Letter

Correct scaling of the correlation length from a theory for concentrated electrolytes

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Abstract

Self-consistent theory for concentrated electrolytes is developed. Oscillatory decay of the charge–charge correlation function with the decay length that shows perfect agreement with the experimentally discovered and so far unexplained scaling is obtained. For the density–density correlations, monotonic asymptotic decay with the decay length comparable with the decay length of the charge correlations is found. We show that the correlation lengths in concentrated electrolytes depend crucially on the local variance of the charge density.

Keywords: structure of ionic liquid mixtures, correlation length in concentrated electrolytes, effects of fluctuations

(Some figures may appear in colour only in the online journal)

According to theoretical predictions, the disjoining pressure (DP) between plates confining the dense electrolyte should decay with increasing distance between the plates with the decay length \(\lambda_S\) equal to the correlation length in the bulk. The results of experimental measurements for dilute electrolytes confirm that the decay length is equal to the Debye screening length, \(\lambda_D\), in perfect agreement with theoretical predictions. \(\lambda_D\) decreases with increasing concentration of ions, \(\rho\). As shown in recent surface force balance experiments [1–3], however, \(\lambda_S\) in concentrated electrolytes increases with increasing \(\rho\) instead of further decreasing, in contrast to theoretical predictions of classical theories [4]. Moreover, \(\lambda_S\) follows the scaling relationship \(\lambda_S/\lambda_D \sim (a/\lambda_D)^3\), where \(a\) is the ion diameter [3]. This relationship was verified for simple salts in water, ionic liquid solutions and alkali halide solutions. Support for the long decay length has been recently provided by using an independent technique in [5].

Several theoretical attempts have been made to tackle the problem. In particular, an explanation of the long decay length has been proposed within the framework of the dressed ion theory extension [6, 7]. The scaling law for the screening length has been confirmed in [8–12] based on different assumptions, introducing e.g., short-range repulsive and attractive non-Coulomb interactions between the ions, and/or solvent structure or some modification of the short-range part of the Coulomb potential. However, the scaling exponents found in these studies as well as in all-atom molecular dynamics simulations [13, 14] appeared to be significantly lower than the experimentally measured one. Unfortunately, molecular simulations have to be performed in a finite size box. Very long correlations cannot be tested there, since when the box size increases, the noise increases too. The puzzle remains unsolved.

In this letter we consider both, the charge–charge and the density–density correlation functions in the mesoscopic theory developed for ionic systems and for mixtures in [15, 16]. In this theory, we consider dimensionless charge and number density of ions in mesoscopic regions around \(\mathbf{r}\), \(c(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})\) and \(\rho(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})\), respectively. \(\pi \rho_i(\mathbf{r})/6\) is the fraction of the volume of the mesoscopic region that is covered by the ions of the \(i\)-type, with \(i = +, -\), and

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may correspond to different distributions of the centers of ions. Hence, \( \epsilon(\mathbf{r}) \) and \( \rho(\mathbf{r}) \) represent a set of microscopic states and can be considered as constraints imposed on the system. The grand potential for fixed \( \epsilon(\mathbf{r}) \) and \( \rho(\mathbf{r}) \) is associated with the allowed microscopic states and takes the standard form

\[
\Omega_{\text{co}}[c, \rho] = U_{\text{co}}[c, \rho] - TS - \mu \int \text{d}\mathbf{r} \rho(\mathbf{r}),
\]

where \( T \) is temperature, \( \mu \) is the chemical potential of the ions, and \( S[c, \rho] \) is the entropy in the presence of the constraints \( \epsilon(\mathbf{r}) \) and \( \rho(\mathbf{r}) \). We make the approximation \(-TS = \int \text{d}\mathbf{r} f_{\text{h}}(\epsilon(\mathbf{r}), \rho(\mathbf{r}))\), where \( f_{\text{h}}(\epsilon, \rho) \) is the free-energy density corresponding to the entropy of mixing of ions and solvent,

