Critical charge and density coupling in ionic spherical models

Jean-Noël Aqua[1] and Michael E. Fisher[2]

[1]*Sorbonne Université, CNRS, Institut des Nanosciences de Paris, INSP, UMR 7588, 4 place Jussieu, 75005 Paris, France*
[2]*Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742, USA*

(Received 27 September 2019; published 27 November 2019)

We investigate ionic criticality on the basis of a specially devised spherical model that accounts both for Coulomb and nonionic forces in binary systems. We show in detail here the consequences of the entanglement of density and charge correlation functions G_{NN} and G_{ZZ} on criticality and screening. We also show on this soluble model how, because of electroneutrality, the long-range Coulomb interactions do not change the universality class of criticality in the model driven primarily by sufficiently attractive nonionic interactions. Near criticality, G_{NN} and G_{ZZ} are fully *decoupled* in charge symmetric systems. However, in more realistic *non*symmetric models, charge and density fluctuations couple in leading order so that the charge and density correlation lengths diverge asymptotically in a similar way. Similarly, the Stillinger-Lovett sum rule, which characterizes a conducting fluid, is violated *at* criticality in nonsymmetric models when the critical-point density-decay exponent η vanishes. In addition, if quantum effects are accounted for semiclassically by incorporating algebraically decaying interactions, G_{ZZ} decays only as a power law in the whole phase space, contrary to the usually expected exponential Debye screening. We expect these results on this soluble toy model to be general and to reveal general mechanisms ruling ionic criticality.

DOI: 10.1103/PhysRevE.100.052145

I. INTRODUCTION

What happens when long-range Coulomb interactions are combined with long-range critical fluctuations? One knows that the universality class of a critical point depends on the range of the interactions: For instance, gas-liquid phase separation belongs to the Ising class when only short-range interactions drive the phenomena [1], while a distinct universality class arises in systems with $1/r^{d+\sigma}$ interactions (with spatial dimension d and a given $\sigma > 0$) [2]. However, when charge-charge $1/r^{d-2}$ interactions are present, e.g., when one considers gas-liquid phase separation in ionic fluids, no current theoretical results establish with full conviction the universality class to be expected [3–6]. Indeed, even though systems with integrable forces are treatable via the renormalization group yielding critical properties that compare successfully with experiments, charged systems characterized by the $1/k^2$ singularity of Coulomb interactions have proved intractable. Might the long range of ionic coupling enforce mean-field behavior, or does the screening effect result in effective short-range interactions, leading again to the Ising class?

To answer these questions, experiments were performed in the early 1990's on electrolyte solutions which allowed exploration of the critical behavior close to the critical point [7,8]. At first, both mean-field and Ising-type behavior seemed to arise! Even though the former results were later shown to be unreliable [9], this controversy engendered the need for a better understanding of the phenomena. More recently, Monte Carlo simulations have unequivocally pointed toward the Ising behavior [10]. But, one must still recognize that no generally accepted theoretical description is available especially as regards the various charge and density correlation functions *at* and *close to* criticality [3–6,11–15]. Yet, some progress has been made as regards the crossover Ginzburg temperature [16–21]. In this situation, exactly soluble models can prove valuable as they can reveal some basic laws. The goal of this article is therefore to describe a model designed to reveal general mechanisms that can rule fluid-fluid criticality in charged systems [22–25]. Even though criticality is ruled here by nonionic interactions, we argue that the structure underlying this exactly soluble model (entanglement between charge and density correlations, cancellation due to electroneutrality, etc.) are general and we intend to describe here the structure of the mechanics of this model.

At first glance, one could expect that the screening effect present in charged fluids might effectively rein in the long range of the Coulomb interactions: In a fluid with Coulomb and short-range interactions, consisting of various species τ of density ρ_τ and carrying charges q_τ, Brydges and Federbush [26] proved that, *in the low-density limit*, the effective interactions are exponentially screened with a screening length $\xi_{Z,\infty}$ that approaches the Debye-Hückel length *defined* by

$$\xi_D \equiv \left(4\pi\beta \sum_\tau q_\tau^2 \rho_\tau\right)^{-1/2}, \tag{1}$$

where $\beta = 1/k_B T$ is the inverse temperature. But, is this property still valid near criticality? And if not, can the Coulomb interactions change the universality class of a system? How does the screening length behave when, near a critical point, the density correlation length $\xi_{N,\infty}$ diverges?

