

Density Fluctuations in an Electrolyte from Generalized Debye-Hückel Theory

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Near-critical thermodynamics in the hard-sphere (1,1) electrolyte is well described, at a classical level, by Debye-Hückel (DH) theory with (+, -) ion pairing and dipolar-pair-ionic-fluid coupling. But DH-based theories do not address *density* fluctuations. Here density correlations are obtained by functional differentiation of DH theory generalized to *nonuniform* densities of various species. The correlation length ξ diverges universally at low density ρ as $(T\rho)^{-1/4}$ (correcting the generalized mean-spherical approximation). When $\rho = \rho_c$ one has $\xi \approx \xi_0^+/t^{1/2}$ as $t \equiv (T - T_c)/T_c \rightarrow 0+$, where the amplitudes ξ_0^+ compare informatively with experimental data.

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There is a major puzzle in the theory of fluid *criticality* in model ionic systems [1] because experiments [1,2] reveal that certain electrolyte solutions exhibit *classical* (i.e., van der Waals as against the usual Ising-type) critical exponents over as much as 1 to 3 decades when $|t| \equiv |T - T_c|/T_c \rightarrow 0$. Probably there is always a scale t_\times *below* which the behavior crosses over from classical to Ising; but attempts to explain how t_\times might vary from ~ 1 to $\sim 10^{-4}$ have so far been unconvincing. Initial efforts have addressed the simplest case: the “restricted primitive model” (RPM), consisting of $N = N^+ + N^- \equiv V\rho$ hard-sphere ions of diameter a , carrying charges $\pm q$ in a medium of dielectric constant D . The hope has been to decide the universality class (and crossover scale t_\times if appropriate) of the RPM [1,3].

To that end Fisher and Levin [3] have shown that the original Debye-Hückel (DH) theory [4] provides a remarkably good, albeit classical account of the critical thermodynamics as judged by current simulations [1,3]. However, for a satisfactory description, pure DH theory must be extended, (i) following Bjerrum (Bj) [1,3], by recognizing bound, neutral but dipolar (+, -) *ion pairs* in equilibrium with the free ions, (ii) by including the dipolar-ionic (DI) solvation free energy [1,3], and (iii) by allowing for hard-core (HC) repulsions. In terms of $T^* \equiv k_B T D a / q^2$, these DHBjDIHC theories yield critical points in the range $T_c^* \approx 0.052$ to 0.057 as compared with 0.052 – 0.056 from recent simulations [3(b)].

Now, following Ebeling and Grigo [5], one can also pursue theories based on the mean spherical approximation (MSA); but, for reasons currently obscure, such theories, even when improved in various ways [3(b),5–8] yield estimates for T_c^* too high by (35–50)% [9]. Note also that the hypernetted chain (HNC) and other integral equations have no solutions in the critical region. Further study of the DH-based theories is thus well justified.

To understand properly the nature of a critical point one must go beyond thermodynamics to study the order-parameter fluctuations. But, even for ionic fluids, the order parameter is just the overall density. Now DH-based theories illuminate the Debye screening of the

bare Coulombic potential, as seen in the exponential decay of the *charge-charge* correlations, but, unfortunately, they say little about the overall *density-density correlation function*, $G_{\rho\rho}(\mathbf{r}) \equiv \langle \rho(\mathbf{r})\rho(\mathbf{0}) \rangle - \rho^2 \equiv \rho \{ \delta(\mathbf{r}) + \rho [g_2(\mathbf{r}) - 1] \}$. Our aim here is to rectify this deficiency.

Note, especially, that the Fourier transform of $G_{\rho\rho}(\mathbf{r})$ yields the \mathbf{k} -dependent susceptibility

$$\chi(\mathbf{k}) = \hat{G}_{\rho\rho}(\mathbf{k})/\rho = \chi(0)/[1 + \xi^2 k^2 + \dots], \quad (1)$$

which diverges at $\mathbf{k} = 0$ at criticality. Indeed, $\chi(\mathbf{k})$ determines the critical opalescence and turbidity [2] and specifies the (second-moment) correlation length $\xi(T, \rho)$ which diverges as ξ_0^+/t^ν when $t \rightarrow 0+$ at $\rho = \rho_c$; furthermore, $\chi(\mathbf{k})$ approaches the reduced compressibility $\chi(0) = \rho k_B T K_T$ (or its solution analog) when $k \rightarrow 0$ [10].