\[
\beta f_{\text{h}}(\epsilon, \rho) = \rho_+ \ln \rho_+ + \rho_- \ln \rho_- + (\rho_{\text{tot}} - \rho) \ln(\rho_{\text{tot}} - \rho)
\]

and \( \beta = 1/k_B T \), with \( k_B \) the Boltzmann constant. For simplicity we assume \( \rho_{\text{tot}} = 1 \). The average diameter of the ions and solvent molecules is denoted by \( a \), and serves as a length unit. In the expression for the internal energy \( U_{\text{co}} \), the Coulomb potential should be multiplied by the pair distribution function \( g(r) \) \(^{[4]}\) for given constraints, i.e. for suppressed large-scale fluctuations. In the dense electrolyte, the key role of \( g(r) \) is to suppress nonphysical states with overlapping cores of the ions. Thus, we approximate \( g(r) \) by the Heaviside \( \theta \) function, and assume

\[
U_{\text{co}}[c, \rho] = \frac{1}{2} \int \text{d}\mathbf{r}_1 \int \text{d}\mathbf{r}_2 \frac{\epsilon^2(\mathbf{r}_1) c(\mathbf{r}_1 + \mathbf{r}) \theta(|\mathbf{r}| - 1)}{\epsilon|\mathbf{r}|},
\]

where \( \epsilon \) is the elementary charge, \( \epsilon \) is the dielectric constant of the medium, and the integrals are performed over the whole space. Note also that in the exact theory, the states with overlapping cores of ions appear with zero probability and do not contribute to the grand potential. In approximate theories, contributions from the forbidden states to the internal energy can be avoided by limiting the integration in \( (2) \) to \( r > a \) \(^{[11, 15, 17]}\). Different regularization of the Coulomb potential leads to similar results \(^{[18]}\).

The subscript \( \text{co} \) indicates that the microscopic states incompatible with the constraints \( \epsilon(\mathbf{r}) \) and \( \rho(\mathbf{r}) \) do not contribute to \( \Omega_{\text{co}} \). When the constraints \( \epsilon(\mathbf{r}) \) and \( \rho(\mathbf{r}) \) are released, such microscopic states, i.e. fluctuations \( \phi \) and \( \eta \) around the fields \( \epsilon \) and \( \rho \), can appear. The average charge and number densities can remain equal to \( \epsilon(\mathbf{r}) \) and \( \rho(\mathbf{r}) \), if the fluctuations cancel one another, i.e. \( \langle \phi \rangle = \langle \eta \rangle = 0 \). Note, however, that these additional microscopic states give additional contribution to the grand potential.

\( c = 0 \) in the absence of electrostatic field independently of the concentration of ions. What distinguishes dilute and concentrated electrolytes is the variance of the charge density, \( \langle \phi^2(\mathbf{r}) \rangle \). Imagine a window at \( \mathbf{r} \) with the size comparable with the size of ions. In the course of time, solvent molecules and ions enter and leave the window. The charge in the window vanishes when it is occupied by the solvent, but when a cation or an anion enters the window, it becomes positively or negatively charged. When the concentration of the ions increases, the window becomes charged more and more often. The average deviation of the local charge from zero is independent of \( \mathbf{r} \), and is given by \( \sqrt{\langle \phi^2 \rangle} \).

