$ is the potential energy at the point $\mathbf{r}$. We get the statistical density

$$n(\mathbf{r}) = C(N/V)e^{-\beta U(\mathbf{r})} , \tag{3}$$

where $C = V/\int d\mathbf{r} e^{-\beta U(\mathbf{r})}$ (such that $\int d\mathbf{r} n(\mathbf{r}) = N$). If the particles are endowed with a charge q,

the charge density is $qn(\mathbf{r})$. It is worth noting that in a continuum model, where the Boltzmann distribution applies, the mean distance between particles should be much smaller than any characteristic distance over which the physical quantities vary (e.g. $U(\mathbf{r})$); this amounts to saying that the physical quantities have a slow spatial variation. We show below that this observation leads to the (linearised) Debye–Huckel model. Phenomenological and semi-empirical models have been extensively developed recently, by combining the Boltzmann distribution (Equation (3)) with the Poisson equation, with the aim of accounting for excluded volume, solvent structure, steric effects, hydration, etc., in highly correlated electrolytes [17–19].

We consider an electrolyte dissolved in a polar solvent, consisting of N identical cations with charge $+q$ and N identical anions with charge $-q$ ($N \gg 1$) in a macroscopic volume V (binary electrolyte) [15]. We denote by $\pm$ the two ionic species (cation/anion) and by $i, j = 1, 2, \ldots N$ the ions of each species. We assume that the ions are spheres with the same radius r_0. Both q and r_0 are viewed as parameters, corresponding to ion solvation; they depend on the nature of the solvent and the ions. Different radii r_0 for the two ionic species may lead to different charges, and specific solvation models are then necessary [20,21]. The results presented below can be extended to distinct ionic charges and numbers of ions (e.g. ternary electrolytes). The interaction of the ions with the solvent molecules is taken into account by a dielectric constant.

The radius r_0 limits the available volume for each particle. We need to consider an excluded volume. This circumstance reflects a type of configurational correlations. We consider non-associated electrolytes, i.e. we assume that the ions are not associated in space in formations of two or more ions (strong electrolytes). The available volume for an ion is $V - (2N - 1)v \simeq V - 2Nv$ ($N \gg 1$), where $v = \frac{4\pi}{3}(2r_0)^3$ ($\ll V$). For instance, we cannot put an ion in a sphere

with a volume strictly smaller than $\frac{4\pi}{3}r_0^3$; if two ions are present, we cannot put one of them in a volume strictly smaller than v. In multiple integrations, where the coordinates of the ions are independent variables, the excluded volumes are counted twice, such that a corresponding factor $1/2$ should be included. Therefore, we consider an available volume $\overline{V}$ which includes $2N$ spherical voids with radius r_0 (multiple voids). If the coordinates $r_i^\pm$ of the cations/anions are determined, the density is defined by

$$n_\pm(\boldsymbol{r}) = \sum_i \frac{1}{2\pi r_0^2} \delta(|\boldsymbol{r} - \boldsymbol{r}_i^\pm| - r_0). \tag{4}$$

The variable $\boldsymbol{r}$ in Equation (4) takes values everywhere in the volume $\overline{V}$, the integration over the volume $\overline{V}$ being performed by means of $\int_{r>r_0} dr\delta(r - r_0) = \frac{1}{2}$, such that we get $\int_{\overline{V}} dr n_\pm(\boldsymbol{r}) = N$. Equation (4) indicates a surface charge distribution, which may be viewed as being appropriate for ion solvation. The Coulomb potential generated by a surface charge in the volume $\overline{V}$ is the same as the potential generated by a pointlike charge or a charge distributed in a sphere with radius r_0. The assumption of an excluded volume is associated with a surface charge.

If the ionic positions are statistical variables, the ionic density is defined by the Boltzmann distribution, as in Equation (3). In order to define the statistical ionic density, we need a continuum model, where contributions of the order of the ionic volume $\sim r_0^3$ should be neglected. We assume the existence of an electrostatic potential $\Phi(\boldsymbol{r})$ in the volume $\overline{V}$, such that the energy of an ion placed in the potential is

$$U(\boldsymbol{r}_i) = \frac{\pm q}{2\pi r_0^2} \int_{\overline{V}} dr \delta(|\boldsymbol{r} - \boldsymbol{r}_i^\pm| - r_0)\Phi(\boldsymbol{r}) = \frac{\pm q}{4\pi} \int do\, \Phi(\boldsymbol{r}_i^\pm + \boldsymbol{r}_0), \tag{5}$$

where do is the element of solid angle and $\boldsymbol{r}_0$ is the vector of length r_0. A series expansion in powers of the coordinates of the vector $\boldsymbol{r}_0$ leads immediately to

$$U(\boldsymbol{r}_i) = \pm q\Phi(\boldsymbol{r}_i) \pm \frac{q}{6}r_0^2 \Delta\Phi(\boldsymbol{r}_i) + O(r_0^4). \tag{6}$$

