Fluctuations in Electrolytes: The Lebowitz and Other Correlation Lengths

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Explicit low-density expansions (using Meeron and hypernetted-chain graphical resummations) are reported for various charge and density correlation lengths in hard-sphere electrolytes with general valences, z_σ, and diameters, $a_{\sigma\tau}$. The "Lebowitz length" quantifies the *area law* for charge fluctuations, $\langle Q_\Lambda^2\rangle$, in a large domain Λ; it approaches but differs from the Debye and other correlation lengths. All corresponding, universal limiting-law predictions of generalized Debye-Hückel (GDH) theory (Lee and Fisher, 1996–1997) prove exact, thus validating GDH theory as a basis for studying anomalies in Coulombic criticality. [S0031-9007(98)08035-1]

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Understanding the structure and equilibrium fluctuations of ionic systems remains a topic of profound theoretical concern [1,2] reinforced in recent years by puzzling experiments on criticality in electrolytes [3]. Of especial interest are the two-point charge and density correlation functions which are most accessibly characterized by a variety of significant *correlation lengths.* In particular, the screening behavior of a conducting electrolyte is embodied in the second-moment charge-charge correlation length, $\xi_{Z,1}(T,\rho)$, where $\rho = \sum_\sigma \rho_\sigma$ denotes the overall number density of ions of species σ and density ρ_σ. Indeed, the Debye-Hückel (DH) approximation [2,3] predicts the *exponential decay* of charge correlations on the scale of the Debye length, $\xi_D(T,\rho)$, given, for ions carrying charges $q_\sigma = z_\sigma q_0$, by

$$1/\xi_D^2 \equiv \kappa_D^2 = 4\pi \bar{z}_2^2 b\rho, \qquad b = q_0^2/Dk_BT, \tag{1}$$

where $b(T)$ is the Bjerrum length defined, say, with q_0 the charge of a proton, while

$$\bar{z}_j = \left[\sum_\sigma z_\sigma^j \rho_\sigma/\rho\right]^{1/j} \tag{2}$$

defines the jth mean valence moment (with $\bar{z}_1 = 0$ by electroneutrality) and D represents the "solvent dielectric constant."

However, screening can also be characterized by considering the total (fluctuating) charge Q_Λ contained in a subdomain Λ of regular shape, with surface $\partial\Lambda$, in a d-dimensional electrolyte. Electroneutrality implies $\langle Q_\Lambda\rangle \equiv 0$; but, in the absence of screening, one expects the charge fluctuations, $\langle Q_\Lambda^2\rangle$, to grow like the volume $|\Lambda|$ as $\Lambda \to \infty$ (i.e., when $|\Lambda|$ diverges through a sequence of self-similar shapes). However, when the system is a conductor and the charge-charge correlation functions decay sufficiently rapidly, Martin and Yalcin [4–6] have proved, instead, that the charge fluctuations in Λ grow only like the *area* $|\partial\Lambda|$.

Lebowitz [5] has interpreted this striking result by picturing the various ions as combined into *neutral* clusters of density $n \propto \rho$ and linear dimensions l. We will call $l \equiv \xi_L(T,\rho)$ the "Lebowitz length" and have slightly extended his picture. In this light, net charge fluctuations can arise in Λ only if some of the neutral clusters are "cut" by the boundary $\partial\Lambda$. If the clusters have no long-range positional or orientational correlations one should thus expect

$$\langle Q_\Lambda^2\rangle/|\partial\Lambda| \approx \mathcal{K}_d(T,\rho) = c_d\rho\bar{z}_2^2 q_0^2 \xi_L(T,\rho), \tag{3}$$

where c_d is a numerical constant. For a classical electrolyte, Lebowitz then argued that ξ_L should be identified with the Debye length, ξ_D defined in (1).

Here we test this conjecture for $d = 3$, evaluating $\xi_L(T,\rho)$ by regarding (3) as a definition in which, indeed, we prove able to specify c_3 so that one has $\xi_L/\xi_D \to 1$ when $\rho \to 0$ for all $T > 0$. However, we also present the leading *corrections* to this behavior for the *extended* primitive model in which the Coulombic potentials, $q_\sigma q_\tau/Dr$, are supplemented by reduced *hard-core potentials* $\bar{u}_{\sigma\tau}^\dagger(r) = 0, \infty$ for $r \gtrless a_{\sigma\tau}$. The diameters $a_{\sigma\tau}$ need *not* be additive, or even nonzero except that the diameter $a \equiv a_{\lambda\mu}$ maximizing $-z_\lambda z_\mu/a_{\lambda\mu}$ must not vanish so that all charges of opposite sign are kept a minimum distance apart.

