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Ionic criticality : an exactly soluble model

Jean-Noël Aqua and Michael E. Fisher

Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742, USA

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Gas-liquid criticality in ionic fluids is studied in exactly soluble spherical models that use interlaced sublattices to represent hard-core *multicomponent* systems. Short range attractions in the uncharged fluid drive criticality but charged ions do not alter the universality class. Debye screening remains exponential *at* criticality in charge-symmetric 1:1 models. However, *asymmetry* couples charge and density fluctuations in a direct manner: the charge correlation length then diverges precisely as the density correlation length and the Stillinger-Lovett rule is violated *at* criticality.

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The nature of gas-liquid (or, more generally fluid-fluid) criticality in systems in which long-range ionic interactions play a significant role has been a focus of attention since still-puzzling experiments questioned the appropriate universality class [1]. Beyond further experiments [1], numerous theoretical [2, 3, 4, 5] and computational [6] studies have been reported; however, basic questions remain open. Certainly, the character of criticality depends on the range of the interactions: One expects an Ising critical point in a fluid with short-range couplings but mean-field behavior for interactions of sufficiently long-range. So, might the introduction of ions interacting via long-range Coulomb forces destroy an Ising-type critical point? Coulomb interactions are exponentially screened in a conducting classical fluid, as proved rigorously at low densities [7]. Charge fluctuations in a fluid of \mathcal{S} species of charges q_σ and valences $z_\sigma = q_\sigma/q$ (where q is an elementary charge), thus decay over a few Debye screening lengths ξ_D , where

$$\xi_D^{-2}(T, \rho) = 4\pi\rho q^2 \sum_{\sigma=1}^{\mathcal{S}} z_\sigma^2 x_\sigma / k_B T, \quad (1)$$

in which $\rho = \sum_\sigma \rho_\sigma$ is the overall density while the mole fractions are $x_\sigma = \rho_\sigma/\rho$. But, does exponential screening on this scale hold near and at criticality?

Indeed, a major open issue is the behavior of the pairwise *charge* correlations near the critical point, where the *density* fluctuations diverge strongly. With

$$G_{\sigma\tau}(\mathbf{r}) = \langle \rho_\sigma(\mathbf{0})\rho_\tau(\mathbf{r}) \rangle - \rho_\sigma\rho_\tau, \quad (2)$$

the correlation functions, G_{NN} , G_{ZZ} , and G_{NZ} for the density, charge, and charge-density, are [4]

$$G_{XY}(\mathbf{r}; T, \rho) = \sum_{\sigma, \tau} q_\sigma^{\vartheta_X} q_\tau^{\vartheta_Y} G_{\sigma\tau}(\mathbf{r}; T, \rho), \quad (3)$$

where X and Y may be N or Z while $\vartheta_N = 0$ and $\vartheta_Z = 1$. Except at the critical point (T_c, ρ_c) , itself, we may suppose that the corresponding structure factor, S_{NN} , has the small $k = |\mathbf{k}|$ expansion

$$S_{NN}(\mathbf{k})/S_{NN}(\mathbf{0}) = 1 + \sum_{p \geq 1} (-)^p \xi_{N,p}^{2p}(T, \rho) k^{2p}. \quad (4)$$

Near criticality, $S_{NN}(\mathbf{0}; T, \rho_c)$ diverges as $1/t^\gamma$ when $t \equiv (T - T_c)/T_c \rightarrow 0+$, while the length $\xi_{N,\infty}$ characterizing the exponential decay of $G_{NN}(\mathbf{r}; T, \rho_c)$ diverges as $\xi_{N,\infty}^2/t^\nu$ (where short-range forces have been assumed). At criticality, density fluctuations are long-ranged and $S_{NN}(\mathbf{k}; T_c, \rho_c) \sim 1/k^{2-\eta}$.

By contrast, the charge structure factor should obey

$$S_{ZZ}(\mathbf{k}) = 0 + \xi_{Z,1}^2 k^2 - \sum_{p \geq 2} (-)^p \xi_{Z,p}^{2p}(T, \rho) k^{2p}, \quad (5)$$

where the first vanishing term results from electroneutrality reflecting the *internal* screening in an ionic fluid, while the Stillinger-Lovett sum-rule [8, 9]

$$\xi_{Z,1}(T, \rho) = \xi_D(T, \rho), \quad (6)$$

characterizes the screening of *external* charges. Does this hold near and at criticality? Finally, we focus also on the charge correlation length $\xi_{Z,\infty}(T, \rho)$, that specifies the exponential decay of $G_{ZZ}(\mathbf{r})$ when $r \rightarrow \infty$. How does $\xi_{Z,\infty}$ vary when $\xi_{N,\infty}$ diverges near criticality?