We assume that the potential Φ is generated by the ionic charges. This is a mean field potential. Since there is no charge at $\boldsymbol{r}_i$, the term with the Laplacian in Equation (6) vanishes, so we are left with $U(\boldsymbol{r}_i) = \pm q\Phi(\boldsymbol{r}_i)$, up to contributions of the order r_0^4. We can see, indeed, that contributions of the order r_0^3 are absent in the potential energy and the ionic density. In all the subsequent calculations, we limit ourselves to terms of the order r_0^2; we define the ionic densities in the whole volume $\overline{V}$, like the potential Φ. Both the ionic density and the electrostatic potential are macroscopic quantities, defined in a continuum model. Finally, we get the ionic densities

$$n_\pm(\boldsymbol{r}) = C_\pm n e^{\mp \beta q \Phi(\boldsymbol{r})} \tag{7}$$

where $n = N/\overline{V}$ and the constants $C_\pm$ are determined by

$$\int_{\overline{V}} dr n_\pm(\boldsymbol{r}) = C_\pm n \int_{\overline{V}} dr e^{\mp \beta q \Phi(\boldsymbol{r})} = N. \tag{8}$$

The charge density is given by $\pm q n_\pm(\boldsymbol{r})$, where $n_\pm(\boldsymbol{r})$ are given either by Equation (4) or by Equation (7), up to contributions of the order r_0^2.

3 Screened potential

The electrostatic potential $\Phi(\boldsymbol{r})$ obeys the Poisson equation

$$\Delta\Phi = -4\pi q[n_+(\boldsymbol{r}) - n_-(\boldsymbol{r})] \tag{9}$$

in the volume $\overline{V}$; the dielectric constant of the solvent is tacitly assumed in Equation (9) (its explicit introduction would complicate the notation). The boundary conditions for this equation are discussed below. In equilibrium, in a continuum model, the densities $n_\pm(\boldsymbol{r})$ and the potential $\Phi(\boldsymbol{r})$ vary slowly in space. In order to apply the equilibrium statistics, we need to assume slowly varying functions. In the close neighbourhood of an ion, the Coulomb potential varies abruptly, so we should subtract the Coulomb self-energy, as shown below, which leads to a smooth variation. Consequently, in the series expansion of the exponentials $e^{\pm\beta q\Phi}$, we may write approximately $\Phi^n = \Phi \cdot \overline{\Phi^{n-1}}$ for any $n \geq 1$, and $\overline{\Phi^n} = \overline{\Phi}^2\overline{\Phi^{n-2}} = \ldots = \overline{\Phi}^n$, such that $\Phi^n = \Phi \cdot \overline{\Phi}^{n-1}$, where $\overline{\Phi^n} = \frac{1}{V}\int_{\overline{V}} d\boldsymbol{r}\Phi^n$, $n = 1, 2, \ldots$. This amounts to avoid interaction self-correlations at the same point, as it is naturally expected for a mean field. By using this approximation, it is easy to see that the exponentials $e^{\pm\beta q\Phi}$ can be written as

$$e^{\pm\beta q\Phi} = 1 + \gamma_{\mp}\beta q\Phi, \tag{10}$$

where

$$\gamma_{\mp} = \frac{e^{\pm\beta q\overline{\Phi}} - 1}{\beta q\overline{\Phi}}. \tag{11}$$

The ionic densities become now

$$n_\pm(\boldsymbol{r}) = C_\pm n e^{\mp\beta q\Phi(\boldsymbol{r})} = C_\pm n[1 + \gamma_\pm\beta q\Phi(\boldsymbol{r})] \tag{12}$$

with the normalisation conditions

$$C_\pm(1 + \gamma_\pm\beta q\overline{\Phi}) = 1; \tag{13}$$

Equation (9) becomes

$$\Delta\Phi = -4\pi qn(C_+ - C_-) - 4\pi(C_+\gamma_+ - C_-\gamma_-)q^2 n\beta\Phi(\boldsymbol{r}), \tag{14}$$