In addition, we report exact calculations of the associated low-density expansions for the charge-charge and density-density second- and fourth-moment correlation lengths [7–9], which are more susceptible to observation (and simulation) than the corresponding exponential screening lengths, $\xi_{Z,\infty}$ and $\xi_{N,\infty}$. The expressions obtained demonstrate that the Lebowitz and all the other correlation lengths are quite distinct at finite densities: see, e.g., Fig. 1.

Furthermore, our results confirm the universal low-density predictions of the recently proposed "generalized Debye-Hückel" (GDH) theory [7]: This approach, in contrast to the original DH analysis [2], yields *density-density* correlations that exhibit a divergent correlation length at criticality [7(a)], as well as charge-charge correlations that display oscillations at higher densities [7(b)] (see Fig. 1) *and* satisfy the Stillinger-Lovett sum rules [1(b),10] (at least when Bjerrum ion pairing is not imposed [7]). This validates GDH theory as, currently, an optimal tool for investigating the critical region [11] of the *restricted*

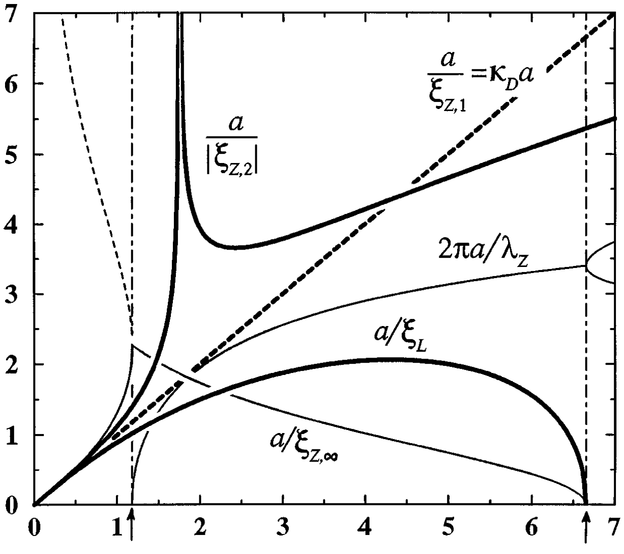

FIG. 1. Inverse charge correlation lengths (and oscillation wavelength λ_Z) for the RPM according to pure GDH theory [7]: x_K and x_X denote the Kirkwood and crystallization values. All plots become exact to order $x^2 \propto \rho$ when $x \to 0$. Note that $\xi_{Z,2}^4$, as defined in (10), is predicted to vanish linearly and change sign at $x \simeq 1.749$.

primitive model (RPM [2,3,12]) despite suggestions to the contrary [13].

To proceed, let $\rho_\sigma(\mathbf{r})$ be the local density of ions of species σ with pair correlation functions

$$G_{\sigma\tau}(\mathbf{r}) = \langle \rho_\sigma(\mathbf{0}) \rho_\tau(\mathbf{r}) \rangle - \rho_\sigma \rho_\tau ,$$
$$= \rho_\sigma [\delta_{\sigma\tau} \delta(\mathbf{r}) + \rho_\tau h_{\sigma\tau}(\mathbf{r})], \qquad (4)$$

where translational invariance is assumed. Then, in terms of the charge-charge correlation function

$$G_{QQ}(\mathbf{r}) = q_0^2 \sum_{\sigma,\tau} z_\sigma z_\tau G_{\sigma\tau}(\mathbf{r}), \qquad (5)$$

the previous analysis [4,5] gives the area-law amplitude as

$$\mathcal{K}_d(T,\rho) = -\alpha_d \int r G_{QQ}(r)\, d\mathbf{r}, \qquad (6)$$

where $\alpha_d = \frac{1}{4}, \pi^{-1}$, and $\frac{1}{2}$ for $d = 3, 2$, and 1, respectively.

To evaluate this and, thence, find ξ_L via (3), consider first the linearized DH approximation for equisized spheres ($a_{\sigma\tau} = a$), namely [2,7],

$$h_{\sigma\tau}(r) \simeq h_{\sigma\tau}^{DH}(r) \equiv -\frac{z_\sigma z_\tau b e^{-\kappa_D (r-a)}}{(1 + \kappa_D a) r}, \qquad r \geq a,$$
$$= -1, \qquad r \leq a. \qquad (7)$$

It is convenient to use the dimensionless parameter

$$x = \kappa_D a \propto q_0 a \sqrt{\rho/T}, \qquad (8)$$

which is *nonuniversal*, i.e., depends explicitly on the hard-core diameters, in contrast to the *universal* combination $\kappa_D b \propto \sqrt{\rho/T^3}$. Then, if we accept $c_3 = \frac{1}{2}$, the DH approximation (7) yields $\xi_L^{DH} = \xi_D [1 + \frac{1}{2} x^2/(1 + x)]$. We may believe the leading behavior, but the correction factor $[1 + O(\rho/T)]$ is suspect and, in fact, incorrect.