To rephrase some of these questions, one can consider the sum rules characterizing conducting fluids: The Stillinger-Lovett (SL) sum rule [27] requires that the charge structure factor S_{ZZ} in Fourier space behaves at small k as

$$S_{ZZ}(\mathbf{k}) = 0 + \xi_{Z,1}^2 k^2 + \cdots \quad \text{with } \xi_{Z,1} = \xi_D, \tag{2}$$

provided the fluid is conducting. Note that the vanishing *at* $\mathbf{k}=\mathbf{0}$ describes the internal screening. Is this sum rule satisfied near a critical point? Finally, one can also consider semiclassical quantum effects described as, e.g., in Lennard-Jones (6,12) pair interactions, by dispersion forces decaying as $1/r^{d+\sigma}$ (with $\sigma > 0$); these are of long range but are integrable. What kind of screening can be expected away from the critical point when dispersion and Coulomb interactions interfere? Are the effective interactions still exponentially screened [28] as in the Debye theory? And what happens when long-range critical fluctuations also come into play?

In the family of the exactly solvable models, the spherical model [29], which corresponds to the $n \to \infty$ limit of an n-dimensional spin model [30], proves to be sufficiently adaptable to encompass many physical situations [24]. It is therefore tempting to use it to study some basic properties of critical charged fluids even though special caution must be exercised before applying the model to a first-order transition [25]. A pioneering approach was made by Smith [31,32] who studied an ionic spherical model in which, however, the Coulomb interactions destroyed the usual gas-liquid phase separation (leading, instead, to a freezing transition to an ionic crystal). As explained below, this feature originated in the use of only a single density variable, namely, the charge density, while density fluctuations were not separately represented.

In order to address this problem, we have devised a *multicomponent* spherical model (see [25] which article will be denoted I in the following) that can be solved for an arbitrary number of species. When one considers a binary lattice fluid with labels + and − (or 1 and 2 in the notation of I), relatively simple expressions can be derived which show that the behavior is driven by the two eigenvalues Λ_N and Λ_Z of an interaction matrix (see I and [22]): In particular, a crucial result we will use below is that all the structure factors can be decomposed according to

$$\frac{S_{XY}(\mathbf{k};\boldsymbol{\lambda})}{k_B T/4\rho v_0} = \frac{B_{XY}^N(\mathbf{k};\boldsymbol{\lambda})}{\Lambda_N(\mathbf{k};\boldsymbol{\lambda})} + \frac{B_{XY}^Z(\mathbf{k};\boldsymbol{\lambda})}{\Lambda_Z(\mathbf{k};\boldsymbol{\lambda})}. \tag{3}$$

Here $\rho = \sum_\tau \rho_\tau$, while v_0 is the volume of the reference lattice unit cell, and X and Y stand for N or Z which, in turn, label neutral number density and charge density, respectively: see Eqs. I(49). The amplitudes B satisfy the relations

$$B_{NN}^N = B_{ZZ}^Z = 1 - B_{NN}^Z = 1 - B_{ZZ}^N \equiv B(\mathbf{k};\boldsymbol{\lambda}) \tag{4}$$

as given in I(50); furthermore, in a charge-symmetric system (defined in terms of the nonionic interactions by $J_{++} = J_{--}$), one has $B(\mathbf{k};\boldsymbol{\lambda}) = 1$. It is noticeable that a similar decomposition was found in Ref. [11] thanks to a random phase approximation of the restricted primitive model.

In this article, we use this model to study systems with symmetric ionic coupling, i.e., $q_+ = -q_-$, but with general short-range nonionic potentials J_{++}, $J_{+-} = J_{-+}$, and J_{--}. When the nonionic interactions are of short range, we find (see also [22]) that, provided the Coulomb interactions are not too strong [as measured by a dimensionless ionicity parameter, see [5] and Eq. (20) below], a fluid-fluid phase separation is driven by the nonionic interactions and the same critical universality class is realized as when no charges are present. Indeed, the slow decay of the Coulomb interactions (characterized by a $1/k^2$ divergence in Fourier space) is exactly canceled from $\Lambda_N(\mathbf{k})$ in Eq. (3) owing to electroneutrality, and hence has no effect on the critical behavior of the density fluctuations.

However, as regards the charge fluctuations, symmetry turns out to be crucial. When the system is fully charge symmetric, with $J_{++}(\mathbf{r}) = J_{--}(\mathbf{r})$, one has $B_{ZZ}^N = B_{NN}^Z = 0$ in Eq. (3), so that the charge and density correlations $G_{ZZ}(\mathbf{r})$ and $G_{NN}(\mathbf{r})$ become completely decoupled being governed separately by Λ_Z and Λ_N, respectively. This ensures that the charge screening length $\xi_{Z,\infty}$ remains finite near and at criticality. By the same token the SL sum rule is satisfied even *at* criticality. Conversely, as soon as some asymmetry appears (so that $J_{++} \neq J_{--}$), as must be the case in a realistic description of most fluids, the charge correlations become infected by the density fluctuations. As a consequence, the charge screening length $\xi_{Z,\infty}$ grows on approach to criticality and *diverges at* criticality. Thus, the usual picture of charge screening being fully effective on a microscopic or nanoscopic length scale is destroyed by this charge-density coupling. Moreover, *at* the critical point, the SL sum rule is now *violated*, indicating, in point of fact, that the fluid is no longer acting as a standard conductor.

