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Rapid Communication

On the electrical double layer capacitance of the restricted primitive model: a link between the mesoscopic theory and the associative mean spherical approximation

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The results for the electrical double layer capacitance and the density of "free ions" obtained from the mesoscopic theory are compared with the corresponding results of the associative mean spherical approximation. While the first theory takes into account the fluctuations of the charge density, the second theory assumes that the free ions and ion pairs are in chemical equilibrium according to the mass action law. Our results demonstrate a fairly good agreement between the two theories at high densities and low temperatures.

Key words: *EDL capacitance, concentrated electrolytes, association, mesoscopic theory, associative mean spherical approximation*

The structure of the electrolyte/electrode interface plays a significant role in electrochemical processes such as electrochemical energy conversion, electrolysis, electrocatalysis, electrochemical devices, etc. This interface is particularly important for energy storage in electric double-layer (EDL) capacitors, or supercapacitors [1–3]. Understanding the structure of EDLs at high ionic concentrations is also important for fundamental reasons.

The study of ion distribution near charged surfaces has a long history and has been carried out using both theoretical and computer simulation methods. The classical approach to electrolytes is the Debye-Hückel theory, which is a linearized mean-field (MF) approximation [1, 4]. The corresponding theory for the EDL is known as the Poisson–Boltzmann (PB) approximation. In this framework, ions are treated as isolated point-like charges in a solvent considered as a continuum dielectric. However, the classical description of EDLs is only valid for dilute electrolytes but it is not suitable for concentrated electrolytes and room-temperature ionic liquids (RTIL). Later, more sophisticated approaches, mostly based on the integral equation theories or different modifications of the PB equation, were developed [5–9]. Initially, these approaches were applied to the simplest possible models, generally charged hard spheres in a uniform dielectric continuum (i. e., primitive models of electrolytes) next to a flat uniformly charged hard wall.

Recently, anomalous underscreening, i.e., unusually long-range screening lengths, was experimentally observed for a number of concentrated electrolytes and RTIL [10, 11], although, it was not detected in some experimental studies [12, 13]. This phenomenon was extensively studied using theory and simulations [14–25]. Unfortunately, different experimental techniques, approximate theories, and simulations yield results that are not consistent with each other and the fundamental question of the structure and the screening length in dense ionic systems remains open.

In this letter, we do not have space enough to cover all theories that have been applied to the EDL. We only mention a few of them, in particular, the mean spherical approximation (MSA) applied to the EDL by Blum [5], the modified Poisson–Boltzmann theory [7], and the associative mean spherical approximation

(AMSA) [26–28] applied for the description of an electrified interface in [8, 29]. The EDL capacitance was also studied using the classical density functional theory (DFT) (see e.g., [30–34]). The DFT requires some approximate expression as a starting point for the intrinsic free-energy functional of the density profile and its implementation is based on the variational principle. The latter makes it a computational tool to study the EDL structure of complex molecular systems. Recently, the mesoscopic theory has been developed for the EDL capacitance [35, 36]. This theory goes beyond the MF approximation by taking into account the variance of the local charge that in concentrated inhomogeneous ionic systems is large.

The purpose of this letter is to compare the results for the EDL capacitance obtained within the mesoscopic theory with the results of the AMSA which appears to be successful for the description of ionic systems [37–39]. To this end, we limited ourselves to the restricted primitive model (RPM) at a flat electrode. In the RPM, spherical ions with equal diameters $a_+ = a_- = a$ and opposite charges are dissolved in a structureless solvent characterized by the dielectric constant ϵ. Below, we present the main expressions for the capacitance of the EDL obtained within the framework of both theories in the limit of the small voltage.

EDL capacitance in the associative mean spherical approximation. The AMSA is based on the theory of associating fluids. In this theory, an ionic model is regarded to be a mixture of free ions and ion pairs which are in chemical equilibrium according to the mass action law (MAL). In this approach, the differential capacitance at the small voltage has the form [8]:

$$C = \frac{\epsilon}{4\pi a} 2\Gamma_B^*, \qquad \Gamma_B^* = \Gamma_B a, \tag{1}$$

where screening parameter Γ_B is calculated from the equation

$$4(\Gamma_B^*)^2(1+\Gamma_B^*)^3 = \kappa^2(\alpha + \Gamma_B^*). \tag{2}$$

In (2), κ is the inverse Debye screening length in $1/a$ units and α is the degree of dissociation which satisfies the MAL:

$$1 - \alpha = \frac{\rho}{2}\alpha^2 K, \tag{3}$$

where $\rho = \rho_+ + \rho_-$ is the dimensionless density of ions. In (3), $K = K_{\text{ass}}^{(0)} K^{\gamma}$ is the association constant where the thermodynamic association constant $K_{\text{ass}}^{(0)}$ is the infinite-dilute limit of K. K^{γ} is the concentration-dependent part which is determined as the ratio of the activity coefficients of free ions to the activity coefficient of the ion pair. In the AMSA, there is a certain kind of arbitrariness in the definition of the ion pair and hence the thermodynamic association constant $K_{\text{ass}}^{(0)}$. We choose $K_{\text{ass}}^{(0)}$ in the form introduced by Ebeling [40]. Ebeling's definition of the ion association constant together with the MSA contribution gives an exact second ionic virial coefficient.

K^{γ} is given by

$$K^{\gamma} = g^{\text{hs}}(r=a)\exp\left[-l_{\text{B}}\frac{\Gamma_B^*(2+\Gamma_B^*)}{(1+\Gamma_B^*)^2}\right],$$

where $l_{\text{B}} = \beta e^2/(a\epsilon)$ is the Bjerrum length in a units and

$$g^{\text{hs}}(r=a) = \frac{1-\eta/2}{(1-\eta)^3}, \qquad \eta = \frac{\pi}{6}\rho,$$

is the contact value of the pair distribution function between the hard-sphere fluid particles of diameter a. It is worth noting that $\rho_{\text{free}} = \alpha\rho$ determines the free ion density.

Without association ($\alpha = 1$), Γ_B reduces to the screening parameter $\Gamma^* = \Gamma a$ in the MSA

$$\Gamma^* = \frac{1}{2}\left(\sqrt{1+2\kappa} - 1\right). \tag{4}$$

In the MSA, the differential capacitance has the form (1) when Γ_B^* is replaced with Γ^*.

EDL capacitance in the mesoscopic theory. Within the framework of the mesoscopic theory, very simple expressions for the EDL capacitance in dilute and concentrated electrolytes were obtained [35, 36]. These expressions for the RPM near a flat metallic electrode are considerably different. They become identical, however, at the Kirkwood line [41] separating the monotonous and oscillatory asymptotic decays of the charge density. The derivation of the formalism of the theory is described in detail in [35, 36, 42].

The charge-density profile on the small-density side of the Kirkwood line has the form:

$$c(z) = A_1\left(\mathrm{e}^{-a_1 z} - \frac{a_2}{a_1}\mathrm{e}^{-a_2 z}\right),$$

where a_1, a_2 are in $1/a$ units and $a_1 > a_2$. For the small voltage, one gets for the capacitance

$$C = \frac{\epsilon a_2(1-\delta)}{4\pi a(1-\frac{a_2}{a_1})} \simeq \frac{\epsilon a_2}{4\pi a} \simeq \frac{\epsilon}{4\pi\lambda_{\mathrm{D}}}, \tag{5}$$

where, for dilute electrolytes, $\delta = 1 - \mathrm{e}^{-a_2/2} + \mathrm{e}^{-a_1/2} \simeq a_2/2 + \mathrm{e}^{-a_1/2} \ll 1$, $1/a_2 \to \lambda_{\mathrm{D}}$ [43, 44] and λ_{D} is the Debye screening length in a units.

On the large-density side of the Kirkwood line, $c(z)$ decays in an oscillatory way,

$$c(z) = A_2 \exp(-\alpha_0 z)\sin(\alpha_1 z + \theta),$$

where α_0 and α_1 are obtained from the pole analysis of the Fourier transform of the charge-charge correlation functions $\langle\tilde{c}(\mathbf{k})\tilde{c}(-\mathbf{k})\rangle$ extended to the complex k plane.

The EDL capacitance for the RPM takes, in the limit of vanishing voltage, the simple form:

$$C = \frac{\epsilon(\alpha_0^2 + \alpha_1^2)}{4\pi a} f, \tag{6}$$

where the factor resulting from the mesoscopic charge distribution at the electrode reads [36]

$$f = \frac{\sin(\alpha_1/2)\exp(-\alpha_0/2)}{\alpha_1}. \tag{7}$$

In the mesoscopic theory, $\langle\tilde{c}(\mathbf{k})\tilde{c}(-\mathbf{k})\rangle$ takes the form:

$$\langle\tilde{c}(\mathbf{k})\tilde{c}(-\mathbf{k})\rangle = \left(\beta\tilde{V}_{\mathrm{C}}(k) + \frac{1}{\rho_{\mathrm{R}}}\right)^{-1}, \tag{8}$$