As stressed by Fisher and Levin [3(a),7], it is valuable to know the amplitude ξ_0^+ even *within* a classical theory since, via the Ginzburg criterion, that offers a route for estimating a crossover range, $\pm t_\times$, outside which close-to-classical critical behavior might be realized [11].

In this Letter we show how DH theory can be generalized to yield, in a natural way, density fluctuations diverging at criticality [12–14]. The method extends straightforwardly to the full DHBjDIHC theories [3] as shown below. In particular, we calculate the correlation length $\xi(T, \rho)$ *explicitly* within the simplest generalized (GDH) theory, and numerically, at improved levels of approximation. At *low* densities a novel, *universal divergence* of $\xi(T, \rho)$ is predicted for all T . In the critical region the results are, as expected, classical with $\nu = \frac{1}{2}$; but the amplitudes ξ_0^+ prove informative and are compared with experiment [2] in classical and Ising domains [11].

Explicitly we proceed, following [3], by approximating the total Helmholtz free energy $F(T, \rho)$ by a sum of terms representing ideal gas, ionic fluid, dipole-ion, and hard-core contributions; but we now aim for a *functional* $\beta F[\{\rho_j\}] = \int d^d r \mathcal{F}$ where $\rho_1(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})$ and $\rho_2(\mathbf{r})$ are slowly varying local free-ion and dipolar densities, while $\beta = 1/k_B T$. Since we wish to probe only the density fluctuations, we follow DH theory and maintain electroneutrality, $\rho_+(\mathbf{r}) = \rho_-(\mathbf{r})$, on long length scales.

Of central concern are the direct correlation functions given by functional differentiation (with $i, j = 1, 2$) as

$$C_{ij}(\mathbf{r} - \mathbf{r}') \equiv \delta^2 \beta F / \delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}') |_{\rho_\lambda(\mathbf{r}'') = \bar{\rho}_\lambda}, \quad (2)$$

where the $\bar{\rho}_\lambda$ ($\lambda = +, -, 2$) are the *overall equilibrium densities*. Note that the various terms in \mathcal{F} contribute *linearly* to the C_{ij} and, in particular, $\hat{C}_{ij}^{\text{ideal}}(\mathbf{k}) = \delta_{ij} / \bar{\rho}_j$. However, since the *total* local density is $\rho(\mathbf{r}) = \rho_1(\mathbf{r}) + 2\rho_2(\mathbf{r})$ [15] one finds, with the aid of the Ornstein-Zernike (OZ) matrix relation for $\hat{C}_{ij}(\mathbf{k})$ [10], the result

$$\frac{1}{\rho \chi(\mathbf{k})} = \frac{1}{\hat{G}_{\rho\rho}(\mathbf{k})} = \frac{\hat{C}_{11}(\mathbf{k})\hat{C}_{22}(\mathbf{k}) - [\hat{C}_{12}(\mathbf{k})]^2}{4\hat{C}_{11}(\mathbf{k}) - 4\hat{C}_{12}(\mathbf{k}) + \hat{C}_{22}(\mathbf{k})},$$

from which ξ follows by expansion in \mathbf{k} . More expeditiously one may impose infinitesimal density variations

$$\rho_j(\mathbf{R}) = \bar{\rho}_j [1 + \Delta_j \cos \mathbf{k} \cdot \mathbf{r}], \quad (3)$$

and expand the reduced free-energy density $\beta F/V$ in powers of Δ_j : The quadratic term is then $\frac{1}{4} \sum_{i,j} \bar{\rho}_i \bar{\rho}_j \hat{C}_{ij}(\mathbf{k}) \Delta_i \Delta_j$, from which the \hat{C}_{ij} follow.