In order to see the role of \( \langle \phi^2 \rangle \) for highly concentrated electrolytes, let us divide the system into windows described above, and assume that the charge in each window is either \( +\sqrt{\langle \phi^2 \rangle} \) or \( -\sqrt{\langle \phi^2 \rangle} \). Entropy favors random distribution of the + and - signs among the cells, but oppositely charged nearest neighbors are favored by the energy. For two windows separated by the distance \( \Delta r \), there are four possible combinations of the +, − signs. When the charge in the considered cells is fixed so that the energy of this pair is negative, +, − and −, + signs are left. The excess free energy in \( k_B T \) units associated with fixing opposite charges is roughly \( \beta \Delta F = -k_B \langle \phi^2 \rangle/\Delta r + \ln 2 \), where \( k_B = \beta^2/\epsilon \) is the Bjerrum length in \( \epsilon \) units. \( \beta \Delta F < 0 \) for \( \Delta r < k_B \langle \phi^2 \rangle/\ln 2 \), and the energy gain due to the charge correlation dominates the entropy loss. For \( \Delta r > k_B \langle \phi^2 \rangle/\ln 2 \), however, the entropy wins, and the charges are not correlated. From \( \beta \Delta F \approx 0 \) we obtain a rough estimation for the correlation length, \( \sim k_B \langle \phi^2 \rangle \). Note that \( \langle \phi^2 \rangle \sim \rho \), since the variance of a fluctuating quantity should be proportional to the number of fluctuating objects. Thus, the correlation length is \( \lambda_s/a \sim k_B \rho \). This scaling is equivalent to \( \lambda_s/\lambda_B \sim (a/\lambda_B)^3 \) because \( a/\lambda_B = \sqrt{\epsilon} \), and is therefore in agreement with experiments \(^{[2, 3, 19]}\). The above considerations highlight the significance of the variance of the charge density, and a need for a first-principles theory that takes it into account.

Fluctuations \( \phi \) and \( \eta \) appear with the probability proportional to \( \exp(-\beta \Delta \Omega_{\phi}) \), where \( \Delta \Omega_{\phi} \) is the excess grand potential associated with appearance of the considered fluctuations \(^{[20]}\). We expect that these fluctuations can be correlated at large distances, as discussed on the physical grounds above. Taking into account the fluctuation contribution, we obtain

\[
\beta \Omega[c, \rho] = \beta \Omega_{\text{co}}[c, \rho] - \ln \int \text{D}\eta \int \text{D}\phi \exp[-\beta \Delta \Omega_{\phi}[c, \rho, \phi, \eta]].
\]

(3)

where \( \Omega_{\text{co}}[c, \rho] \) is given in \((1)-(2)\) and \( \int \text{D}\Omega \) denotes the functional integral. The leading-order contributions to \( \Omega \) coming from the fluctuation term in \((3)\) are proportional to \( \langle \phi^2 \rangle \) when periodic \( \phi(\mathbf{r}) \) minimizes the energy \(^{[21, 22]}\). The correlation functions \( G_{\phi\phi}(\mathbf{r}) = \langle \phi(\mathbf{r}) \phi(\mathbf{r} + \mathbf{r}) \rangle \) and \( G_{\phi\eta}(\mathbf{r}) = \langle \eta(\mathbf{r}) \eta(\mathbf{r} + \mathbf{r}) \rangle \) can be calculated with the probability distribution proportional to \( \exp(-\beta \Delta \Omega_{\phi}) \). On the other hand, \( G_{\phi\phi} \) and \( G_{\phi\eta} \) are inverse to the second functional derivative of \( \beta \Omega[c, \rho] \) with respect to the corresponding fields. \( G_{\phi\phi} = 0 \) for \( c = 0 \).

We make the self-consistent Gaussian approximation

\[
\beta \Delta \Omega_{\phi}[c, \rho, \phi, \eta] \approx \beta H_{\phi\phi}[c, \rho, \phi, \eta]
\]

with

\[
\beta H_{\phi\phi}[c, \rho, \phi, \eta] = \frac{1}{2} \int \text{d}\mathbf{r}_1 \int \text{d}\mathbf{r}_2 \left[ \phi(\mathbf{r}_1) C_{c,\phi}(\mathbf{r}_1) \phi(\mathbf{r}_2) + \eta(\mathbf{r}_1) C_{\rho,\phi}(\mathbf{r}_1) \eta(\mathbf{r}_2) \right],
\]
where $C_{cc}$ and $C_{pp}$ are the second functional derivatives of $\beta \Omega$ with respect to $c$ and $\rho$, respectively, and $r = |r_1 - r_2|$. HQ incorporates higher-order terms in the expansion of $\beta \Delta \Omega_{\rho\rho}$, when the fluctuation contribution is present in (3). With this approximation, both ways of calculating the correlation functions lead to the same results.