where $\beta = 1/(k_{\mathrm{B}}T)$, and $\beta V_{\mathrm{C}}(r) = l_{\mathrm{B}}\theta(r-1)/r$ is the Coulomb potential truncated for distances smaller than the ionic diameter (the unit step function is $\theta(r-1) = 1$ for $r > 1$ and $\theta(r-1) = 0$ for $r < 1$). l_{B} is the Bjerrum length in a units. The Fourier transform $\beta\tilde{V}_{\mathrm{C}}(k)$ takes a negative minimum for $k = k_0 > 0$. The "effective" density ρ_R satisfies, in the Gaussian approximation, the equation [19]

$$\frac{1}{\rho_{\mathrm{R}}} = \frac{1}{\rho} + \frac{\langle c^2\rangle}{\rho^3}, \tag{9}$$

where $\rho = \rho_+ + \rho_-$ and $\langle c^2\rangle$ is the variance of the local charge given by

$$\langle c^2\rangle \approx \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\langle\tilde{c}(\mathbf{k})\tilde{c}(-\mathbf{k})\rangle. \tag{10}$$

Equations (8)–(10) should be solved self-consistently.

In dense electrolytes $\rho_R < \rho$ due to spontaneous formation of oppositely charged neighboring regions with the size $\sim a$. In turn, it means that aggregates are formed with oppositely charged nearest neighbors and fewer free ions remain in the system. Therefore, ρ_R is related to the number density of free ions.

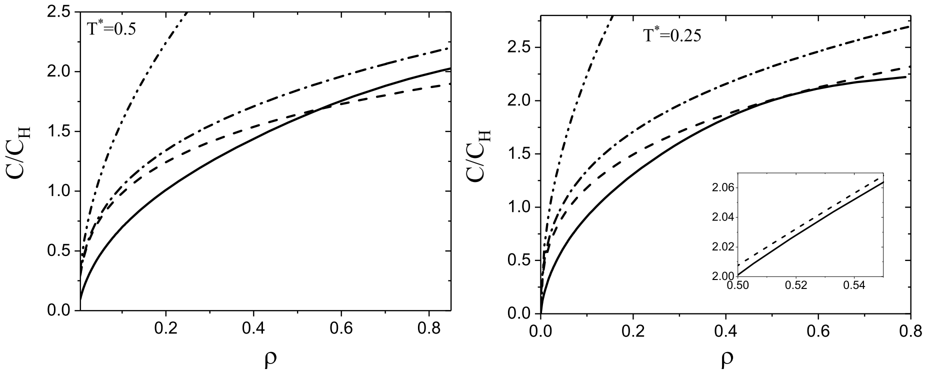

Figure 1. The EDL capacitance C of the RPM in units of the Helmholtz capacitance $C_{\mathrm{H}} = \epsilon/(4\pi a)$ obtained from the mesoscopic theory (solid line), MSA (dash-dotted line), AMSA with Ebeling's association constant (dashed line) for $T^* = 0.5$ (left-hand panel) and $T^* = 0.25$ (right-hand panel). The Debye capacitance, equation (5), is shown by a dash-dot-dotted line. ρ is the dimensionless density of ions, $T^* = 1/l_{\mathrm{B}}$, l_{B} is the Bjerrum length in a units (a is the ion diameter). The inset in the right-hand panel shows the magnified plot of the range $0.5 < \rho < 0.55$ where the capacitance obtained from the mesoscopic theory and from the AMSA takes almost the same values.

Results. Using the above-mentioned equations we calculated the EDL capacitance C at small voltage as a function of the bulk number density of ions ρ for the fixed dimensionless temperature $T^* = 1/l_{\mathrm{B}}$. In figure 1, the capacitance C in units of the Helmholtz capacitance $C_{\mathrm{H}} = \epsilon/(4\pi a)$ obtained from the mesoscopic theory, MSA and AMSA is shown as a function of the bulk number density of ions for $T^* = 0.5$ and $T^* = 0.25$. The ρ-dependence of the Debye capacitance, equation (5), is also shown for comparison. It is seen that the results obtained from the mesoscopic theory are rather in good agreement with the AMSA results when ρ increases. Moreover, for $T^* = 0.25$ and $\rho \geqslant 0.4$ the results obtained from both theories are very close and almost coincide for $0.5 < \rho < 0.55$ (see the inset in the right-hand panel).