To obtain insight into these questions, we study *multicomponent* lattice gas generalizations of the spherical model [10, 11, 12] specifically designed to represent hard-core interactions and thus avoid the mutual “annihilation” of oppositely charged ions on the same site. This crucial feature, which (in contrast to [11]) allows gas-liquid criticality to survive in the presence of Coulomb interactions, is accomplished by using a set of equivalent interlacing sublattices (with sites i at \mathbf{R}_i^σ with spacing a), one for each of the $\sigma = 1, 2, \dots, \mathcal{S}$ distinct particle species [13]. Thereby unlike charges cannot approach closer than an effective hard-core diameter a_0 : see, e.g., Fig.1.

To specify the models more fully, consider a multicomponent grand canonical lattice gas with site occupancy variables $n_i^\sigma = 0, 1$; this is equivalent to an Ising magnet with spins $s_i^\sigma = 2n_i^\sigma - 1 = \pm 1$, subject to fields h_σ (linearly related to the chemical potentials, μ_σ). For attractive interparticle potentials, the corresponding spin-spin couplings, $J_{\sigma\tau}(\mathbf{R})$, at lattice separations \mathbf{R} , are positive. We decompose these couplings as

$$J_{\sigma\tau}(\mathbf{R}) = J_{\sigma\tau}^0(\mathbf{R}) - \frac{1}{4} q_\sigma q_\tau \varphi^C(\mathbf{R}), \quad (7)$$

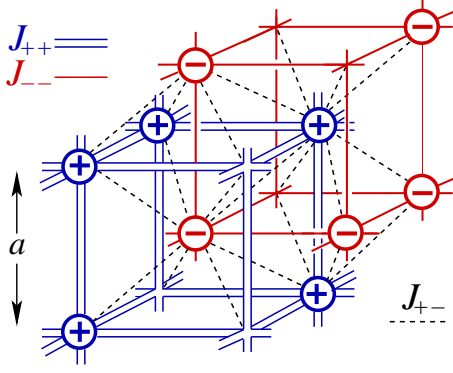


FIG. 1: Interlaced + and - sc sublattices with $a_0 = \frac{1}{2}\sqrt{3}a$.

where $J_{\sigma\tau}^0(\mathbf{R})$ represents short-range or, more generally, integrable interparticle interactions which we suppose suffice to drive gas-liquid criticality (even if the charges q_σ vanish). We take the d -dimensional Coulomb potential, $\varphi^c(\mathbf{R}) \sim 1/R^{d-2}$ ($d > 2$), as the solution of an appropriate discrete Laplace equation [14] (with, for convenience, a uniform neutralizing background so that electroneutrality, $\sum_\sigma x_\sigma q_\sigma = 0$, must be imposed). Fourier transforms, $\hat{J}_{\sigma\tau}(\mathbf{k})$, are defined by summing over one sub-lattice, with Brillouin zone \mathcal{B} , and it is useful to introduce

$$\Delta J_{\sigma\tau}(\mathbf{k}) \equiv \frac{1}{2}[\hat{J}_{\sigma\tau}(\mathbf{0}) - \hat{J}_{\sigma\tau}(\mathbf{k})]. \quad (8)$$

To model a simple 1:1 electrolyte one needs only $\mathcal{S} = 2$ components, say + and - with $q_\pm = \pm q$. We may then identify basic energy and range scales, j_0 and R_0 , via

$$\hat{J}_{+-}^0(\mathbf{0}) \equiv k_B T_0 \equiv 2j_0 > 0, \quad (9)$$

and, assuming short-range isotropic nonionic couplings,

$$\Delta J_{++}^0 + 2\Delta J_{+-}^0 + \Delta J_{--}^0 \approx 2j_0 R_0^2 k^2 > 0, \quad (10)$$

as $k \rightarrow 0$. Now, if $J_{++}(\mathbf{R}) = J_{--}(\mathbf{R})$, the model is (fully) *charge symmetric* (as is the well known continuum Restricted Primitive Model or RPM [1, 2, 3, 6]). A suitable *charge asymmetry* parameter is then [14]