This ionic spherical model can be generalized easily to consider also $1/r^{d+\sigma}$ nonionic interactions which may in fact mimic quantum effects semiclassically [23]. Away from any critical point, we find that the charge correlations $G_{ZZ}(\mathbf{r})$ decay only algebraically as $1/r^{d+\sigma+4}$. Hence, the $1/r^{d-2}$ Coulomb interactions are still screened, but only by the algebraic factor $1/r^{\sigma+6}$. Once again, the classical picture of the exponential Debye screening is destroyed, but this time because of the coupling between Coulomb interactions and power-law forces. In such long-range spherical models, the critical behavior of the density fluctuations matches that found for the short-range models: (i) The critical universality class is not affected by the Coulomb interactions; and (ii) when the system is charge symmetric, the charge and density fluctuations are decoupled; conversely, (iii) they are coupled, so that $\xi_{Z,\infty}$ diverges, in an asymmetric system. However, (iv) in asymmetric fluids, the validity of the SL sum rule *at* criticality is now controlled by the long-range decay of the density correlation function as $1/r^{d-2+\eta}$: specifically, when $\eta = 0$, which corresponds to longer-ranged critical fluctuations, the SL rule is violated, while $\eta > 0$ ensures its satisfaction.

In the following, we first define the binary ionic spherical model, with due attention to important details, in Sec. II. Coulomb interactions are computed in the lattice geometry of concern and significant general properties are stated. In Sec. III, we analyze the charge symmetric models with only short-range and Coulomb interactions. To ensure normal critical behavior we impose some general conditions on the ionicity. The critical singularities are then given by the vanishing of Λ_N which, as explained, is independent of the $1/k^2$ Coulomb divergence since electroneutrality is required. The charge correlations are computed and shown to remain free of the critical singularity because of their decoupling from the density fluctuations. A particular model devised to simplify numerical estimates is also presented. Charge asymmetry, introduced by supposing $J_{++}(\mathbf{r}) \neq J_{--}(\mathbf{r})$, is introduced in Sec. IV. The universality class of criticality is still not affected by ionic forces since $\Lambda_N(\mathbf{k})$ is still free of the $1/k^2$ Coulomb singularity; however, charge and density correlations are coupled to both eigenmodes via the factors $1/\Lambda_N$ *and* $1/\Lambda_Z$. The consequences for the charge and charge-density structure functions, etc., are analyzed. A particular asymmetric model convenient for numerics is also introduced. Section V is devoted to both symmetric and asymmetric fluids but with power-law interactions in addition to the ionic coupling. The structure of the charge correlations resulting from both $1/\Lambda_N$ and $1/\Lambda_Z$ enforces weak, i.e., algebraic screening over the whole phase diagram. Near criticality, the coupling between charge and density correlations depends on the nature of the decay of the density fluctuations. Finally, in Appendix A, the SL sum rule is generalized for long-range systems while various correlation lengths are derived rigorously in Appendix B. The algebraic decay of $G_{ZZ}(\mathbf{r})$ in ionic-plus-power-law systems is supported by a diagrammatic expansion in Appendix C.

II. BINARY CHARGED SPHERICAL MODELS

A. Coulomb interactions

In order to consider an ionic lattice gas, we first need to appropriately define Coulomb interactions in the corresponding geometry. Thanks to the work of Lieb and Lebowitz [33], one knows that the thermodynamic limit of a Coulomb fluid in the grand-canonical ensemble exists for all chemical potentials μ_τ for species τ. The fluid then satisfies bulk electroneutrality while any excess charge, linked to the chemical potentials [34], is repelled to the vicinity of the system boundaries. If we wished to consider surface effects, we would need to specify the nature of the boundary conditions, Dirichlet vs Neumann, etc.; but, because they are not relevant for bulk properties, we eliminate such effects by considering a uniform background which neutralizes the system. At equilibrium, this affects the properties of a Coulomb fluid only near its boundaries. (One may refer to [31,35] for some insights regarding the surface properties of an ionic spherical model.)