where we recognise the (linearised) Debye–Huckel model. The potential $\Phi(\boldsymbol{r})$ changes the local densities from their uniform-distribution values n to $n_\pm(\boldsymbol{r}) = C_\pm n[1 + \gamma_\pm\beta q\Phi(\boldsymbol{r})]$; the change is proportional to the potential, $\delta n_\pm(\boldsymbol{r}) \sim \Phi(\boldsymbol{r})$. Since the number of ions is conserved $\left(\int_{\overline{V}} d\boldsymbol{r}n_\pm(\boldsymbol{r}) = N\right)$, the average potential is zero, $\overline{\Phi} = 0$. This condition leads to $C_\pm = 1$ (Equation (13)), $\gamma_\pm = \mp 1$ (Equation (11)) and

$$\Delta\Phi = \kappa^2\Phi(\boldsymbol{r}), \tag{15}$$

where $\kappa^2 = 8\pi\beta q^2 n$. We can see that the potential Φ is a self-consistent potential.

This equation is solved by using the boundary conditions provided by Equation (4), according to the charge conservation. The solution is a superposition of potentials vanishing at infinity, given by

$$\Phi(\boldsymbol{r}) = q^* \sum_i \left(\frac{e^{-\kappa|\boldsymbol{r}-\boldsymbol{r}_i^+|}}{|\boldsymbol{r}-\boldsymbol{r}_i^+|} - \frac{e^{-\kappa|\boldsymbol{r}-\boldsymbol{r}_i^-|}}{|\boldsymbol{r}-\boldsymbol{r}_i^-|} \right), \tag{16}$$

where the constant of integration q^* (an effective charge) is determined shortly from the charge conservation. Before this, we analyse the condition $\overline{\Phi} = 0$. Equation (16) defines the well-known Debye–Hückel screened potential [1,15]. We can see that in the close neighbourhood of an ion the main contribution to the potential given by Equation (16) is $q^* e^{-\kappa r}/r$, for r close to r_0. For small values of r_0 this contribution has an abrupt variation, arising from the Coulomb self-potential q^*/r for $r \simeq r_0$ in the expansion $q^* e^{-\kappa r}/r = q^*/r - q^*\kappa + \ldots$. This Coulomb self-potential should be removed, such that the assumption of a smooth potential in the Poisson equation is preserved.

The calculation of the average potential $\overline{\Phi} = \frac{1}{V} \int_{\overline{V}} d\boldsymbol{r} \Phi(\boldsymbol{r})$ can be done, most conveniently,

by integrating over the whole volume V and subtracting the contribution of the volume V_{int} of the spheres with radius r_0 (the volume of the voids). In the integral over the volume V_{int}, for a fixed sphere, we need to separate the contribution of that sphere from the contributions of the other spheres. For instance, we get

$$\int_{V_{int}} d\boldsymbol{r} \sum_i \frac{q^* e^{-\kappa|\boldsymbol{r}-\boldsymbol{r}_i^+|}}{|\boldsymbol{r}-\boldsymbol{r}_i^+|} = \frac{4\pi q^*}{\kappa^2} N[1 - (1 + \kappa r_0)e^{-\kappa r_0}] + $$
$$+ \frac{4\pi q^*}{\kappa^2}(\kappa r_0 \cosh \kappa r_0 - \sinh \kappa r_0)\left(\sum_{i \neq j} \frac{e^{-\kappa r_{ij}^{++}}}{\kappa r_{ij}^{++}} + \sum_{ij} \frac{e^{-\kappa r_{ij}^{+-}}}{\kappa r_{ij}^{+-}}\right),$$
(17)

where $r_{ij}^{++} = |\boldsymbol{r}_i^+ - \boldsymbol{r}_j^+|$ and $r_{ij}^{+-} = |\boldsymbol{r}_i^+ - \boldsymbol{r}_j^-|$. A similar contribution arises from the other term of the potential in Equation (16), such that the average potential is

$$\overline{\Phi} = -\frac{4\pi q^*}{\kappa^2 V}(\kappa r_0 \cosh \kappa r_0 - \sinh \kappa r_0) \sum_{i \neq j} \left(\frac{e^{-\kappa r_{ij}^{++}}}{\kappa r_{ij}^{++}} - \frac{e^{-\kappa r_{ij}^{--}}}{\kappa r_{ij}^{--}}\right)$$
(18)

(where $r_{ij}^{--} = |\boldsymbol{r}_i^- - \boldsymbol{r}_j^-|$). Since $\kappa r_0 \cosh \kappa r_0 - \sinh \kappa r_0 = (\kappa r_0)^3/3 + \ldots$, we can see that $\overline{\Phi} = 0$ within our approximation of a small excluded volume. This condition defines the equilibrium state of the electrolyte. Also, it follows that κr_0 should be much less than unity.