Evidently, the crucial issue is to extend DH theory to nonuniform but slowly varying mean densities of the various species. Note first that the free-ion contribution becomes [16], via the Debye charging process [4],

$$F^{\text{DH}} = \int d^d r_1 \rho_1(\mathbf{r}_1) \int_0^q dq_1 \psi_1(\mathbf{r}_1, q_1), \quad (4)$$

where $\psi_1(\mathbf{r}_1; q_1)$ is the mean electrostatic potential at the site \mathbf{r}_1 of a fixed ion due to all the other ions when each carries charges $\pm q$. If $\phi(\mathbf{r}, \mathbf{r}_1)$ is the mean electrostatic potential at a general point \mathbf{r} when the ion 1 is fixed at \mathbf{r}_1 , one has [4] $\psi_1(\mathbf{r}_1) = \lim_{\mathbf{r} \rightarrow \mathbf{r}_1} [\phi(\mathbf{r}, \mathbf{r}_1) - q_1/D|\mathbf{r} - \mathbf{r}_1|]$. DH derived their celebrated equation for ϕ by approximating the probability density for a particle of species λ ($= +, -, 2$) with charge q_λ by $\bar{\rho}_\lambda \exp[-\beta q_\lambda \phi(\mathbf{r})] \approx \bar{\rho}_\lambda [1 - \beta q_\lambda \phi(\mathbf{r})]$ [4]. (Note $q_2 = 0$.) In the same spirit we now propose to replace the constant partial (species) density $\bar{\rho}_\lambda$ by $\rho_\lambda(\mathbf{r})$ the (slowly varying) *nonuniform* density [16]. Our generalized (GDH) equation then reads

$$[\nabla_r^2 - \tilde{\kappa}^2(\mathbf{r})\Theta_1(\mathbf{r})]\phi(\mathbf{r}; \mathbf{r}_1) = -4\pi q_1 \delta(\mathbf{r} - \mathbf{r}_1)/D, \quad (5)$$

where, utilizing $\theta(y)$, the Heaviside step function $\Theta_1(\mathbf{r}) \equiv \theta(|\mathbf{r} - \mathbf{r}_1| - a)$ embodies the crucial hard-core boundary condition [4], while the spatially varying coefficient

$$\tilde{\kappa}^2[\{\rho_j\}] = 4\pi\beta \sum_\lambda q_\lambda^2 \rho_\lambda(\mathbf{r})/D = 4\pi\beta q^2 \rho_1(\mathbf{r})/D, \quad (6)$$

reduces to the standard expression for κ^2 , the inverse Debye length squared, when $\rho_\lambda(\mathbf{r}) = \bar{\rho}_\lambda$ is constant [4].

To solve (5), we adopt (3) and expand ϕ in powers of Δ_1 . The coefficient of Δ_1^n can be found recursively, setting $\tilde{\kappa} = \kappa$ and $\mathbf{r}_1 = 0$, using the Green's function

$$\mathcal{G}(\mathbf{r}; \mathbf{r}') = \frac{\kappa}{4\pi} \sum_{\ell=0}^{\infty} \mathcal{G}_\ell(\kappa r, \kappa r') P_\ell\left(\frac{\mathbf{r} \cdot \mathbf{r}'}{rr'}\right), \quad (7)$$

where, employing modified spherical Bessel functions,

$$\begin{aligned} \mathcal{G}_\ell(s, s') &= \frac{s_\leq^\ell}{s_\>^{\ell+1}} - \frac{k_{\ell-1}(x)s^\ell s'^\ell}{k_{\ell+1}(x)x^{2\ell+1}}, & s, s' < x, \\ &= (2\ell + 1) \frac{s_\leq^\ell k_\ell(s_\>)}{k_{\ell+1}(x)x^{\ell+2}}, & s_\leq \leq x \leq s_\>, \end{aligned}$$

where $x = \kappa a$, $s_\> = \max(s, s')$, $s_\leq = \min(s, s')$, while

$$\frac{\mathcal{G}_\ell(s, s')}{2\ell + 1} = \frac{i_{\ell+1}(x)}{k_{\ell+1}(x)} k_\ell(s)k_\ell(s') + i_\ell(s_\leq)k_\ell(s_\>), \quad (8)$$

for $s, s' > x$, and $P_\ell(\mu)$ denotes a Legendre polynomial.