We consider the geometry of a d-dimensional binary lattice gas (as described generally in I) where the two species labeled $\sigma = +$ and $-$ lie on two sublattices which are images of a hypercubic reference sublattice with lattice spacing a, after translation with the vectors $\boldsymbol{\delta}_+ = \mathbf{0}$ and $\boldsymbol{\delta}_- = (a/2, \dots, a/2)$. For simplicity here, we specialize to "body centered" interlacing of the two sublattices based on a hypercubic reference lattice of spacing a. We define Coulomb interactions as solutions of the Laplace equation but discretized on the lattice geometry with periodic boundary conditions and including a neutralizing background. Explicitly, the Coulomb potential $\varphi^C(\mathbf{r})$ is thus the solution of

$$D_{\mathbf{r}}\varphi^C(\mathbf{r}-\mathbf{r}') = -S_d\left[\frac{\delta_{\mathbf{r},\mathbf{r}'}}{(a/2)^d} - \frac{1}{L^d}\right], \tag{5}$$

with periodic boundary conditions in the Cartesian directions of the sublattices (before the thermodynamic limit $L \to \infty$ is taken). The term $-1/L^d$ describes the uniform neutralizing background, while $\delta_{\mathbf{r},\mathbf{r}'}$ is the discrete Kroenecker symbol and $S_d = 2\pi^{d/2}/\Gamma(d/2)$ (with $S_3 = 4\pi$) is the surface of a sphere of radius unity. The factor $(a/2)^d$ is introduced to preserve dimensions but also ensures that the limit $a \to 0$ leads to the standard continuum Coulomb potential. Finally, $(a/2)^2 D_{\mathbf{r}}$ is the *appropriate lattice* Laplacian defined as follows: We need the electrostatic potential to "live" on both the interlaced sublattices; thus, for simplicity, we define $\varphi^C(\mathbf{r})$ at all lattice sites $\mathbf{R} = (R_\alpha)$ with $\mathbf{R}_\alpha/a = 1, 1\frac{1}{2}, 2, \dots, L/a + \frac{1}{2} (\alpha = 1, \dots, d)$, i.e., on a lattice of spacing $\frac{1}{2}a$ that hence includes the two $+$ and $-$ sublattices. Hence, the operator $D_{\mathbf{r}}$ is defined by

$$D_{\mathbf{r}}F = \frac{1}{(a/2)^2}\sum_{\alpha=1}^{d}\left[F\left(\mathbf{r}+\frac{1}{2}a\mathbf{e}_\alpha\right) - 2F(\mathbf{r}) + F\left(\mathbf{r}-\frac{1}{2}a\mathbf{e}_\alpha\right)\right], \tag{6}$$

where $\mathbf{e}_\alpha$ is the unit vector in the direction α of the reference sublattice. The solution of (5) with appropriate boundary conditions is

$$\varphi^C(\mathbf{r}-\mathbf{r}') = \frac{S_d a^2}{4L^d} \sum_{\mathbf{k}'=(2\pi/L)\mathbf{p}'}^{*} e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')}\frac{1}{K^2(\mathbf{k}')}, \tag{7}$$

where $\mathbf{p}'_\alpha = 0, \pm 1, \pm 2, \dots, [2L/a]$, and the summation $\sum^*$ is performed over nonzero vectors, and

$$K^2(\mathbf{k}') = 2\sum_{\alpha=1}^{d}\left[1 - \cos\left(\frac{1}{2}\mathbf{k}'_\alpha a\right)\right]. \tag{8}$$

[Note that the spacing $\frac{1}{2}a$ used in the discrete Laplacian means that the summation in Eq. (7) runs over vectors which belong to a Brillouin zone larger by a factor 2^d than that associated with the reference sublattice, namely, $\mathcal{B}$; see I.) The Fourier transforms of the Coulomb potential over the reference sublattice, as defined in I, are, with $\tau = +, -$, then

$$\widehat{\varphi}^C_{\tau\tau}(\mathbf{k}) = \frac{S_d}{4a^{d-2}}\sum_{b_\alpha=0,1}^{\dagger}\frac{1}{K^2(\mathbf{k}-2\pi\mathbf{b}/a)}, \tag{9}$$

$$\widehat{\varphi}^C_{+-}(\mathbf{k}) = \frac{S_d}{4a^{d-2}}\sum_{b_\alpha=0,1}^{\dagger}\frac{(-1)^{\sum_\alpha b_\alpha}}{K^2(\mathbf{k}-2\pi\mathbf{b}/a)}, \tag{10}$$

where the sum $\sum^\dagger$ includes nonzero $\mathbf{b}$ if and only if $\mathbf{k} = \mathbf{0}$. Naturally, the small-k expansions of the Coulomb potential, which reveal its crucial long range, display the usual $1/k^2$ divergence; specifically, for $\mathbf{k} \neq \mathbf{0}$, we find

$$\widehat{\varphi}^C_{\tau\upsilon}(\mathbf{k}) = v_d\left\{\frac{1}{k^2} + a^2\left[\Sigma_4(\hat{\mathbf{k}}) + \frac{\widehat{\varphi}^C_{\tau\upsilon}(\mathbf{0})}{S_d a^{2-d}} + O(k^2a^2)\right]\right\}, \tag{11}$$

where $v_d = S_d/a^d$. Depending only on the unit vector $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$, the anisotropy factor satisfies

$$0 \leqslant \Sigma_4(\hat{\mathbf{k}}) = \frac{1}{48}\sum_{\alpha=1}^{d}\mathbf{k}_\alpha^4/k^4 \leqslant \frac{1}{48}. \tag{12}$$