The effective charge q^* is determined from the condition that the integral $\int d\boldsymbol{r} \Delta \Phi$ over the volume $\overline{V}$ is equal to 4π multiplied by the total charge. The integral $\int d\boldsymbol{r} \Delta \Phi$ reduces to a sum of surface integrals of $grad\Phi$ over the spherical surfaces with radius r_0 surrounding the ions (the contribution of the surface at infinity is zero). Let us assume a cation placed at $\boldsymbol{r}_i^+$. The surface integrals can be effected straightforwardly, with the result

$$q^*(1 + \kappa r_0)e^{-\kappa r_0} - q^*(\kappa r_0 \cosh \kappa r_0 - \sinh \kappa r_0)\left(\sum_{j,1pt j \neq i} \frac{e^{-\kappa r_{ij}^{++}}}{\kappa r_{ij}^{++}} - \sum_j \frac{e^{-\kappa r_{ij}^{+-}}}{\kappa r_{ij}^{+-}}\right) = q.$$
(19)

For an anion placed at $\boldsymbol{r}_i$ the result is the same with q^*, q changed to $-q^*, -q$ and r_{ij}^{++} changed in r_{ij}^{--}. The summation over all the cations and separately over all the anions leads to the same charge q^*, providing the condition $\overline{\Phi} = 0$ given above (Equation (18)) is satisfied. Therefore, the effective charge is given by

$$q^*(1 + \kappa r_0)e^{-\kappa r_0} - q^*(\kappa r_0 \cosh \kappa r_0 - \sinh \kappa r_0)\left(\frac{1}{N}\sum_{i \neq j} \frac{e^{-\kappa r_{ij}^{++}}}{\kappa r_{ij}^{++}} - \frac{1}{N}\sum_{i,j} \frac{e^{-\kappa r_{ij}^{+-}}}{\kappa r_{ij}^{+-}}\right) = q,$$
(20)

i.e.

$$q^* = q\frac{e^{\kappa r_0}}{1 + \kappa r_0} \simeq 1 + \frac{1}{2}(\kappa r_0)^2.$$
(21)

We note that a non-zero ionic radius $r_0 \neq 0$ leads to an enhanced effective charge $q^* > q$.

4 Correlation energy

We pass now to computing the electrostatic energy E of the electrolyte. It is given by $E = \frac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})\Phi(\mathbf{r})$ (without including the self-energy), where $\rho(r)$ is the charge density. If we use

$$\rho = q(n_+ - n_-) = -2n\beta q^2\Phi \tag{22}$$

(according to Equations (12)), we get $E = -\frac{\kappa^2}{8\pi}\int d\mathbf{r}\Phi^2(\mathbf{r}) = 0$. This is too crude an approximation, because the potential Φ given by Equation (16) shows that the main contribution arises from the regions near the ionic positions, where $|\mathbf{r} - \mathbf{r}_i^\pm| \simeq r_0$, which indicates the use of the ionic density given by Equation (4), instead of the statistical density. According to Equation (4), the charge densities of the ionic spheres are

$$\rho_\pm(\mathbf{r}) = \pm\sum_i \frac{q}{2\pi r_0^2}\delta(|\mathbf{r} - \mathbf{r}_i^\pm| - r_0); \tag{23}$$

the potential given by Equation (16) can be written as

$$\begin{aligned}\Phi(\mathbf{r}) &= \sum_i \left[\Phi_i^+(\mathbf{r}) + \Phi_i^-(\mathbf{r})\right], \\ \Phi_i^\pm(r) &= \pm q^* \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}_i^\pm|}}{|\mathbf{r}-\mathbf{r}_i^\pm|},\end{aligned} \tag{24}$$

such that the electrostatic energy is given by

$$E = \int_V d\mathbf{r}\left[\frac{1}{2}\sum_{i\neq j}\rho_i^+\Phi_j^+ + \frac{1}{2}\sum_{i\neq j}\rho_i^-\Phi_j^- + \sum_{ij}\rho_i^+\Phi_j^-\right], \tag{25}$$

where we avoid the self-energy of the screened ions; Equation (25) accounts only for the electrostatic interaction energy of the screened ionic charges. The integration in this equation is performed immediately; we get

$$E = \frac{qq^*}{2\kappa r_0}\sinh\kappa r_0\left[\sum_{i\neq j}\left(\frac{e^{-\kappa r_{ij}^{++}}}{r_{ij}^{++}} + \frac{e^{-\kappa r_{ij}^{--}}}{r_{ij}^{--}}\right) - 2\sum_{ij}\frac{e^{-\kappa r_{ij}^{+-}}}{r_{ij}^{+-}}\right], \tag{26}$$

where $\frac{q^*\sinh\kappa r_0}{\kappa r_0} = q\left[1 + \frac{1}{3}(\kappa r_0)^2\right]$.