Substituting in (4) and expanding $\hat{C}_{\rho\rho} \equiv 1/\hat{G}_{\rho\rho}$ to $O(k^2)$ yields ξ^2 . This requires only the $\ell = 0$ and 1 terms in (7). Consequently, within pure DH theory the correlation length is given explicitly by (recall $x = \kappa a$)

$$\frac{\xi^2}{a^2} = \frac{\chi^{\text{DH}}(0)}{24T^*x^2} \left[\ln \frac{(1+x)^{10}}{(1+x+\frac{1}{3}x^2)^9} - \frac{x-5x^2-8x^3}{2(1+x)^2} \right] \quad (9)$$

where $1/\chi^{\text{DH}}(0) = 1 - x/4T^*(1+x)^2$ [3].

Now corrections to this result enter only in $O(x^2) = O(\rho)$, i.e., beyond the leading low-density behavior which, in fact, exhibits the novel *divergence*

$$\xi(T, \rho) = \frac{1}{4}(b/36\pi\rho)^{1/4} [1 + \frac{1}{8}\kappa b + O(\rho^*)], \quad (10)$$

when $\rho \rightarrow 0$, where $b = q^2/Dk_B T$ is Bjerrum's length. This expression for the density-density correlation length is *independent* of the hard-core diameter a and is thus *universal!* We believe it represents the *exact* limiting behavior not previously noted. At low densities Debye's screening length $\xi_D = 1/\kappa$ controls the decay of the charge correlations [4(b),17]. It also diverges universally when $\rho \rightarrow 0$; but since we find $\xi \approx \sqrt{b}\xi_D/48$, the density correlations then decay on a *shorter* scale than the charge correlations.

Our conclusion (10) can be checked further by using the HNC relation $c_{ij} \approx -\beta u_{ij} + \frac{1}{2}h_{ij}^2$ [4(b),17,18], which is probably generally valid in the low-density limit [17] when $h_{ij} \equiv g_{ij} - 1$ decays fast. This leads to [16,19]

$$1/\chi(\mathbf{k}) \approx 1 - \frac{1}{2}\kappa^2 b \tan^{-1}(k/2\kappa)/k \quad (\rho \rightarrow 0), \quad (11)$$

which, expanding to order k^2 , yields the DH limiting law for $\chi(0)$ and reproduces (10). However, the *true correlation length*, $\xi_\infty(T, \rho)$, that determines the OZ-like exponential decay of $G_{\rho\rho}(\mathbf{r})$ is determined by the dominant zeros of (11). These give the different expression

$$\xi_\infty \approx \frac{1}{2}\xi_D \{1 + 2 \exp[-4/(\pi\rho b^3)^{1/2}] + \dots\}, \quad (12)$$

[16,19] which diverges as $(T/\rho)^{1/2}$. Thus $G_{\rho\rho}(\mathbf{r})$ has a small but longer-range tail decaying slightly *more slowly* than $e^{-2\kappa r}/r^2$, the *squared* charge-charge correlation.

By contrast to (10) and (11), one finds [16] that the GMSA or generalized mean-spherical approximation [7,18] predicts $1/\chi(\mathbf{k}) \approx 1 - \frac{1}{2}\kappa b/[2 + k^2 a/\kappa]$ when $\rho \rightarrow 0$. This gives $\chi(0)$ correctly to $O(\rho^{1/2})$ but leads to

$$\xi_{\text{GMSA}} \approx \xi_{\infty\text{GMSA}} \approx (\frac{1}{2}a\xi_D)^{1/2} = \frac{1}{2}(a^2/\pi\rho b)^{1/4}. \quad (13)$$

Thus ξ_{GMSA} also diverges as $\rho^{-1/4}$, but the power of T differs and the result is *nonuniversal*, depending on a . This reveals an unsuspected defect of the GMSA [20], which was especially devised to satisfy a variety of correlation-function sum rules [18]. (The original MSA gives only a hard-sphere result for $G_{\rho\rho}(\mathbf{r})$; see, e.g., [10].)