When calculating the functional derivatives of $\Omega$ up to the second order, we take into account the fluctuation contribution in (3), but neglect it for higher-order derivatives, and obtain in Fourier representation

$$
\tilde{C}_{cc}(k) = I_0 \frac{4\pi k \cos(k)}{k} + A_{02} + A_{04} \langle \phi^2 \rangle + A_{22} \langle \eta^2 \rangle - A_{12}^2 \int d\mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} C_{cc}(r) C_{pp}(r)
$$

(4)

$$
\tilde{C}_{pp}(k) = A_{20} + A_{22}^2 \langle \phi^2 \rangle + A_{40} \langle \eta^2 \rangle - A_{12}^2 \int d\mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} C_{cc}(r)^2 - A_{20}^2 \int d\mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} C_{pp}(r)^2
$$

(5)

where $\tilde{C}_{cc}(k) = 1/\tilde{G}_{cc}(k)$, $\tilde{C}_{pp}(k) = 1/\tilde{G}_{pp}(k)$ and

$$
A_{mn}(c, \rho) = \frac{\partial^{m+n}}{\partial c^m \partial \rho^n}.
$$

(6)

Note that both, $\int d\mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} C_{cc}(r)^2$ and $\int d\mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} C_{pp}(r)^2$ take a maximum for $k = 0$, and for $k \to 0$, (5) takes the form $\tilde{C}_{pp}(k) \approx R_0 + R_2 k^2 + \cdots$. From the $k \to 0$ form of $\tilde{C}_{pp}(k)$, we obtain the asymptotic decay of correlations in the real space

$$
\tilde{C}_{pp}(r) = A_{p} \exp(-r/\xi_{p}),
$$

(7)

where $4\pi A_{p}^2 R_0 = 1$ and $4\pi A_{p} R_2 = 1$.

Let us focus on concentrated electrolytes where charge waves with the wavenumber $k_0 \sim \pi$ (oppositely charged nearest neighbors) are energetically favored. A field theory with the Hamiltonian taking a minimum for the field that oscillates in space was developed by Brazovskii [23]. He noted that a local variance of an oscillatory field is large, because the field is typically either larger or smaller from its average value. Thus, $\langle \phi^2 \rangle = (2\pi)^3 \int d\mathbf{k} \tilde{C}_{cc}(k)$ should be taken into account, but $\langle \eta^2 \rangle$ can be neglected. Using the above assumptions and (6) we obtain

$$
\tilde{C}_{pp}(k) \approx \frac{1}{\rho(1 - \rho)} + \frac{1}{\rho^2} \int \frac{d\mathbf{k}}{(2\pi)^3} \tilde{G}_{cc}(k)
$$

$$
- \frac{1}{2\rho^2} \int d\mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} C_{cc}(r)^2
$$

$$
- \frac{(2\rho - 1)^2}{2\rho^2(1 - \rho)^2} \int d\mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} C_{pp}(r)^2.
$$

(8)

Note that for $\rho \to 1$ the first and the last terms in (8) diverge. Neglecting the remaining terms and using (7), we obtain the result, valid in the asymptotic regime

$$
\xi_{p} \approx \rho^{-1} \left( \frac{1.54}{(1 - \rho)^{1/3}} \right) \quad \text{and} \quad A_{p} \approx \rho^{-3} 0.44(1 - \rho)^{5/3}.
$$