In general, the calculation of the summations in Equation (26) can be done by using two-particle correlation functions [22–24]. For a uniform distribution of ions, Equation (26) leads to $E = 0$, such that a non-vanishing contribution may result from self-energies. For higher densities (or low temperature), the summations in Equation (26) can be performed by taking into account the excluded volumes indicated by $i\neq j$ and r_{ij}^{+-} in a uniform distribution of ions. For like ions a volume $\overline{V}/N = \frac{4\pi}{3}a^3$ is assigned to each ion, where $2a$ is the mean separation distance between these ions ($a > r_0$); the corresponding excluded volume is $\frac{4\pi}{3}(2a)^3$. For counterions, a volume $\overline{V}/2N = \frac{4\pi}{3}\overline{a}^3$ is assigned to each ion, the excluded volume is $\frac{4\pi}{3}(2\overline{a})^3$, where $\overline{a} = a/2^{1/3}$. This assumption of excluded volumes reflects a type of configurational correlations. We give here the computation of the first summation in Equation (26) (for a fixed r_i), omitting the superscripts $++$:

$$\begin{aligned}{\sum_j}' \frac{e^{-\kappa r_{ij}}}{r_{ij}} &= n\int_{\overline{V}_1}d\mathbf{r}\frac{e^{-\kappa|r_i-r|}}{|r_i-r|} - n\int_{2r_0 < r < 2a}d\mathbf{r}\frac{e^{-\kappa r}}{r} = \\ &= \sum -\frac{4\pi n}{\kappa^2}\left[(1 + 2\kappa r_0)e^{-2\kappa r_0} - (1 + 2\kappa a)e^{-2\kappa a}\right],\end{aligned} \tag{27}$$

where $\Sigma = n \int_{\overline{V}_1} d\mathbf{r} \frac{e^{-\kappa r}}{r} = \sum_i \frac{e^{-\kappa r_i}}{r_i}$ (and the prime means the excluded volume); the volume $\overline{V}_1$ is the whole volume V minus the spherical volumes with radius $2r_0$. The calculation of Σ leads to

$$
\begin{aligned}
\Sigma &= n \int_V d\mathbf{r} \frac{e^{-\kappa r}}{r} - n \sum_i \int_{r < 2r_0} d\mathbf{r} \frac{e^{-\kappa|r_i+r|}}{|r_i+r|} = \\
&= \frac{4\pi n}{\kappa^2} - \frac{4\pi n}{\kappa^3} \left(2\kappa r_0 \cosh 2\kappa r_0 - \sinh 2\kappa r_0\right) \sum \,,
\end{aligned}
\tag{28}
$$

i.e. $\Sigma = 4\pi n/\kappa^2$. The quantity Σ does not enter the final result of Equation (26). Introducing all the three summations in Equation (26), we get

$$
E = \frac{4\pi q q^* n}{\kappa^3 r_0} N \sinh \kappa r_0 \left[(1 + 2\kappa a)e^{-2\kappa a} - (1 + 2\kappa \overline{a})e^{-2\kappa \overline{a}}\right].
\tag{29}
$$

It is easy to see that E given by Equation (29) is always negative (for $\overline{a} < a$), indicating the tendency towards a bound state. Formally, we may get a simplified expression of E in the limits $\kappa r_0 \ll 1$ and $\kappa a, \kappa \overline{a} \ll 1$; it is the Coulomb energy

$$
E \simeq -\frac{6q^2}{a}(1 - 2^{-2/3})N + \ldots = -2.2\frac{q^2}{a}N + \ldots .
\tag{30}
$$

The error introduced in the above calculation by the continuum approximation of a uniform ionic distribution with excluded volume (in comparison with the discrete summations) may change slightly the numerical coefficient $1 - 2^{-2/3}$ in Equation (30); however, the counterions are always closer to each other than the like ions, such that the energy is always negative. The fluctuations of the parameter $\overline{a}$ about the equilibrium position, $\overline{a} \to \overline{a} + \delta \overline{a}$ ($< \delta \overline{a} > = 0$), lead to a positive change $\delta E = 8\pi q^2 nN(\delta \overline{a})^2 > 0$ in energy, which shows that the equilibrium is stable. For moderately low temperatures or dilutions the electrolyte solute looks like a liquid, while lowering further the temperature or increasing the concentrations, where the Debye length becomes comparable to, or shorter than the mean inter-ion separation distance a ($\kappa a \geq 1$), the ions may stabilise themselves in equilibrium positions (in estimating the numerical values of the energy in Equation (30) we should include the dielectric constant of the solvent). An estimate of these critical values of the temperature and the concentration is given shortly below. In this case, the equilibrium state should be re-constructed, by including the repulsive ionic interaction. Such a long-range order in electrolytes has been suggested a long time ago [25]. The stabilisation of the ions in equilibrium positions indicates an associated electrolyte, similar to an ionic solid (e.g. the factor 2.2 in Equation (30) is a Madelung constant [26]). It is difficult to illustrate such an ionic solid by numerical calculations, because of the finite spatial extension of the ionic sample, which generates instabilities. The factor $1/2$ in $\overline{a}^3 = a^3/2$ is reminiscent of the correlation factor introduced by Bjerrum for associated electrolytes [27].