In spite of the $1/k^2$ divergence of $\widehat{\varphi}^C_{\tau\upsilon}$ at small k, the neutralizing background ensures that the values of $\widehat{\varphi}^C_{\tau\upsilon}$ precisely at $\mathbf{k} = \mathbf{0}$ are finite; their values for $d = 3$ are $\widehat{\varphi}^C_{\tau\tau}(\mathbf{0}) = 29\pi/24a$ and $\widehat{\varphi}^C_{+-}(\mathbf{0}) = -11\pi/24a$. These values, together with (9) and (10), are independent of the lattice size L^d and remain valid in the thermodynamic limit. The finiteness of $\widehat{\varphi}^C_{\tau\upsilon}(\mathbf{0})$ ensures that, in the correspondence between lattice gas and Ising spins developed in I, the sums in I(7) and I(8) remain finite in the thermodynamic limit even when long-range Coulomb interactions are present. Hence, the thermodynamic limit of the system remains well defined whatever the total charge of the fluid: i.e., there is no need to impose electroneutrality. However, the fluid-plus-background system is always electroneutral by our construction. Nevertheless, we will require electroneutrality in the following. (Without the neutralizing background, an ambiguity in the chemical potential differences would arise at this stage, related to the bulk electroneutrality condition [34].)

Finally, at order k^2, the difference between the two Fourier transforms when $d = 3$ reduces to

$$a\{\widehat{\varphi}^C_{+-}(\mathbf{0}) - \widehat{\varphi}^C_{\tau\tau}(\mathbf{0}) - [\widehat{\varphi}^C_{+-}(\mathbf{k}) - \widehat{\varphi}^C_{\tau\tau}(\mathbf{k})]\} = -\tfrac{1}{36}\pi k^2 a^2 + O(k^4 a^4). \quad (13)$$

Notice that $\widehat{\varphi}^C_{+-}(\mathbf{k}) > 0$ when $|\mathbf{k}_\alpha| < \pi/a$ whereas $\widehat{\varphi}^C_{+-}(\mathbf{k}) = 0$ when one coordinate satisfies $|\mathbf{k}_\alpha| = \pi/a$. Note also that $\varphi^C(\mathbf{R})$ as defined via (7) is a decreasing function of $|\mathbf{R}_\alpha|$.

B. Total interactions

We consider a system where *both* nonionic and Coulomb interactions are present so that

$$J_{\tau\upsilon} = J^0_{\tau\upsilon} + J^C_{\tau\upsilon} \quad (\tau, \nu = +, -), \quad (14)$$

where $J^C_{\tau\upsilon}$ describes the Coulomb interaction $J^C_{\tau\upsilon}(\mathbf{R}^\tau_i, \mathbf{R}^\upsilon_j) = -q_\tau q_\upsilon \varphi^C(\mathbf{R}^\tau_i - \mathbf{R}^\upsilon_j)/4$, while the nonionic interactions $J^0_{\tau\upsilon}(\mathbf{R}^\tau_i - \mathbf{R}^\upsilon_j)$ are supposed to be integrable, either short or long range decaying as $1/r^{d+\sigma}$ with $\sigma > 0$, so that $\widehat{J}^0_{\tau\upsilon}(\mathbf{k} = \mathbf{0})$ is well defined. We suppose the interaction $J^0_{+-}(\mathbf{R})$ is sufficiently attractive so that

$$j_0 \equiv \tfrac{1}{2} k_B T_0 \equiv \tfrac{1}{2} \widehat{J}^0_{+-}(\mathbf{0}) > 0, \quad (15)$$

where $\widehat{J}^0_{+-}(\mathbf{0})$ is the only maximum of $|\widehat{J}^0_{+-}(\mathbf{k})|$ over the Brillouin zone. Moreover, we also impose a global condition of attraction

$$2\widehat{J}^0_{+-}(\mathbf{0}) + \widehat{J}^0_{++}(\mathbf{0}) + \widehat{J}^0_{--}(\mathbf{0}) > 2|\widehat{J}^0_{+-}(\mathbf{k})| + \widehat{J}^0_{++}(\mathbf{k}) + \widehat{J}^0_{--}(\mathbf{k}), \quad (16)$$

for all $\mathbf{k} \neq \mathbf{0}$. A sufficient condition for the validity of this inequality is that the mean interaction is globally positive in the sense that

$$\Delta \bar{J}^0(\mathbf{k}) \geqslant 0 \quad \text{in } \mathcal{B}, \quad (17)$$

where, following I, for any function $\widehat{g}(\mathbf{k})$ we write

$$\Delta g(\mathbf{k}) = \tfrac{1}{2}[\widehat{g}(\mathbf{0}) - \widehat{g}(\mathbf{k})], \quad (18)$$