$$\delta_J = \max_{\mathbf{k} \in \mathcal{B}} |\Delta J_{++}(\mathbf{k}) - \Delta J_{--}(\mathbf{k})| / k_B T_0, \quad (11)$$

which might, e.g., be used to represent distinct ionic sizes, a_+ and a_- [6(a)]. As the simplest “*Basic Ionic Model*” it suffices to take only nearest neighbor couplings, $J_{+-}^0 > 0$ and $J_{++}^0 = -J_{--}^0$; then one has $j_0 = 2^{d-1} J_{+-}^0$ and $\delta_J = d|J_{++}^0|/2^{d-2}|J_{+-}^0|$. Finally, as a dimensionless measure of the relative strength of the Coulomb interactions, it is helpful to introduce the *ionicity* [15]

$$\mathcal{I}_0 = q^2 / a^{d-2} k_B T_0. \quad (12)$$

Of course, even this Basic Ionic Model is insoluble for $d \geq 2$. Accordingly, in the standard way [10, 11, 12],

we “sphericalize” these multicomponent models by taking the spins s_i^σ as unbounded continuous variables subject only to \mathcal{S} *spherical constraints*, $\langle s_\sigma^2 \rangle = 1$, enforced with the aid of \mathcal{S} Lagrange multipliers which, for later convenience, we write as $\lambda_\sigma + \frac{1}{2}\hat{J}_{\sigma\sigma}(\mathbf{0})$. In full generality, the singular part of the total free energy $f[T, \mathbf{h}; \boldsymbol{\lambda}(T, \mathbf{h})]$ in the thermodynamic limit, is then [14]

$$f_s(T; \boldsymbol{\lambda}) = \frac{1}{2} k_B T \int_{\mathbf{k}} \ln \{ |\boldsymbol{\Lambda}(\mathbf{k}; \boldsymbol{\lambda})| / (k_B T)^{\mathcal{S}} \}, \quad (13)$$

where $\int_{\mathbf{k}} \equiv (a/2\pi)^d \int_{\mathbf{k} \in \mathcal{B}} d^d \mathbf{k}$ and $\mathbf{h} = (h_\sigma)$ and $\boldsymbol{\lambda} = (\lambda_\sigma)$, while the $\mathcal{S} \times \mathcal{S}$ matrix $\boldsymbol{\Lambda}$ has elements

$$\Lambda_{\sigma\tau} = [\lambda_\sigma + \Delta J_{\sigma\sigma}(\mathbf{k})] \delta_{\sigma\tau} - \frac{1}{2}(1 - \delta_{\sigma\tau}) \hat{J}_{\sigma\tau}(\mathbf{k}). \quad (14)$$

The field-dependent contribution to the free energy is

$$f_h = -\frac{1}{4} \langle \mathbf{h} | \boldsymbol{\Lambda}^{-1}(\mathbf{0}; \boldsymbol{\lambda}) | \mathbf{h} \rangle \quad \text{with} \quad \mathbf{h} = 2\boldsymbol{\Lambda}(\mathbf{0}; \boldsymbol{\lambda}) \mathbf{m}, \quad (15)$$

where $\mathbf{m} = (m_\sigma)$ and $m_\sigma = \langle s_\sigma \rangle = 2\langle n_\sigma \rangle - 1$ so that $\rho_\sigma = \frac{1}{2} \rho_\sigma^{max} (1 + m_\sigma)$. Finally, the Lagrange multipliers $\boldsymbol{\lambda}(T, \mathbf{h})$ are determined implicitly via the \mathcal{S} spherical constraints $\langle s_\sigma^2 \rangle = (\partial f / \partial \lambda_\sigma) = 1$. These results are valid while the eigenvalues of $\boldsymbol{\Lambda}$ remain positive; the vanishing of any one of them signals a thermodynamic singularity.