The characteristic length of variation of the screened potential given by Equation (16) is the Debye length κ^{-1}. According to the assumption of the continuum model and the statistical equilibrium, this screening length should be much longer than the mean separation distance $2\overline{a}$ between counterions, i.e. $2\kappa\overline{a} \ll 1$, or, approximately, $\frac{q^2}{a} \ll T$: the Coulomb energy should be much smaller than the temperature. q^2/T is the Bjerrum length. For $q = -4.8 \times 10^{-10} esu$ (electron charge) and $T = 300K$ we get $q^2/T = 5.5 \times 10^{-6} cm$; if we allow for a dielectric constant $\varepsilon = 80$ (water), we get $q^2/T = 7 \times 10^{-8} cm$. For mean separation distances smaller than the Bjerrum length, interaction correlations appear and the above description, based on the existence of a mean-field potential, is no longer valid [28–30]. In this case, the change in position of an ion modifies the potential, such that the removal of the self-correlations (in $\Phi^n = \Phi\overline{\Phi}^n$) is not valid anymore. We need to solve for the effects of the interaction, repulsive ionic interactions included, and expect elementary excitations like plasmons, or sound-like waves.

For high temperatures or high dilutions ($\kappa a \ll 1$) the electrolyte behaves as a (non-ideal) gas. The excluded volumes discussed above (associated to the mean distances a and $\bar{a}$) are practically zero, as a consequence of the thermal motion, the interaction energy given by Equation (26) is vanishing, and we are left with the self-energy of the screened ions (not included in Equation (26)), which is given by

$$E_{ion} = \frac{qq^*}{2\pi r_0^2} \int_{r > r_0} d\mathbf{r} \frac{e^{-\kappa r}}{r} \delta(r - r_0) = \frac{qq^*}{r_0} e^{-\kappa r_0} = \frac{q^2}{r_0(1 + \kappa r_0)} \; ; \tag{31}$$

subtracting the Coulomb self-energy and multiplying by $\frac{1}{2} \cdot 2N$, we get the well-known total interaction (or correlation) energy [1,15]

$$E_{int} = -\frac{q^2 \kappa N}{1 + \kappa r_0} \simeq -q^2 \kappa N \left[1 - \kappa r_0 + (\kappa r_0)^2\right]. \tag{32}$$

Using $E_{int}/T^2 = -\frac{\partial}{\partial T}(F_{int}/T)$, we get the interaction free energy F_{int} (up to a T-independent term in F_{int}/T, arising from the excluded volume). According to the theorem of small increments, F_{int} gives also the interaction contribution to the Gibbs free energy at constant pressure and temperature for the electrolyte solution (in computing the Gibbs free energy it is convenient to introduce the number of particles and the molecular volume of the solvent) [31]. The statistical equilibrium requires an estimation of the interaction effects up to relative corrections of the order $q^2/aT = (\kappa a)^2 \ll 1$, where a is the mean inter-ionic separation distance. The energy given by Equation (32) satisfies this criterion, since $E_{int}/N(q^2/a)$ is of the order κa. Also, the energy given by Equation (30) satisfies this criterion, although the energy given by Equation (29) may lead to $\kappa a \geq 1$, which requires the re-construction of the equilibrium state. Higher-order correlations may bring contributions, which infringe upon this criterion, or are irrelevant.