To go further we focus on the general charge-charge structure factor $S_{ZZ}(\mathbf{k}) = \hat{G}_{QQ}(\mathbf{k})/\rho q_0^2$. One can then rewrite [6] the Lebowitz length as

$$\xi_L(T,\rho) = \frac{2}{\pi \bar{z}_2^2} \int_0^\infty \frac{dk}{k^2} S_{ZZ}(k), \qquad (9)$$

where the convergence of the integral at the lower limit is ensured by electroneutrality [2,7].

Now GDH theory for the RPM [7] provides closed expressions of the expected form [2], namely,

$$S_{ZZ}(k) = \bar{z}_2^2 [\xi_{Z,1}^2 k^2 - \xi_{Z,2}^4 k^4 + O(k^6)], \qquad (10)$$

with [1(b),10] $\xi_{Z,1} \equiv \xi_D$ (when Bjerrum ion pairing is not explicitly included [7]), and a *fourth-moment correlation length* $\xi_{Z,2}^{\mathrm{GDH}} = \xi_D [1 - \frac{1}{8} x^2 + \frac{1}{18} x^3 + \cdots]$; the exponential decay of $G_{QQ}(r)$ is controlled by $\xi_{Z,\infty} = \xi_D [1 - \frac{1}{4} x^2 + \frac{1}{9} x^3 + \cdots]$. For the GDH Lebowitz length we find $\xi_D [1 + \frac{1}{4} x^2 - \frac{5}{18} x^3 + \frac{31}{96} x^4 + \cdots]$: The leading behavior is again as hoped for but the correction factor differs from that based on (5).

More interesting, however, are the GDH plots of a/ξ vs x presented in Fig. 1. The "true" correlation length, $\xi_{Z,\infty}$, exhibits a bifurcation at a "Kirkwood value," $x_K \simeq 1.178$, beyond which charge-charge *oscillations* with a wavelength $\lambda_Z(T,\rho)$ are predicted [7(b)]. At a higher value, $x_X \simeq 6.652$, the amplitude of oscillation no longer vanishes when $r \to \infty$; this may be interpreted loosely as indicating crystallization. On the other hand, one finds that the Lebowitz length ξ_L decreases smoothly to a minimum of about $0.485\,89a$ at $x_m \simeq 4.3166$ but then increases again, diverging as $1/(x_X - x)$ on approach to "crystallization." Although these GDH predictions cannot be trusted quantitatively for $x \gtrsim 1$, the increase of ξ_L in a dense electrolyte—physically a "molten salt"—could well be qualitatively correct.

To check the validity of these and further GDH results, we have appealed to the diagrammatic resummations constructed by Meeron [14] for $h_{\sigma\tau}(\mathbf{r}; T, \rho)$. At fixed $\mathbf{r}$ these yield density expansions correct up to error terms of order $\rho^{3/2}(\ln \rho)^j$ (where j is a small integer) [8,9]; but on integration to obtain Fourier transforms and correlation-function moments, precision is normally lost by factors of $\xi_D \propto \rho^{-1/2}$ [9(b)]. Furthermore, in the absence of charge symmetry, specifically when $\bar{z}_3 \neq 0$, it proves necessary in order to maintain accuracy, even in reduced order, to include two five-bond graphs dropped by Meeron: the (2, 1, 2) chain and the leading bridge diagram [14,15]. Care is needed in evaluating the many primary integrals; a tedious technical task [9(b)] is bounding classes of integrals that may be neglected.