For brevity hereon we focus on the two-species, 1:1 case (with $q_\pm = \pm q$), the + and - ions residing on one of two hypercubic sublattices displaced by $\frac{1}{2}(a, a, \dots, a)$: see Fig.1 for $d = 3$. The eigenvalues of $\boldsymbol{\Lambda}$, to be called Λ_Z and Λ_N for reasons soon to be evident, are then simply the + and - roots of the quadratic equation $|\boldsymbol{\Lambda} - x\mathbf{I}| = 0$,

$$\Lambda_x(\mathbf{k}; \boldsymbol{\lambda}) = \bar{\lambda} + \Delta \bar{J}(\mathbf{k}) - (-)^{\theta_x} \mathcal{D}(\mathbf{k}; \boldsymbol{\lambda}) \quad \text{with} \quad (16)$$

$$\mathcal{D}^2(\mathbf{k}; \boldsymbol{\lambda}) \equiv [\lambda^\dagger + \Delta J^\dagger(\mathbf{k})]^2 + \frac{1}{4} \hat{J}_{+-}^2(\mathbf{k}), \quad (17)$$

where, for each variable g_+ , g_- , g_{++} , etc., we have introduced the mean $\bar{g} = \frac{1}{2}(g_+ + g_-)$ and difference $g^\dagger = \frac{1}{2}(g_+ - g_-)$, while the square root is chosen so that $\mathcal{D}(\mathbf{0}; \boldsymbol{\lambda}) > 0$ and $\Lambda_x(\mathbf{k})$ is analytic.

A pivotal result now transpires [14], namely, the linear decomposition of the structure factors via

$$\frac{S_{XY}(\mathbf{k}; \boldsymbol{\lambda})}{k_B T / 4\rho a^d} = \frac{B_{XY}^N(\mathbf{k}; \boldsymbol{\lambda})}{\Lambda_N(\mathbf{k}; \boldsymbol{\lambda})} + \frac{B_{XY}^Z(\mathbf{k}; \boldsymbol{\lambda})}{\Lambda_Z(\mathbf{k}; \boldsymbol{\lambda})}, \quad (18)$$

in which $B_{NN}^N = B_{ZZ}^Z = 1 - B_{NN}^Z = 1 - B_{ZZ}^N$, while

$$B_{NN}^N(\mathbf{k}; \boldsymbol{\lambda}) = \frac{1}{2} + \frac{1}{4} |\hat{J}_{+-}(\mathbf{k})| / \mathcal{D}(\mathbf{k}; \boldsymbol{\lambda}), \quad (19)$$

and $B_{NZ}^N + B_{NZ}^Z = 0$. In the *charge symmetric cases*, all the g^\dagger variables vanish by definition, so $B_{NN}^N \equiv 1$ and $B_{NN}^Z = B_{ZZ}^N \equiv 0$: this implies that S_{NN} is entirely governed by Λ_N , and, likewise, S_{ZZ} by Λ_Z , so justifying the notation. Conversely, in *nonsymmetric models*, both Λ_N and Λ_Z contribute to *all* the structure functions.

Finally, the spherical constraints reduce, first, to

$$k_B T \mathcal{J}_d(\boldsymbol{\lambda}) + \bar{h}^2 / 4\lambda^2 = 1 \quad \text{with} \quad \lambda = \bar{\lambda} - j'_0, \quad (20)$$

where $j'_0 = \frac{1}{2}\widehat{J}_{+-}(\mathbf{0})$ [14], while the basic integral

$$\mathcal{J}_d(\boldsymbol{\lambda}) = \frac{1}{4} \int_{\mathbf{k}} [\Lambda_N^{-1}(\mathbf{k}; \boldsymbol{\lambda}) + \Lambda_Z^{-1}(\mathbf{k}; \boldsymbol{\lambda})], \quad (21)$$

becomes singular, typically as $\Delta\mathcal{J}_d \sim -\lambda^{1/\gamma}$, when λ ($\sim t^\gamma$) vanishes, where γ is the appropriate critical exponent [10, 12, 14]; lastly λ^\dagger is given (implicitly) by

$$\lambda^\dagger \int_{\mathbf{k}} 1/|\Lambda(\mathbf{k}; \boldsymbol{\lambda})| = - \int_{\mathbf{k}} \Delta\mathcal{J}^\dagger(\mathbf{k})/|\Lambda(\mathbf{k}; \boldsymbol{\lambda})|. \quad (22)$$

Recall, however, that λ^\dagger vanishes identically in charge symmetric cases: more generally, this result relates λ^\dagger to the asymmetry parameter δ_J [see Eq. (11)] via

$$\lambda_c^\dagger \approx c_\delta[J_{\sigma\tau}] \delta_J, \quad (23)$$

where, however, $c_\delta[J_{\sigma\tau}]$ might vanish “accidentally”.