5 van der Waals equation

By using the above results, we can arrive at a van der Waals-type equation for the non-ideal electrolyte gas. According to our assumptions, the excluded volume $\sim r_0^3$ should be omitted in this equation ($\overline{V} = V$); also, the small terms κr_0 and $(\kappa r_0)^2$ in Equation (32) may be neglected, since E_{int} should be a small correction to the energy, which implies $a \gg q^2/T$ ($\kappa a \ll 1$). We get the correction to the free energy $F_{int} = -\frac{2}{3} q^2 \kappa N$ and the total (osmotic) pressure (at an interface with the solvent, van't Hoff's law)

$$p = \frac{2NT}{V} - \frac{2\sqrt{2\pi}}{3} T \left(\frac{q^2 N}{TV}\right)^{3/2}. \tag{33}$$

The function $p(V)$ given by this equation has a maximum at $V_1 = a_1^3$, $a_1 = (\pi/2)^{1/3}(q^2/T)$, where the pressure is $p_1 = \frac{4}{3\pi} T(T/q^2)^3$ and a zero at $V_0 = a_0^3$, $a_0 = (2\pi/9)^{1/3}(q^2/T)$. Close to these points (where the correction to the energy is no longer small) the negative pressure generated by the Coulomb interaction dominates the thermal pressure; in this region, the electrolyte has the tendency to collapse in a bound state, first as a liquid, followed by an ionic solid. The values $a_{0,1}$ can be taken as an estimate of the parameter a used in Equation (29) for an associated electrolyte. Equation (33) can be written as $p_r = 1/\bar{v} - \sqrt{\pi}/3\bar{v}^{3/2}$ in the reduced variable $\bar{v} = V/2Nv_b$, where $p_r = pv_b/T$ and $v_b = (q^2/T)^3$ is the Bjerrum volume; the curve $p_r(\bar{v})$ is shown in Figure 1.

In order to compute the Gibbs free energy Φ we need to introduce the molecular volume $v_0 = V/N_0$ of the solvent, where N_0 is the number of solvent molecules; v_0 is a function of the pressure p and the temperature T. For a weak electrolyte ($N \ll N_0$), the Gibbs free function is given by
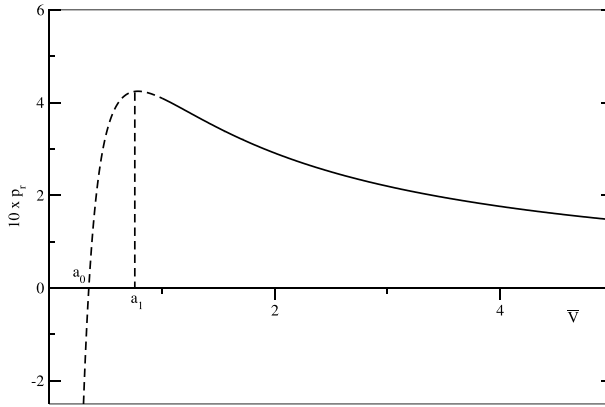
Figure 1. Reduced pressure *vs* reduced volume $p_r = 1/\bar{v} - \sqrt{\pi}/3\bar{v}^{3/2}$ (van der Waals-type curve for electrolytes, Equation (33)). The parameters $a_{0,1}$ are of the order of the Bjerrum length q^2/T. In this concentration region the electrolyte has the tendency to collapse into a correlated state (ionic liquid, ionic solid).

$$\Phi = N_0\mu_0 + 2NT\ln(N/eN_0) + N(\psi_+ + \psi_-) - \frac{2}{3}N_0\sqrt{\frac{\pi}{v_0 T}}\left(\frac{2q^2 N}{N_0}\right)^{3/2}, \qquad (34)$$

where μ_0 is the chemical potential of the pure solvent and $\psi_{\pm}$ are undetermined functions of p and T [31]. Hence, we can compute the chemical potentials of the solvent and the ions, as well as the change in the freezing point, the boiling point, the vapour pressure, etc. For instance, the heat released by dilution is

$$Q = \frac{2\sqrt{\pi}}{3}N_0\left(\frac{2q^2 N}{N_0}\right)^{3/2}T^2\frac{\partial}{\partial T}\left(\frac{1}{v_0^{1/2}T^{3/2}}\right) \qquad (35)$$

(the dielectric constant should be included under the temperature derivative).