Defining density correlation lengths via

$$S_{NN}(k)/S_{NN}(0) = 1 - \xi_{N,1}^2 k^2 + \xi_{N,2}^4 k^4 - \cdots, \qquad (11)$$

we find [9] the universal results

$$\xi_{N,1} = \bar{z}_2(b\xi_D/48)^{1/2}[1 + \tfrac{1}{8}\,\eta_1\kappa_D b + \cdots], \tag{12}$$

$$\xi_{N,2} = (\bar{z}_2^2 b\xi_D^3/320)^{1/4}[1 + \tfrac{7}{72}\,\eta_2\kappa_D b + \cdots], \tag{13}$$

where $\eta_1\bar{z}_2^4 = 2\bar{z}_2^2\bar{z}_4^4 - \bar{z}_2^6 - \frac{116}{9}\,\bar{z}_3^6$ and

$$\eta_2\bar{z}_2^4 = \tfrac{23}{14}\,\bar{z}_2^2\bar{z}_4^4 - \tfrac{9}{14}\,\bar{z}_2^6 - \tfrac{1\,045\,621}{17\,010}\,\bar{z}_3^6\,, \tag{14}$$

while the nonuniversal corrections are of order $\kappa_D^2 b^2 \ln x$. For 1:1 and 2:1 electrolytes one has $\eta_1, \eta_2 = 1, 1$, and $-8\,\frac{8}{9}$, -57.8_3, respectively.

None of these results match the *charge* correlation lengths even when $\rho \to 0$; but for the RPM they precisely reproduce the corresponding GDH predictions [7(a)]. For *nonsymmetric* models, charge and density fluctuations mix [9(c),16] so that $G_{NN}(\mathbf{r})$ should display the charge-charge decay length. $\xi_{Z,\infty}$ (see below), when $r \to \infty$. However, the exponential decay length of the density correlations in *species symmetric* cases obeys $\xi_{N,\infty} \approx \frac{1}{2}\,\xi_D$ $(\rho \to 0)$ [7(a),9].

For $S_{NN}(0)$ we find the expression

$$1 + \tfrac{1}{4}\,\bar{z}_2^2\kappa_D b + \tfrac{1}{16}\,\kappa_D^2 b^2\left[\eta_0 + \sum_{\sigma,\tau} y_\sigma y_\tau \mathcal{L}_{\sigma\tau}^N(\kappa_D, b)\right], \tag{15}$$

with corrections of order $\rho^{3/2}\ln^j\rho$, while $\eta_0 = \bar{z}_4^4 - \bar{z}_3^6/\bar{z}_2^2$, $y_\sigma \equiv \rho_\sigma/\rho$, and the nonuniversal term varies as $\ln\rho$ since

$$\mathcal{L}_{\sigma\tau}^X = \tfrac{8}{3}\,(z_\sigma^3 z_\tau^3/\bar{z}_2^2)[\ln\kappa_D a_{\sigma\tau} + e_X - \mathcal{E}(\theta_{\sigma\tau})], \tag{16}$$

where, with $X = N$, one has $e_N = \gamma_E + \ln 3 + \frac{3}{4} \simeq 2.42_6$ and

$$\theta_{\sigma\tau} = -z_\sigma z_\tau b/a_{\sigma\tau} \propto q_\sigma q_\tau/a_{\sigma\tau}T\,. \tag{17}$$

We also need the "second-virial function"

$$\tfrac{1}{6}\,\theta^3\mathcal{E}(\theta) = \sum_{n=0}^{\prime}\theta^n/n!\,(n - 3) \equiv \int_1^{\dagger} e^{\theta/r}r^2\,dr\,, \tag{18}$$

where the divergent term in the sum is excluded and the integrated ionic Boltzmann factor is suitably subtracted. This yields the low-temperature $(\theta \to +\infty)$ asymptotic expansion $\mathcal{E}(\theta) \approx (e^\theta/\theta^4)[3! + 4!/\theta + \cdots]$; the exponential divergence when $T \to 0$ directly reflects Bjerrum $(+,-)$ ion pairing [3,6,11,14(b)].

Because nonadditivity is allowed (e.g., $a_{++} + a_{--} \neq 2a_{+-}$), effective short-range attractions between like and unlike ions can be represented. At first sight, however, taking a "point-charge" limit in (16) (e.g., $a_{++} \to 0$) produces a logarithmic divergence, but since $\mathcal{E}(\theta) \approx -\ln|\theta| + \mathcal{E}_\infty$ when $\theta \to -\infty$ [14(b)], that cancels and yields well defined results.

Now, the overall isothermal bulk compressibility, K_T, of a mulitcomponent fluid should satisfy $S_{NN}(0) = \rho k_B T K_T$, *provided* the interactions decay sufficiently rapidly. However, for an ionic fluid this sum rule is valid *only* for *two*-component systems [17]. In that special case η_0 reduces to $\bar{z}_2^4$ in (15) which then reproduces the general expression for $\rho k_B T K_T$ following from the virial expansions for the pressure [18,19]. This represents a stringent check which, in particular, needs the five-bond "non-Meeron" graphs mentioned above.