We are now in a position to answer, with explanations, the questions posed after Eqns. (1)-(6). For specific numerical results we will invoke the *Basic Ionic Spherical Model* (BISM), i.e., the sphericalized version of the $d = 3$, $\mathcal{S} = 2$, 1:1 model with $\rho_+ = \rho_- = \frac{1}{2}\rho$ and nearest-neighbor interactions as set out with Eqns. (9)-(12). When $\delta_J = \mathcal{I}_0 = 0$ one readily finds from the vanishing of $\Lambda_N(\mathbf{0})$ when $\lambda \rightarrow 0$ [10, 11, 12, 14] that standard spherical-model criticality and scaling pertains, with exponents $\beta = \frac{1}{2}$ and $\gamma = 1 - \alpha = (2 - \eta)\nu$, where short-range (non-Coulomb) interactions [16] lead to $\eta = 0$ and $\gamma = \max\{2/(d-2); 1\}$ (for $d \geq 2$).

For \mathcal{I}_0 and δ_J not too large, the *same* situation prevails—contrary to speculations (for hard-core continuum ionic models) that lack of symmetry might lead to mean-field criticality [3]. This follows most directly from the small \mathbf{k} behavior of the eigenvalues, namely,

$$\begin{aligned} \Lambda_N(\mathbf{k}; \boldsymbol{\lambda}) &= \lambda + j_0 R_N^2(\boldsymbol{\lambda}) k^2 + \mathcal{O}(k^4), \\ \Lambda_Z(\mathbf{k}; \boldsymbol{\lambda}) &= (S_d q^2 / 4a^d) [1/k^2 + R_Z^2 + \mathcal{O}(k^2)], \end{aligned} \quad (24)$$

where S_d is the area of a unit d -sphere, while [14]

$$\begin{aligned} R_N^2(\boldsymbol{\lambda}) &= R_0^2 - S'_d a^2 \mathcal{I}_0 - 2a^2 \lambda^{\dagger 2} / S_d \mathcal{I}_0 j_0^2, \\ R_Z^2(\boldsymbol{\lambda}, \hat{\mathbf{k}}) &= 2a^2 (\lambda + j'_0) / S_d \mathcal{I}_0 j_0 + a^2 \Sigma_4(\hat{\mathbf{k}}), \end{aligned} \quad (25)$$

in which $S'_3 = \pi/144$ and $\Sigma_4 \equiv \frac{1}{48} \sum_{\alpha} k_{\alpha}^4 / k^4$. The crucial feature, following directly from (16), is that the Coulomb singularity, characterized by $\widehat{\varphi}^c(\mathbf{k}) \sim 1/k^2$, cancels out of Λ_N exactly thanks to electroneutrality. (The absence of this possibility for $\mathcal{S} = 1$ results in the destruction of gas-liquid criticality by Coulomb interactions [11(b)].)

To ensure the stability of the critical point, one also needs [14]: (i) $\mathcal{I}_0 < \mathcal{I}_d^{max}$, with $\mathcal{I}_3^{max} = \frac{96}{11}\pi \simeq 2.77$; (ii) $R_N^2 > 0$, which restricts \mathcal{I}_0 and δ_J to the interior of an ellipsoid with a vertex at $\delta_J = \mathcal{I}_0 = 0$, which, for $d = 3$, is $\frac{1}{72}\delta_J^2 + [\frac{1}{72}\pi\mathcal{I}_0 - (R_0^2/a^2)]^2 < R_0^4/a^4$; and (iv) the absence of competing minima in $\Lambda_N(\mathbf{k})$,

which is satisfied for sufficiently small δ_J , specifically by $\delta_J < 1 - \frac{1}{12}\pi\mathcal{I}_0$ in the BISM. The solution $\lambda^\dagger(\lambda)$ of (22) then varies smoothly when $\lambda \rightarrow 0$ and (23) applies. By (20) criticality is restricted to $\bar{h} = 0$ and occurs at $k_B T_c = 1/\mathcal{J}_d(0, \lambda_c^\dagger)$ and $\rho_c = a^{-d} = \frac{1}{2}\rho_{max}$. For the BISM, we find $T_c \approx T_0/K_{bcc}$, to lowest order in δ_J and \mathcal{I}_0 , with $K_{bcc} \simeq 1.39$ [10]. It transpires [14] that $T_c(\delta_J)$ is a *decreasing* function of the asymmetry in accord with recent simulations of hard-core continuum electrolyte models [6(a)] that, however, contradict various approximate theories. Furthermore, a term varying as $\mathcal{I}_0^{3/2}$ (in $d = 3$) appears [14], in accord with [15] and in analogy with [17].