Besides the capacitance curves, it is also interesting to compare the "effective" density of ions ρ_R in the mesoscopic theory given by equations (9)–(10) with the density of free ions $\rho_{\mathrm{free}} = \alpha\rho$ (α and ρ are the dissociation constant and the number density of ions, respectively) obtained within the framework of the AMSA theory [see equations (2)–(3)]. The corresponding dependence of ρ_R and ρ_{free} on ρ is shown in figure 2 for two values of the reduced temperature. It is clearly seen that the both curves are very close to each other for $T^* = 0.25$ and $\rho \geqslant 0.3$ (figure 2, right-hand panel).

Conclusions. We compared the results for the EDL capacitance and the density of free ions obtained from two different theories, namely the associative mean spherical approximation (AMSA) and the mesoscopic theory. The first theory assumes that the free ions and ion pairs in the ionic system are in chemical equilibrium according to the MAL, whereas the second theory takes into account the fluctuations in the local charge density.

First, we compared the results for the EDL capacitance in the limit of small voltage as a function of the bulk number density of ions ρ for two values of the reduced temperature, $T^* = 0.5$ and 0.25, where T^* is the inverse reduced Bjerrum length. Overall, the results demonstrate fairly good agreement at higher densities, and the agreement is better at lower temperatures.

We also compared the "effective" density of ions $\rho_R < \rho$, which appeared in the mesoscopic theory as a result of fluctuations being taken into account, with the density of free ions $\rho_{\mathrm{free}} = \alpha\rho$ in the AMSA where α is the degree of dissociation. We obtained a fairly good agreement between the theories for $T^* = 0.25$ in the range of the reduced density $\rho \geqslant 0.3$.

Our result suggests that the self-consistent Gaussian approximation is equivalent to the equilibrium between free ions and ion pairs. For large density of ions, however, larger neutral clusters can also be formed. We can suppose that taking into account the equilibrium between different aggregates would

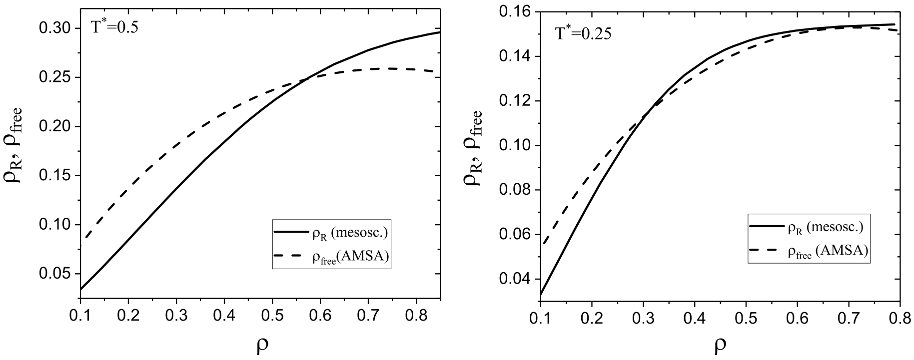

Figure 2. Effective density of ions ρ_R obtained from the mesoscopic theory, equation (9), (solid line) and the density of free ions $\rho_{\text{free}} = \alpha\rho$ (α is the degree of dissociation) obtained from the AMSA with Ebeling's association constant (dashed line) for $T^* = 0.5$ (left-hand panel) and $T^* = 0.25$ (right-hand panel). ρ is the dimensionless density of ions, $T^* = 1/l_{\text{B}}$, l_{B} is the Bjerrum length in a units (a is the ion diameter).

correspond to the mesoscopic theory beyond the Gaussian approximation. One should also note that the AMSA modified by including ion trimers and tetramers satisfactorily reproduces the thermodynamic measurement data up to high concentrations for nonaqueous solutions with solvents of lower permittivity [45, 46]. It will be interesting to compare the results obtained from both theories accounting for the equilibrium between larger clusters in a future work.

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Щодо ємності подвійного електричного шару обмеженої примітивної моделі: зв’язок між мезоскопічною теорією та асоціативним середньосферичним наближенням

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Результати для ємності подвійного електричного шару та густини “вільних іонів”, отримані з використанням мезоскопічної теорії, порівнюються з відповідними результатами асоціативного середньосферичного наближення. У той час як перша теорія враховує флуктуації густини заряду, друга теорія припускає, що вільні іони та іонні пари знаходяться в хімічній рівновазі згідно із законом діючих мас. Наші результати демонструють досить добру узгодженість між двома теоріями при високих густинах та низьких температурах.

Ключові слова: *ємність подвійного електричного шару, концентровані електроліти, асоціація, мезоскопічна теорія, асоціативне середньосферичне наближення*