It also transpires [9(b)] that Meeron's approach *fails* to generate the charge-charge structure factor $S_{ZZ}(\mathbf{k}; T, \rho)$ satisfactorily. To overcome this, we have used the hypernetted-chain (HNC) *resummation* analysis [15]. This expresses the *direct* correlation functions, $c_{\sigma\tau}(\mathbf{r})$, in terms of the interaction potentials and a functional expansion in powers of $h_{\sigma\tau}(r; T, \rho)$. One may thus use Meeron's analysis to calculate $c_{\sigma\tau}(\mathbf{r})$, and thence, via the matrix Ornstein-Zernike relations, obtain $S_{ZZ}(k)$ [9(b)].

By this route (as known [20]) one reconfirms the Stillinger-Lovett relations [10] with $\xi_{Z,1} = \xi_D$. Furthermore, for the *unrestricted two-component* models, we obtain [see (8)]

$$\begin{aligned}\xi_{Z,2}^4/\xi_D^4 = 1 &+ \tfrac{1}{4}\,\eta_3\kappa_D b + \tfrac{1}{16}\,\kappa_D^2 b^2 \\ &\times\left[\eta_3\eta_4 + \tfrac{8}{3}\,\eta_5 - \sum_{\sigma,\tau}(y_\sigma\delta_{\sigma\tau} - y_\sigma y_\tau)\mathcal{L}_{\sigma\tau}^Z\right] \\ &+ O(\rho^{3/2}\ln^j\rho)\,,\end{aligned} \tag{19}$$

with valence coefficients given by $\eta_3\bar{z}_2^2 = \bar{z}_2^4 - \bar{z}_4^4$ and

$$\eta_4\bar{z}_2^4 = \bar{z}_2^6 - \tfrac{2}{3}\,\bar{z}_3^6, \qquad \eta_5\bar{z}_2^4 = \bar{z}_3^6\bar{z}_2^2 - \bar{z}_5^5\bar{z}_3^3\,, \tag{20}$$

while $\mathcal{L}_{\sigma\tau}^Z$ follows from (16) with $e_Z = \gamma_E + \ln 3 \simeq 1.67_6$. For the RPM one has $\eta_3 = \eta_5 = 0$ so that GDH theory is verified to $O(\rho^{1/2})$, but, of course, the nonuniversal $\rho\ln\rho$ term is *not* predicted.

We can also calculate the Lebowitz length at low densities for *charge-symmetric* two-component models by using the HNC + Meeron form for $S_{NN}(k)$ in (9): this yields [9(b)]

$$\xi_L/\xi_D \approx 1 + \tfrac{1}{32}\,\kappa_D^2 b^2\sum_{\sigma,\tau}(y_\sigma\delta_{\sigma\tau} - y_\sigma y_\tau)\,\mathcal{L}_{\sigma\tau}^L\,, \tag{21}$$

where, in (16), $e_L = \gamma_E + \ln 4 \simeq 1.96_3$. In summary, one sees that our original claim that $\xi_L/\xi_D \to 1$ when $\rho \to 0$ is fully justified, but, equally, at *nonzero* densities ξ_L does *not* match any of the other charge or density correlation lengths that we have evaluated.

Finally, we remark that our results to order $\rho\ln\rho$ (but *not* order ρ) can be generated by dropping the bridge function in the HNC resummation and using the leading Meeron-based [14] approximation

$$h_{\sigma\tau}(r) \simeq h_{\sigma\tau}^D(r) = \exp[-\bar{u}_{\sigma\tau}^{\dagger}(r) + w_{\sigma\tau}(r)], \tag{22}$$

where the reduced screened Coulomb interaction is

$$w_{\sigma\tau}(r) = -z_\sigma z_\tau b \exp[-\kappa_D r]/r \,. \tag{23}$$

On this basis, the nearest pole of $S_{ZZ}(k)$ on the imaginary axis leads to [9(b)]

$$\xi_{Z,\infty}/\xi_D = 1 - \tfrac{1}{12}\,\bar{z}_2^4 \kappa_D^2 b^2 \ln x + O(\kappa_D^2 b^2)\,, \tag{24}$$

for the RPM. Remarkably, although derived by a truncation not designed to ensure precision in determining the correlation decay when $r \longrightarrow \infty$, this agrees precisely (for the RPM) with the long-distance analysis of Kjellander and Mitchell [20(b)] (which required a study of the bridge function for $r \longrightarrow \infty$). Of course, it is not surprising that the leading correction term in (24), of order $(\rho/T^3)\ln\rho$, is *not* found by GDH theory [7]; but, as shown, the GDH approximation does predict precisely *all* the universal forms to relative order $\rho^{1/2}$.

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