As regards the density correlation lengths, (18) yields

$$\xi_{N,1}(T, \rho) = R_N[\boldsymbol{\lambda}(T, \rho)] [j_0/\lambda(T, \rho)]^{1/2}, \quad (26)$$

for all acceptable \mathcal{I}_0 and δ_J ; when $\rho = \rho_c$, this diverges as ξ_N^0/t^ν . Furthermore, all higher moments [see (4)], including the “true” correlation length $\xi_{N,\infty}$ [18], satisfy $\xi_{N,p}/\xi_{N,1} \rightarrow 1$ when $(T, \rho) \rightarrow (T_c, \rho_c)$. For the BISM, with small \mathcal{I}_0 and δ_J we have $\xi_N^0 \approx a/\pi K_{bcc} \simeq 0.229a$, close to the $d = 3$, nearest neighbor Ising model value [18].

By contrast, the near-critical *charge correlation lengths* depend radically on symmetry. In *charge symmetric models*, where $B_{ZZ}^z = 1$, it follows from (18) and (24) that the Stillinger-Lovett sum-rule (6) is valid for all fluid regimes *including* the critical point. However, the true charge screening length is given by

$$\xi_{z,\infty}(T, \rho) = R_z(T, \rho) [1 + \mathcal{O}(\mathcal{I}_0^2)], \quad (27)$$

where, from (25) we find $R_z/\xi_D \rightarrow 1$ as $\rho \rightarrow 0$ whereas near criticality one has $R_{z,c}/\xi_{D,c} \approx 2\sqrt{T_0/T_c}$; that yields $R_{z,c}/\xi_{D,c} \simeq 2.36$ for the BISM (for \mathcal{I}_0 and δ_J not too large). Furthermore, when $t \rightarrow 0$, the screening length, $\xi_{z,\infty}(\rho_c, T)$ gains, in general, a singular correction factor $[1 + c_{1-\alpha} t^{1-\alpha}]$ [14]. Up to $\mathcal{O}(\mathcal{I}_0)$, the higher moments of S_{ZZ} satisfy $(\xi_{z,p})^p \approx \xi_D R_Z^{p-1}$.

On the other hand, in *nonsymmetric cases* B_{ZZ}^N in (18) does *not* vanish: rather one has

$$B_{ZZ}^N(\mathbf{k}; \boldsymbol{\lambda}) = 4\lambda^{\dagger 2} k^4 a^4 / S_d^2 \mathcal{I}_0^2 j_0^2 [1 + \mathcal{O}(k^2)] > 0. \quad (28)$$

Consequently, *all* charge correlations become infected by the divergent density fluctuations controlled by $\Lambda_N(\mathbf{k})$. Nevertheless, because of the factor k^4 , the Stillinger-Lovett relation (6) remains valid in the fluid regime except *at* criticality where it fails and we find [14, 16]

$$(\xi_{z,1}/\xi_D)_c^2 = 1 + w_c^2 \lambda_c^{\dagger 2} = 1 + w_c^2 c_\delta^2 \delta_J^2 + \dots, \quad (29)$$

where $w^2 = 2a^2/S_d \mathcal{I}_0 R_N^2 j_0^2$ and, recalling (23), we note that $c_\delta[J_{\sigma\tau}] \neq 0$ for the BISM. This critical point failure implies a breakdown of full screening that is necessarily associated with slow decay of certain ionic correlations [9]. Indeed, when $(T, \rho) \rightarrow (T_c, \rho_c)$ the charge decay

TABLE I: Charge correlation lengths near criticality where ξ_N diverges, while $R_Z/\xi_D = \mathcal{O}(1)$. The ionicity, $\mathcal{I}_0 \propto q^2$, and asymmetry factor $w_c c_\delta \delta_J$, are defined in (12), (23) and (29).