while we also adopt the notation of I for averages and differences, namely,

$$\bar{g} = \tfrac{1}{2}(g_+ + g_-), \quad g^\dagger = \tfrac{1}{2}(g_+ - g_-) \quad (19)$$

for any g_σ. The condition (17) is fulfilled, e.g., when both J^0_{++} and J^0_{--} are attractive interactions. We consider in this article only *charge-symmetric* systems where the species bear the charges $q_+ = -q_- = q$ with q the elementary charge. However, we will allow *asymmetry* in the sense that $J^\dagger \propto (J_{++} - J_{--})$ need *not* vanish. The relative importance of the Coulomb forces vs the nonionic interactions is conveniently measured by the ionicity [5]

$$\mathcal{I}_0 = \frac{q^2}{a^{d-2}} \frac{1}{k_B T_0}, \quad (20)$$

where, via (15), T_0 is defined in terms of the short-range $(+, -)$ attractions.

As observed above, the presence of neutralizing backgrounds means that the Coulomb interactions alone will not enforce bulk electroneutrality whatever the chemical potentials may be. On the other hand, one knows [33] that a grand-canonical Coulomb fluid will realize bulk electroneutrality in the absence of any background potentials. In order to reproduce this situation, we impose electroneutrality "by hand," which means that we consider only systems where the ionic densities

$$\rho_\sigma = \tfrac{1}{2}(1 + m_\sigma)/a^d \quad (\sigma = +, -) \quad (21)$$

satisfy

$$\rho_+ = \rho_- \quad \text{or} \quad m^\dagger = \tfrac{1}{2}(m_+ - m_-) = 0. \quad (22)$$

Consequently, in contrast to general nonionic spherical model fluids, our ionic lattice model is defined by the set of only two variables, e.g., $(T, \bar{m})$ where the overall ion density is set by

$$\rho = \rho_+ + \rho_- = (1 + \bar{m})/a^d. \quad (23)$$

This greatly simplifies the further analysis.

III. SYMMETRIC IONIC FLUIDS

A. General properties

In this section, we consider *symmetric* ionic fluids with Coulomb and nonionic interactions which are of short range as is conveniently stated via the analyticity of their Fourier transforms at small k and is usefully embodied in the expansions

$$\widehat{J}^0_{\tau\upsilon}(\mathbf{k}) = \widehat{J}^0_{\tau\upsilon}(\mathbf{0})[1 - k^2 R^2_{\tau\upsilon} + O(k^4)], \quad (24)$$

where $R_{\tau\upsilon}$ is the range of $J^0_{\tau\upsilon}(r)$. Moreover, we assume "perfect charge symmetry" in the sense $J^0_{++} = J^0_{--}$ so that $J_{++} = J_{--}$; this common simplification (as in the restricted primitive model [3–6]) has dramatic and special consequences for the physical properties of the model as explained below; one must be aware of these features when trying to comprehend more realistic models of ionic fluids.

As explained in I, a general binary spherical model requires two spherical fields, here λ_+ and λ_-, one for each sublattice. However, the electroneutrality condition (22), requiring $m^\dagger = 0$, ensures as in I that $\lambda^\dagger \equiv \frac{1}{2}(\lambda_+ - \lambda_-)$ must also vanish so that only the mean spherical field $\bar{\lambda} = \frac{1}{2}(\lambda_+ + \lambda-)$ plays a role. It is convenient then to define the net spherical field by

$$\lambda \equiv \bar{\lambda} - j_0' \quad \text{with} \quad j_0' \equiv \tfrac{1}{2}\widehat{J}_{+-}(\mathbf{0}), \quad (25)$$

where j_0' differs only slightly from the short-range parameter defined in Eq. (15). Specifically, for $d = 3$ we have

$$j_0' = j_0\left(1 - \tfrac{11}{96}\pi \mathcal{I}_0\right). \quad (26)$$

To present the spherical condition, which then determines λ as a function of T and the overall ionic density $\rho \propto (1+\bar{m})$, we require the eigenvalues of the basic interaction matrix. These, as seen in I, are given by

$$\Lambda_{\pm}(\mathbf{k};\boldsymbol{\lambda}) = \bar{\lambda} + \Delta\bar{J}(\mathbf{k}) \pm D(\mathbf{k};\boldsymbol{\lambda}), \tag{27}$$

where

$$D(\mathbf{k};\boldsymbol{\lambda}) \equiv \sqrt{[\lambda^{\dagger} + \Delta J^{\dagger}(\mathbf{k})]^2 + \tfrac{1}{4}[\widehat{J}_{+-}(\mathbf{k})]^2}\,. \tag{28}$$