6 Ion mobility

The non-zero ionic radius r_0 brings a small correction to the relaxation change in the mobility of the ions. We give here a simple derivation of the relaxation change in mobility for high dilution. According to Onsager [14], this change consists of two factors. The first factor arises from the change brought about by the external electric field in the localisation probability. This change is $-\beta\int dr\rho\delta\Phi$, where ρ is the charge distribution of an ion and $\delta\Phi = -\kappa q^* e^{-\kappa r_0}\delta x/r$ is the change in the potential of a counterion, with δx the change in position along the electric field (removing the Coulomb contribution). It is easy to see that δx is the projection along the direction of the electric field of the displacement $r\cos\theta$ produced by the field along $\mathbf{r}$, i.e. $r\cos^2\theta$, where θ is the angle between $\mathbf{r}$ and the direction of the field. Averaging over directions, we get $\delta x = \frac{1}{3}r$, such that $\delta\Phi = -\frac{1}{3}\kappa q^* e^{-\kappa r_0}$ and the change in probability is $-\frac{1}{3}\beta qq^*\kappa e^{-\kappa r_0}$. The second factor arises from the change in the mean correlated mobility. The mobility μ, defined as velocity divided by force, $v = \mu F$, implies a correlated mobility arising from the product of two velocities, $v_1 v_2 = \mu_1\mu_2 F^2$. The correlated mobility S is given by $S = \bar{\mu} - \sqrt{\bar{\mu}}S$, where $\bar{\mu}$ is the average mobility (for counterions) [14]. In general, for two counterions with charges $q_{1,2}$ and mobilities $\mu_{1,2}$ the average mobility is $\bar{\mu} = (q_1\mu_1 - q_2\mu_2)/(q_1 - q_2)(\mu_1 + \mu_2)$; for

binary electrolytes $q_1 = -q_2 = q$ and $\bar{\mu} = 1/2$ [32]. It follows that the mobility factor is $S = 1 - 1/\sqrt{2}$. Finally, we get the mobilities corrected by the counterion relaxation (Kohlrausch law)

$$\mu_{1,2} \to \mu_{1,2}\left(1 - \frac{S}{3}\beta qq^* \kappa e^{-\kappa r_0}\right) = \mu_{1,2}\left[1 - \frac{S\beta q^2 \kappa}{3(1 + \kappa r_0)}\right]; \qquad (36)$$

we can see that a non-zero ionic radius further reduces the ion mobility [33]. A similar result is valid for the electrophoretic part of the change in the mobility, by replacing the screening length κ^{-1} by $\kappa^{-1} + r_0 = \kappa^{-1}(1 + \kappa r_0)$. These formulae should be limited by $(1 + \kappa r_0)^{-1} \simeq 1 - \kappa r_0 + (\kappa r_0)^2$.

In the opposite limit of higher concentrations, or lower temperatures, there may appear two distinct behaviours of the conductance. If the configurational correlations and association dominate, especially in solvents with small dielectric constants, we may have a further decrease in conductance; their effect may be diminished in solvents with larger dielectric constants, such that the conductance may exhibit a tendency of increasing with increasing concentration.

7 Conclusions

The main assumption of the above calculations is the existence of an electrostatic, self-consistent mean-field potential $\Phi(\mathbf{r})$, generated by the ionic charge distribution in the volume $\overline{V}$, i.e. for all points $\mathbf{r}$ except those belonging to the ions with radius r_0. In equilibrium, the cation/anion charge density is given by the Boltzmann distribution $n_{\pm}(\mathbf{r}) \sim e^{\mp \beta q \Phi(\mathbf{r})}$. These charge densities are defined for all points $\mathbf{r}$ where the potential is defined. Consequently, the electrolyte is viewed as a continuous medium (with multiple voids), and we need to consider only smooth spatial variations of the potential and the density. This observation leads straightforwardly to the linearised form of the density given by Equation (12) (with $C_{\pm} = 1$ and $\gamma_{\pm} = \mp 1$). Usually, this result is valid for an external potential, which varies smoothly in space. For our potential, generated by interacting charges, we need to take into account the potential in the close neighbourhood of the ions, where it is a Coulomb potential. The ionic voids act like multiple boundary conditions. Since the Coulomb potential varies abruptly near the ions, we need to remove the Coulomb self-interaction. This way we arrive at the screened potential (Equation (16)) and the interaction energy given by Equation (26) (without self-energy) for moderately higher concentrations or the screened self-energy given by Equation (32) for dilute concentrations.

In conclusion, the equilibrium state of the electrolytes implies a vanishing average electrostatic potential ($\overline{\Phi} = 0$) and the absence of the interaction self-correlations ($\gamma_{\pm} = \mp 1$); the main role in their interaction properties is played by screening and configurational correlations. For higher concentrations (or lower temperatures) the Coulomb interaction dominates. Its minimisation leads to ionic excluded volumes, which reflect a type of configurational correlations, such that the ions tend to stabilise themselves in equilibrium positions. This situation may correspond to associated electrolytes (similar to ionic solids). For higher dilutions, or higher temperatures (which is the current situation in electrolyte solutions), the screening correlations dominate, and the interaction energy is the self-energy of the screened ions (correlation energy). A non-zero ionic radius, which reflects another type of configuration correlations, may account for solvation effects; it leads to well-known corrections to the screening, the interaction energy and the ionic mobility, through an effective charge occurring in the electrostatic potential.

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