In the critical region the pure GDH result (11) diverges with exponent $2\nu = 1$ at $T_c^* = \frac{1}{16}$, $x_c = 1$, $\rho_c^* = 1/64\pi$. The correlation length amplitude is found to be

$$(\xi_0^+/a)_{\text{DH}} = [1 + \frac{20}{3} \ln 2 - 6 \ln \frac{7}{3}]^{1/2} \approx 0.7329. \quad (14)$$

This is surprisingly close to the GMSA value 0.75 [7], although T_c^* and ρ_c^* differ significantly [9].

Although the pure GDH theory based on (4)–(6) is sufficient at low density, one must, as mentioned above [3], include *ion pairing* to study the critical region. Bjerrum's ansatz for the association constant is appealing but Ebeling's result is superior [3] and used here. (Near criticality the numerical changes are minor.) In simple "DHBj" theory the ion pairs are supposed *ideal* [3] and one finds $\hat{C}_{22} = 1/\bar{\rho}_2$, $\hat{C}_{12} = 0$, and $\hat{C}_{11}(\mathbf{k})$ is unaltered. But that is too naive and proves unphysical: It is essential to include the *dipole-ionic* (DI) interactions [3].

We calculate the new *nonuniform* DI effects by using the GDH equation, (5), but with a dipolar source term, i.e., + and - point charges at $\mathbf{r}_1 = \pm \frac{1}{2} \mathbf{a}_1$, where \mathbf{a}_1 specifies the orientation and typical charge separation, $a_1(T) \equiv |\mathbf{a}_1|$ [3]. The associated bispherical exclusion zone is approximated by a sphere of radius a_2 [3]. Thus the Green's function (8) still applies, but with $x \rightarrow x_2 \equiv \kappa a_2$. At low T , $a_1 = a$ ("contact") and $a_2 = 1.16198a$ (angular average) are reasonable [3] and the sensitivity to these values is readily tested [3(b)].

Angular integration over the dipole orientations is complicated, yielding the solution $\phi_{\text{dip}}(\mathbf{r}; \mathbf{r}_1)$ as a multiple sum with Clebsch-Gordan coefficients, $C_{\ell_1 \ell_2}(m_1, m_2 | \ell, m)$. To obtain $\psi_2(\mathbf{r}; q)$ for use in the pair analog of (4), the self-potential of the source dipole is subtracted. To $O(k^2)$ one needs only $\ell = 0, 1, 2$, which gives explicit results with low-density expansions

$$\hat{C}_{11}^{\text{DI}}(\mathbf{k}) = \frac{xx_1^2 \rho_2}{20T^* \rho_1^2} \left\{ 1 - \frac{40}{27}x_2 + \frac{25}{21}x_2^2 + O(x_2^3) - \frac{5}{36} \frac{k^2}{\kappa^2} [1 + \frac{7}{15}x_2^2 + O(x_2^3)] + O(k^4) \right\},$$

$$\hat{C}_{12}^{\text{DI}}(\mathbf{k}) = -\frac{xx_1^2}{12T^* x_2 \rho_1} \left\{ 1 - \frac{6}{5}x_2 + \frac{8}{9}x_2^2 + O(x_2^3) - \frac{5}{18} \frac{k^2}{\kappa^2} [x_2 - \frac{3}{5}x_2^2 + \frac{1}{5}x_2^3 + O(x_2^4)] + O(k^4) \right\},$$

where $x_1 \equiv \kappa a_1$ while $\hat{C}_{22}^{\text{DI}}(\mathbf{k}) = 0$ [16].

Finally, hard-core exclusion may be approximated by local, free-volume terms $\mathcal{F}^{\text{HC}} = -\sum_i \rho_i \ln[1 - \sum_j B_j \rho_j]$ with (i) $B_1 = \frac{1}{2}B_2 = 4a^3/3\sqrt{3}$ to yield bcc close packing or (ii) $B_1 = \frac{1}{2}B_2 = 2\pi a^3/3$ for the exact ion-ion second virial coefficient [3]; or (iii), perhaps preferably, by the lo-

cal Carnahan-Starling mixture form [21]

$$\frac{6}{\pi} \left[\left(\zeta_0 - \frac{\zeta_2^3}{\zeta_3^2} \right) \ln(1 - \zeta_3) - \frac{3\zeta_1 \zeta_2}{1 - \zeta_3} - \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2} \right],$$

where $\zeta_n \equiv \frac{1}{6}\pi \sum_i \rho_i \sigma_i^n$ with σ_i the hard-core diameter of species i ; we take $\sigma_1^3 = \frac{1}{2}\sigma_2^3 = a^3$. For densities near critical, only the second virial coefficients prove significant. Being local, the approximations (i)–(iii) give $\hat{C}_{ij}^{\text{HC}}(\mathbf{k})$ independent of \mathbf{k} . Nonlocal effects are easily included at the second-virial-coefficient level; but that changes the critical amplitude ξ_0^+ by less than 1%.