In terms of them we may define the basic integral

$$\mathcal{J}_d(\lambda) = \frac{1}{4}\int_{\mathbf{k}} [\Lambda_{+}^{-1}(\mathbf{k};\lambda) + \Lambda_{-}^{-1}(\mathbf{k};\lambda)], \tag{29}$$

where for brevity we have written $\int_{\mathbf{k}} \equiv \int_{\mathbf{k}\in\mathcal{B}} a^d d^d\mathbf{k}/(2\pi)^d$ the integral running over the reference lattice Brillouin zone $\mathcal{B}$. This form follows directly from I(42) and I(52) (but is simpler than the integrals $\mathcal{G}$ and $\mathcal{L}_{\sigma}$ that we had to consider in detail in I in order to handle the general case with $\rho_{+} \neq \rho_{-}$).

In this symmetric system and thanks to the electroneutrality condition (22), the most convenient variables are defined with the usual average and difference values [see (19)], and one can check that the spherical condition (50b) of I enforces the equivalence

$$m^{\dagger} = 0 \Leftrightarrow \lambda^{\dagger} = 0, \tag{30}$$

as Λ_{+} and Λ_{-} are non-negative. Hence, the system is uniquely characterized by only one Lagrange multiplier λ, implicitly defined by the spherical condition

$$1 = k_B T\,\mathcal{J}_d(\boldsymbol{\lambda}) + \frac{\bar{h}^2}{4\lambda^2}. \tag{31}$$

The field $\bar{h}$, related to the species chemical potential and defined in I(7), is merely given here by

$$\bar{h} = 2\bar{m}\lambda, \tag{32}$$

as the conditions (22) and (30), together with Eqs. (54) of I ensure that $h^{\dagger} \equiv 0$ in this symmetric system. The spherical condition (31) involves the functions

$$\mathcal{J}_d \equiv (\mathcal{J}_{+} + \mathcal{J}_{-})(\boldsymbol{\lambda}) \quad \text{with} \quad \mathcal{J}_{\pm}(\boldsymbol{\lambda}) \equiv \frac{1}{4}\int_{\mathbf{k}} 1/\Lambda_{\pm}(\mathbf{k};\boldsymbol{\lambda}), \tag{33}$$

which depend here on only one variable λ (as $\lambda^{\dagger}=0$). When (30) is met, the interaction matrix eigenvalues (see I) are given merely by

$$\Lambda_{\pm}(\mathbf{k};\boldsymbol{\lambda}) = \bar{\lambda} + \Delta\bar{J}(\mathbf{k}) \pm \tfrac{1}{2}|\widehat{J}_{+-}(\mathbf{k})|. \tag{34}$$

For small (but nonzero) vectors $\mathbf{k}$, $\Lambda_N \approx \Lambda_{-}$ behaves as

$$\Lambda_N(\mathbf{k};\boldsymbol{\lambda}) = \lambda + j_0 R_N^2\, k^2 + O(k^4), \tag{35}$$

where we define the new characteristic length

$$R_N^2 = R_0^2 - \tfrac{1}{576} S_d a^2 \mathcal{I}_0, \tag{36}$$

with the nonionic global range

$$j_0 R_0^2 = \frac{1}{4}\sum_{\tau} R_{\tau\tau}^2\, \widehat{J}_{\tau\tau}^{\,0}(\mathbf{0}) + \frac{1}{2} R_{+-}^2\, \widehat{J}_{+-}^{\,0}(\mathbf{0}), \tag{37}$$

which is positive thanks to (16). The crucial point of the expansion (35) is that even if Λ_N *a priori* involves Coulomb interactions with their $1/k^2$ divergence [see (34)], its behavior at small k is free of this singularity, due to the exact cancellation of the divergence of $2\Delta\bar{J}(\mathbf{k}) \approx -v_d q^2/k^2$ and of $\widehat{J}_{+-}(\mathbf{k}) \approx v_d q^2/k^2$; in fact, this cancellation can be seen as a consequence of electroneutrality and will ensure that Coulomb interactions do not change the universality class of the model as seen in the following. On the other hand, the behavior of $\Lambda_Z = \Lambda_{+}$ near the origin is drastically different, as the divergences of $\Delta\bar{J}(\mathbf{k})$ and $\widehat{J}_{+-}$ sum up and lead to

$$\Lambda_Z(\mathbf{k};\boldsymbol{\lambda}) = \frac{S_d q^2}{4a^d}\frac{1}{k^2}\big[1 + R_Z^2(\boldsymbol{\lambda},\hat{\mathbf{k}})\,k^2 + O(k^4)\big], \tag{38}$$

where

$$R_Z^2(\boldsymbol{\lambda};\hat{\mathbf{k}}) = \frac{2a^2}{S_d\mathcal{I}_0}\frac{\lambda + 2j_0'}{j_0} + a^2\Sigma_4(\hat{\mathbf{k}}). \tag{39}$$