Let us consider $\tilde{C}_{cc}(k)$ and focus on the last term in (4). From the charge neutrality it follows that $\int d\mathbf{r} \tilde{G}_{cc}(r) = 0$. If $\xi_{c}^2$ is large, $\int d\mathbf{r} \tilde{G}_{cc}(r) C_{pp}(r)$ is close to zero, because $C_{pp}(r)$ is almost constant for $r$ such that $C_{cc}(r)$ differs significantly from zero. On the large density side of the Kirkwood line [24–26] $\tilde{C}_{cc}(r)$ shows exponentially damped oscillations around zero, and we assume that the last term in (4) is significantly smaller than the first three terms for moderate $\xi_{c}$, as well. Based on the above observation, we assume that the last term in (4) can be neglected for the considered thermodynamic states, and obtain

$$
\tilde{C}_{cc}(k) \approx I_0 \frac{4\pi k \cos(k)}{k} + \frac{1}{\rho} + \frac{1}{\rho^2} \int \frac{d\mathbf{k}}{(2\pi)^3} \tilde{G}_{cc}(k)
$$

(9)

The integral in (9) is regularized by a cutoff associated with the size of the ions. In the case of oscillatory decay of $\tilde{G}_{cc}(r)$, however, $1/\tilde{C}_{cc}(k)$ has a peak at $k = k_0 \approx 2.46$ that for the considered range of $\rho$ and $I_0$ is high and narrow. The main contribution to the integral comes from the vicinity of $k_0$, and as long as the cutoff has physically significant values, the dependence on it is weak [27]. $\beta \tilde{V}(k) = I_0 \pi \cos(k^2)/k^2$ can be Taylor-expanded about its minimum, and for $k \approx k_0$ the expansion can be truncated. We take into account that $\tilde{V}(k)$ is an even function of $k$, and assuming $\beta \tilde{V}(k) \approx \beta \tilde{V}(k_0) + \beta \nu (k^2 - k_0^2)^2$, where $\beta \nu \approx 0.044 I_0$, obtain the result [23]

$$
\langle \phi^2 \rangle = \int \frac{d\mathbf{k}}{(2\pi)^3} \left[ \tilde{G}_{cc}(k_0) + \beta \nu (k^2 - k_0^2)^2 \right] \approx \frac{k_0}{4\pi \tilde{C}_{cc}(k_0) \beta \nu}.
$$

(10)

$\tilde{C}_{cc}(k_0)$ is the self-consistent solution of (9) with $k = k_0$ and (10), and its lengthy explicit expression is given in [21, 28]. In this approximation

$$
\tilde{G}_{cc}(r) \approx A_{c} \sin(k_0 r) \exp(-\alpha_0 r),
$$

(11)

with

$$
A_{c} \approx \langle \phi^2 \rangle / k_0 \quad \text{and} \quad \alpha_0^{-1} \approx 8\pi \beta \nu \approx 1.1 I_0 \langle \phi^2 \rangle.
$$

(12)

The analytical solution and (10)–(12) were obtained under the assumption of small $\tilde{C}_{cc}(k_0)$, and can be valid for thermodynamic states such that $\tilde{C}_{cc}(k_0) < 1$. We found that $\tilde{C}_{cc}(k_0) < 1$ for $\rho \geq 0.75$ and $I_0 \geq 1$, and only for such parameters our results are presented.

(11) and (12) allow us to compute $\xi_{p}$ and $A_{p}$ for intermediate $\rho$. In figure 1(a), the dependence of the decay lengths of the correlation functions on $\rho$ is shown for several values of $I_0$ ($1.38 \leq I_0 \leq 2.07$) similar to $I_0$ in experiments. In figure 1(b), the decay lengths as functions of $I_0$ are shown for several values of $\rho$ ($0.75 \leq \rho \leq 0.9$). In figure 2, the density–density and the charge–charge correlation functions are shown for $\rho = 0.9$, and for $I_0 = 1$ (panel (a)) and $I_0 = 1.55$ (panel (b)).