For the DHBjDI theories the equilibrium equations require numerical solution. Figure 1 shows the resulting inverse square correlation lengths vs T^* on the critical isochore for various levels of approximation. The linear approach of all plots to $\xi^{-2} = 0$ represents the expected classical prediction $\nu = \frac{1}{2}$. The effects of the DI coupling are less dramatic near T_c than might have been guessed. With the assignments $a_1 = a$, $a_2 \approx 1.162a$ [3] the critical amplitudes are $\xi_0^+/a \approx 0.7511, 0.7776, 0.8186$, and 0.8147 for pure DHBjDI theory and with HC treatments (i)–(iii), respectively. Increasing a_1 to $1.15a$ lowers ξ_0^+ by no more than 8.3%. Similarly, taking a_2 to be $1.150a$ leads to a reduction of less than 1.1%. (The changes in T_c^* , ρ_c^* , etc. can be found in [3(b)].)

To compare our results for ξ_0^+ with experiments on systems that might plausibly be modeled by the RPM, one needs not only data for ξ_0^+ [2] but also some estimate of the effective hard-core diameter, a . That might be obtained by matching the ρ_c^* predictions to experiment. To that end, we re-express our results above as $\xi_0^+ \rho_c^{1/3} \approx 0.2275, 0.2302, 0.2375$, and 0.2368 (in contrast to 0.1251 for pure DH theory and 0.1828 for the GMSA [7]).

Beyond that one must recall that our theory is classical with $\nu = \nu_{\text{MF}} = \frac{1}{2}$, whereas observations indicate the Ising value $\nu_{\text{Is}} \approx 0.63$ or crossover to that for $t \leq t_\times$.

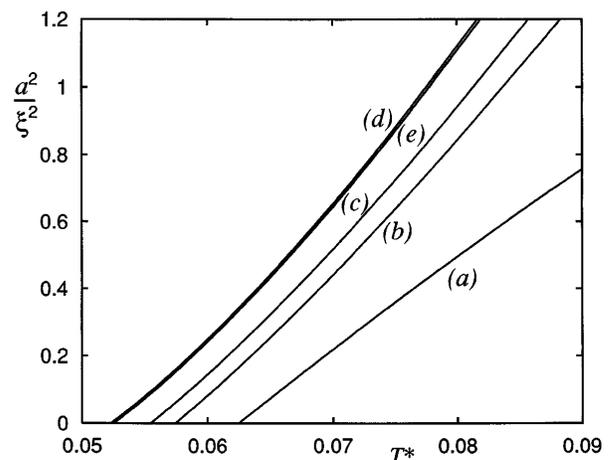


FIG. 1. Inverse square of the density-density correlation length, $\xi(T, \rho)$, on the critical isochore according to (a) pure DH theory; (b) with Bjerrum association and dipole-pair-ionic-fluid coupling (DHBjDI) with $a_1 = a$, $a_2 = 1.16198a$; (c)–(e) with hard-core terms (i)–(iii); see text.

