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Ionic criticality : an exactly soluble model

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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 longrange. 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

$$\xi_{D}^{-2}(T,\rho) = 4\pi\rho q^{2} \sum_{\sigma=1}^{S} z_{\sigma}^{2} x_{\sigma} / k_{B} T , \qquad (1)$$

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 pairwize *charge* correlations near the critical point, where the *density* fluctuations diverge strongly. With

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

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

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

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

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

Near criticality, $S_{NN}(\mathbf{0}; T, \rho_c)$ diverges as $1/t^{\gamma}$ when $t \equiv (T - T_c)/T_c \to 0+$, while the length $\xi_{N,\infty}$ characterizing the exponential decay of $G_{NN}(\mathbf{r}; T, \rho_c)$ diverges as ξ_N^0/t^{ν} (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

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

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

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

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 $r \to \infty$. How does $\xi_{Z,\infty}$ vary when $\xi_{N,\infty}$ diverges near criticality?

To obtain insight into these questions, we study *mul*ticomponent lattice gas generalizations of the spherical model [10, 11, 12] specifically designed to represent hardcore interactions and thus avoid the mutual "annihilation" of oppositely charged ions on the same site. This crucial feature, which (in contrast to [11]) allows gasliquid 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 $\sigma = 1, 2, \ldots, S$ 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

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



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

where $J^0_{\sigma\tau}(\mathbf{R})$ 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

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

To model a simple 1:1 electrolyte one needs only 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

$$\widehat{J}_{+-}^{0}(\mathbf{0}) \equiv k_{\scriptscriptstyle B} T_0 \equiv 2j_0 > 0 \,,$$
(9)

and, assuming short-range isotropic nonionic couplings,

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

as $k \to 0$. 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]

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

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]

$$\mathcal{I}_0 = q^2 / a^{d-2} k_B T_0 \,. \tag{12}$$

Of course, even this Basic Ionic Model is insoluble for $d \ge 2$. 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 S spherical constraints, $\langle s_{\sigma}^2 \rangle = 1$, enforced with the aid of S Lagrange multipliers which, for later convenience, we write as $\lambda_{\sigma} + \frac{1}{2} \widehat{J}_{\sigma\sigma}(\mathbf{0})$. 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]

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

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

$$\Lambda_{\sigma\tau} = \left[\lambda_{\sigma} + \Delta J_{\sigma\sigma}(\mathbf{k})\right] \delta_{\sigma\tau} - \frac{1}{2}(1 - \delta_{\sigma\tau}) \widehat{J}_{\sigma\tau}(\mathbf{k}) \,. \tag{14}$$

The field-dependent contribution to the free energy is

$$f_h = -\frac{1}{4} \langle \mathbf{h} | \mathbf{\Lambda}^{-1}(\mathbf{0}; \boldsymbol{\lambda}) | \mathbf{h} \rangle$$
 with $\mathbf{h} = 2\mathbf{\Lambda}(\mathbf{0}; \boldsymbol{\lambda}) \mathbf{m}$, (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 Λ , to be called Λ_z and Λ_N for reasons soon to be evident, are then simply the + and - roots of the quadratic equation $|\Lambda - x\mathbf{I}| = 0$,

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

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

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

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

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

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

and $B_{NZ}^{N} + B_{ZZ}^{Z} = 0$. 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 *non*symmetric 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

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

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

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

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

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 Spheri*cal Model (BISM), i.e., the sphericalized version of the d = 3, S = 2, 1:1 model with $\rho_+ = \rho_- = \frac{1}{2}\rho$ and nearestneighbor 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 $\lambda \to 0$ [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 shortrange (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 meanfield criticality [3]. This follows most directly from the small **k** behavior of the eigenvalues, namely,

$$\Lambda_{N}(\mathbf{k};\boldsymbol{\lambda}) = \lambda + j_{0}R_{N}^{2}(\boldsymbol{\lambda})k^{2} + \mathcal{O}(k^{4}),$$

$$\Lambda_{Z}(\mathbf{k};\boldsymbol{\lambda}) = (S_{d}q^{2}/4a^{d})[1/k^{2} + R_{Z}^{2} + \mathcal{O}(k^{2})], \quad (24)$$

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

$$R_N^2(\boldsymbol{\lambda}) = R_0^2 - S_d' a^2 \mathcal{I}_0 - 2a^2 {\lambda^{\dagger}}^2 / S_d \mathcal{I}_0 j_0^2 ,$$

$$R_z^2(\boldsymbol{\lambda}, \hat{\mathbf{k}}) = 2a^2 (\lambda + j_0') / S_d \mathcal{I}_0 j_0 + a^2 \Sigma_4(\hat{\mathbf{k}}) , \qquad (25)$$

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 $\hat{\varphi}^{_{\rm C}}(\mathbf{k}) \sim 1/k^2$, 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 $\lambda \to 0$ 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

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

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 $\xi_{N,p}/\xi_{N,1} \to 1$ when $(T,\rho) \to (T_c,\rho_c)$. For the BISM, with small \mathcal{I}_0 and δ_J we have $\xi_N^0 \approx a/\pi K_{bcc} \simeq 0.229 a$, 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

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

where, from (25) we find $R_z/\xi_D \to 1$ as $\rho \to 0$ 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 $t \to 0$, 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

$$B_{ZZ}^{N}(\mathbf{k}; \boldsymbol{\lambda}) = 4\lambda^{\dagger^{2}} k^{4} a^{4} / S_{d}^{2} \mathcal{I}_{0}^{2} j_{0}^{2} [1 + \mathcal{O}(k^{2})] > 0.$$
 (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]

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

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

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

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

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 $\xi_{Z,p}^{2p} \approx -\xi_{N,\infty}^{2(p-1)} \xi_{D,c}^2 w_c^2 \lambda_c^{\dagger^2}$ 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, $\xi_{Z,\infty} \approx \xi_N \to \infty$, 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

$$\xi_{NZ,p}^{2p}(T,\rho) \approx \left(\lambda^{\dagger}\xi_{D}^{2}/j_{0}R_{N}^{2}\right)\xi_{N,\infty}^{2p}(T,\rho),\qquad(32)$$

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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