$\xi_{p}$ increases for increasing $\rho$ in a strongly nonlinear way, and its dependence on $I_0$ is nonmonotonic. For sufficiently small $I_0$ (high temperature) and large $\rho$, $\xi_{p} > 1/\alpha_0$, i.e. the number density fluctuations are correlated over larger distances than the charge fluctuations. Moreover, $G_{pp}(r)$ decays
Figure 1. The correlation length of the density–density correlations $\xi_\rho$ (solid lines) and of the charge–charge correlations $1/\alpha_0$ (dashed lines) as a function of $\rho$ for $l_B = 1.38, 1.55, 1.77, 2.07$, black, green, blue and red lines (from the bottom to the top, solid lines) respectively (panel (a)) and as a function of $l_B$ for $\rho = 0.75, 0.8, 0.85, 0.9$ from the bottom to the top line, respectively (panel (b)). $\rho = a^3 N/V$, where $a, N, V$ are the ion diameter, the number of ions and the volume, respectively, and $l_B = \beta e^2/\epsilon$ is the Bjerrum length. $l_B, \xi_\rho$ and $1/\alpha_0$ are in units of the ion diameter $a \sim 0.5–1$ nm.

Figure 2. The density–density (solid line) and the charge–charge (dashed line) correlation functions. (a) $\rho = 0.9$ and $l_B = 1$. Note that the oscillatory decay of charge correlations dominates for $r < 6$, and the monotonic decay of density correlations dominates for $r > 6$ (see the inset). (b) The same correlation functions but for $\rho = 0.9$ and $l_B = 1.55, \rho = a^3 N/V$, where $a, N, V$ are the ion diameter, the number of ions and the volume, respectively, and $l_B = \beta e^2/\epsilon$ is the Bjerrum length. $l_B$ and $r$ are in units of a $0.5–1$ nm.

monotonically. We should stress, however that $G_{pp}$ depends strongly on the assumed form of the entropy associated with the packing effects, and is therefore model (and experimental system) dependent. $G_{cc}$, in contrast, depends only on the entropy associated with mixing, and our result for this function should be more universal. As shown in figure 1, $1/\alpha_0 > \xi_\rho$ for large $l_B$. Notably, $1/\alpha_0$ has a nearly linear dependence on $\rho$ for fixed $l_B$, with the slope increasing with $l_B$, and a nearly linear dependence on $l_B$ for fixed $\rho$, with a slope increasing with $\rho$, indicating that $\alpha_0^{-1} \sim l_B \rho$, in agreement with experiments. This result and (12) confirm the conjecture $\langle \phi^2 \rangle \propto \rho$ and show the crucial role of the variance of the charge density, as already discussed on the heuristic level. Our approximate theory is not expected to predict accurately the constant $C$ in the relation $\alpha_0^{-1}/l_B = C \rho$. $C$ depends significantly on the assumed average diameter of the ions in the experimental relation $\rho = a^3 c_{ion}$, and may also depend on the other microscopic details. Nevertheless, we can make some estimates using the results presented in figure 1(b). For example, for $l_B = 2.5 a$, typical for experiment, and $\rho = 0.9$ (corresponding to the volume fraction of ions $\sim 0.47$), we get $\alpha_0^{-1} \sim 6 \alpha$ or $\alpha_0^{-1} = 3 – 6$ nm in the range of $a = 0.5–1$ nm. Although the value obtained is not very large, the order of magnitude correlates with the experimental findings [1, 2, 19].

The DP between plates confining the dense electrolyte exhibits damped oscillations at short distances, and a monotonic decay at large separations [2, 3]. We obtain the correct scaling of the correlation length of the charge–charge correlations, which, however, decay in an oscillatory way. A monotonic decay is found for the density–density correlation function, but $\xi_\rho$ is not proportional to $\rho l_B$. To obtain the DP in our theory, one should calculate $\Delta \Omega(c, \rho + \Delta \rho) = \Omega(c, \rho + \Delta \rho) - \Omega(0, \rho)$ for the system confined between two plates at a distance $L$. The expected asymptotic decay length of $\Delta \Omega$ for
increasing \( L \) is \( \max \{ \alpha_0^{-1}, \xi_\rho \} \). Beyond the Gaussian approximation for \( \Delta \Omega \), \( c \) and \( \Delta \rho \) are coupled, and this coupling can modify the amplitude associated with the decay length \( \alpha_0^{-1} \) [29]. This will be a subject of a separate study.

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**Data availability statement**

No new data were created or analysed in this study.

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