However, for 3D lattice gases, which are described by ν_{Is} for all $t \leq 1$, the mean-field estimates for ξ_0^+ , say ξ_0^{MF} , agree with numerical estimates, say ξ_0^{Is} , to within 10% [22] (for various lattice structures). On the other hand, if crossover is found, the fits for $t < t_{\times}$ and $t > t_{\times}$ should roughly obey the matching formula $\xi_0^{\text{Is}}/\xi_0^{\text{MF}} = (t_{\times})^{\nu_{\text{Is}} - \nu_{\text{MF}}}$. Data for Na+ND₃ with $t_{\times} \approx (7-9) \times 10^{-3}$ have been fitted in both regions [2(a),2(c)] and confirm the relation. For this system we find $\xi_0^{\text{Is}} \rho_c^{1/3} = 0.34 \pm 0.03$, which is some 40% to 50% above our estimates. For Pitzer's salt [2(b),2(e)] we may postulate a crossover at $t_{\times} \approx 1 \times 10^{-4}$ [1]: This yields $\xi_0^{\text{Is}} \rho_c^{1/3} = 0.21 \pm 0.04$ which encompasses our values. Tetra-*n*-butyl-ammonium picrate in *n*-tridecanol [2(d)] displays crossover and we find $\xi_0^{\text{Is}} \rho_c^{1/3} \approx 0.22$, close to our prediction. Finally, for the same salt in other solvents [2(f)] quite similar values of ξ_0^{Is} fit the turbidity data. Overall the agreement is encouraging when using the Ising-fitted amplitudes. It is puzzling, but perhaps significant, that in the mean-field region outside t_{\times} the values of $\xi_0^{\text{MF}} \rho_c^{1/3}$ are all larger (by factors of 2–3) than our classical theory predicts!

In conclusion, we have shown how to calculate density-density correlations within DH theory and its extensions [3]. At low densities the correlation length, $\xi(T, \rho)$, diverges in unexpected but universal fashion potentially amenable to experimental check. In the critical region comparison with experiments on electrolytes proves instructive and raises further questions. More concretely, the present theory enables the observed classical-to-Ising crossover to be addressed via the Ginzburg criterion [3,11].

A naive extension of the functional approach outlined is not sufficient for studying the charge correlations at higher densities since, when $\mathbf{k} \rightarrow 0$, the associated density perturbations, even when infinitesimal, induce a macroscopic charge imbalance. However, approaches which separate out the long-range Coulombic contributions [17,23] should lead to progress.

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 [13] M. Grigo and W. Ebeling [*J. Solution Chem.* **13**, 321 (1984); *Z. Phys. Chem. (Leipzig)* **265**, 1072 (1984)] sought to derive $G_{\rho\rho}(\mathbf{r})$ by functional differentiation with respect to ion-ion interactions. They used MSA and DH theory, with ion pairs (but not DI effects). However, the method also fails to give $\xi \rightarrow \infty$ at criticality.
 [14] Cluster expansion techniques [G. Stell *et al.*, *Phys. Rev. Lett.* **37**, 1369 (1976)] might be used for $\xi(T)$ above T_c . The approach is potentially powerful but not easy; so far it has led to poor (T_c^*, ρ_c^*) values [1].
 [15] For simplicity the density of an ion pair is taken at its center of mass. This approximation can be corrected, but should not matter for small $|\mathbf{k}|$.
 [16] B.P. Lee and M.E. Fisher (to be published). Extending [4(b)] yields a statistical mechanical basis for (5)–(7).
 [17] R. Kjellander and D.J. Mitchell, *J. Chem. Phys.* **101**, 603 (1994). The bridge function is shown to modify the simple HNC relation at higher order in the density.
 [18] B. Hafskjold and G. Stell, in *The Liquid State of Matter*, edited by E.W. Montroll and J.L. Lebowitz (North-Holland, Amsterdam, 1982), p. 175. See, especially, Sec. 4.3 and, for the GMSA, G. Stell and S.F. Sun, *J. Chem. Phys.* **63**, 5333 (1975).
 [19] J. Ennis, R. Kjellander, and D.J. Mitchell, *J. Chem. Phys.* **102**, 975 (1995), Eqs. (42) and (A15).
 [20] Ennis *et al.* [19] (*Note added in proof*) remark that the GMSA does not predict $\xi_{\infty} \rightarrow \frac{1}{2} \xi_D$ when $\rho \rightarrow 0$.
 [21] See, e.g., G. Jackson, *Mol. Phys.* **72**, 1365 (1991); but the result stated here may not be in the literature.
 [22] H.B. Tarko and M.E. Fisher, *Phys. Rev. B* **11**, 1217 (1975).
 [23] H. van Beijeren and B.U. Felderhof, *Mol. Phys.* **38**, 1179 (1979).