charge symmetric	non-symmetric
$\xi_{Z,1} = \xi_D = (4\pi\rho q^2/k_B T)^{1/2}$, the Debye length,	$= \xi_D$ for $(T, \rho) \neq (T_c, \rho_c)$, $> \xi_{D,c}$ at (T_c, ρ_c) ,
$\xi_{Z,2}^4 = \xi_D^2 R_Z^2(T, \rho) = \mathcal{O}(\xi_D^4)$,	$= -\xi_D^2 [(w_c c_\delta \delta_J)^2 \xi_N^2 - R_Z^2]$,
$\xi_{Z,p}^{2p} = \xi_D^2 R_Z^{2(p-1)} [1 + \mathcal{O}(\mathcal{I}_0)]$,	$\approx -(w_c c_\delta \delta_J)^2 \xi_D^2 \xi_N^{2(p-1)}$,
$\xi_{Z,\infty} = R_Z [1 + \mathcal{O}(\mathcal{I}_0^2)] = \mathcal{O}(\xi_D)$,	$\approx \xi_N \sim 1/t^\nu$.

length $\xi_{Z,\infty}$ *asymptotically approaches* the density correlation length, $\xi_{N,\infty}$, and thus *diverges* as ξ_N^0/t^ν (for $\rho = \rho_c$).

However, the fourth charge correlation moment is given (except *at* criticality) by

$$\xi_{Z,2}^4(T, \rho) = \xi_D^2 [R_Z^2 - \xi_{N,1}^2 w^2 \lambda^{\dagger 2}], \quad (30)$$

so that $|\xi_{Z,2}(\rho_c, T)|$ diverges more weakly as $1/t^{\nu/2}$. Note also that on approaching criticality, $\xi_{Z,2}^4$ changes sign (with respect to the symmetric case); for small δ_J this crossover occurs in the BISM at $t = t_\times \approx 0.265 \delta_J$. More generally the higher moments in nonsymmetric systems satisfy $\xi_{Z,p}^{2p} \approx -\xi_{D,c}^{2(p-1)} \xi_{D,c}^2 w_c^2 \lambda^{\dagger 2}$ leading to a hierarchy of critical exponents $|\xi_{Z,p}| \sim 1/t^{\nu(1-1/p)}$. Notwithstanding the divergence of the charge correlation length, $\xi_{Z,\infty} \approx \xi_N \rightarrow \infty$, the charge-charge *pair correlation function*, $G_{ZZ}(\mathbf{r})$, decays *exponentially at* (T_c, ρ_c) ! Indeed on approach to criticality we obtain

$$G_{ZZ}(\mathbf{r}) \propto 2\delta_J^2 \frac{T_0}{T_c} \frac{c_\delta^2}{j_0^2} \frac{\xi_D^4}{R_N^2} \frac{e^{-r/\xi_N}}{\xi_N^4(T, \rho)r} - \frac{\xi_D^2}{R_Z^4} \frac{e^{-r/R_Z}}{r}, \quad (31)$$

to leading orders for $d = 3$. At T_c only the second term survives since the first vanishes as $t^{4\nu}$.

Finally, as regards the cross-correlations embodied in the charge-density structure factor S_{NZ} , we find $S_{NZ}(\mathbf{k} = \mathbf{0}; T, \rho) \equiv 0$ except at (T_c, ρ_c) where the value $(\lambda^{\dagger 2} \xi_D^2 / j_0 R_N^2)_c$ is realized. Moreover, on defining moments in analogy to (5), one obtains

$$\xi_{NZ,p}^{2p}(T, \rho) \approx (\lambda^{\dagger 2} \xi_D^2 / j_0 R_N^2) \xi_{N,\infty}^{2p}(T, \rho), \quad (32)$$

near criticality; of course, all these moments vanish identically in charge symmetric models since $\lambda^{\dagger} \equiv 0$.

In summary, we have analyzed a class of exactly soluble spherical models for 1:1 ionic systems and shown that the Coulomb interactions do not change the gas-liquid critical universality class—contrary to some suggestions [1, 3]. The couplings between the charge correlations and the divergent critical density fluctuations [14, 16] follow mainly from a remarkable structure-function decomposition, Eq. (18), that respects the Stillinger-Lovett (SL)

sum rule (unlike [5]). Our principal results are collected in Table I: they are broadly consistent with Ornstein-Zernike-based arguments advanced for hard-core continuum electrolytes [3]. In *charge-symmetric* models density fluctuations are not directly coupled to two-point charge correlations which remain of short-range and obey SL near and *at* criticality; but in more realistic *nonsymmetric* systems the density fluctuations “infect” the charge correlations which hence exhibit the same diverging correlation length. Moreover, the SL rule is then violated *at* criticality [14, 16] indicating an anomalous conducting state [9].

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