B. Criticality

The free energy per site is given by Eq. (26) of I, and involves $\ln[\Lambda_{-}\Lambda_{+}(\mathbf{k};\boldsymbol{\lambda})]$ in a binary system, so that its singularities, which signal criticality, happen when $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda})$ vanishes (recall that $\Lambda_{-} \leqslant \Lambda_{+}$). In fact, we can show that these singularities occur (a) when $\lambda = 0$ and (b) for $\mathbf{k} \to \mathbf{0}$, provided the conditions (15) and (16) are met, and for bounded ionicities. To establish this result, we first need to ensure the positiveness of j_0', which can be done by imposing

$$\mathcal{I}_0 < \mathcal{I}_i(d) \quad \text{where} \quad \mathcal{I}_i(3) = 96/11\pi \simeq 2.78 \tag{40}$$

[see (26)]. The second condition ensures that the small-k expansion (35) of $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda})$ is convex, which, thanks to (36), is fulfilled when

$$\mathcal{I}_0 < \mathcal{I}_{ii}(d) \quad \text{where} \quad \mathcal{I}_{ii}(3) = \frac{144}{\pi}\frac{R_0^2}{a^2}. \tag{41}$$

When this condition is met, the limit $\mathbf{k} \to \mathbf{0}$ is the strict minimum of Λ_{-} in the zone where (35) is valid, i.e., typically for vectors $\mathbf{k}$ such as $|\mathbf{k}_{\alpha}| \leqslant k_{-}$ with some given k_{-}. The last condition ensures that no other minimum of $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda})$ can compete with $\mathbf{k} \to \mathbf{0}$ in the rest of the Brillouin zone. Let us define $\mathcal{B}'$ the close subdomain of the Brillouin zone made of vectors with at least one component such as $|\mathbf{k}_{\alpha}| \geqslant k_{-}$. We compare $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda})$ to its value when $q = 0$ (which case is referred to with superscripts 0). The minimum of the continuous function $\Lambda_{-}^{0}(\mathbf{k};\boldsymbol{\lambda})$ is reached on the close domain $\mathcal{B}'$ and is so strictly positive thanks to (16),

$$\delta\Lambda_{-}^{0} \equiv \min_{\mathbf{k}\in\mathcal{B}'}\{\Lambda_{-}^{0}(\mathbf{k};\boldsymbol{\lambda}) - (\bar{\lambda} - j_0)\} > 0, \tag{42}$$

with some given constant $\delta\Lambda_{-}^{0}$, independent of q. Moreover, as $\widehat{\varphi}_{\tau\upsilon}^{C}$ is continuous and bounded on the close interval $\mathcal{B}'$, one can check that $\widehat{J}_{\tau\upsilon}^{C}(\mathbf{k}) = O(\mathcal{I}_0)$, $j_0' = j_0 + O(\mathcal{I}_0)$, and

$$\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda}) = \Lambda_{-}^{0}(\mathbf{k};\boldsymbol{\lambda}) + O(\mathcal{I}_0). \tag{43}$$

Hence, in B',

$$\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda}) - \lambda > \delta\Lambda_{-}^{0} + O(\mathcal{I}_0), \tag{44}$$

so that for ionicities not too strong, let us say $\mathcal{I}_0 \leqslant \mathcal{I}_{iii}$, $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda}) - \lambda > 0$ in the domain $\mathcal{B}'$. As a conclusion, as soon as $\mathcal{I}_0 < \mathcal{I}_{\max} = \inf(\mathcal{I}_i, \mathcal{I}_{ii}, \mathcal{I}_{iii})$, the minimum of $\Lambda_{-}(\mathbf{k};\boldsymbol{\lambda})$ is

λ and is reached only when $\mathbf{k} \to \mathbf{0}$ so that $\lambda = 0$ signals the singularities of the model.

In fact, these conclusions mean that criticality is mainly governed by the nonionic attractive interactions. Indeed, first note that the conditions (a) and (b) are similar to the ones describing criticality in purely short-range spherical models (see I). Moreover, the critical condition $\bar{\lambda} = j_0' = j_0 + O(\mathcal{I}_0)$ shows that Coulomb interactions enter only via a perturbation in the critical localization. In fact, the origin of this mechanism lies in the properties of Λ_N: As the $1/k^2$ Coulomb divergence is exactly canceled in Λ_N, and as criticality is governed by the vanishing of this eigenvalue, the long range of Coulomb interactions is ruled out of the critical behavior. This result is very different from the conclusions of the ionic spherical model recently proposed by Smith [32]. The main difference is that in the latter analysis, only one variable, the charge density, is considered at each lattice site: The interactions between every site are both short range and ionic, but the latter destroy the gas-liquid phase separation as the $1/k^2$ divergence dominates the calculation and breaks the usual spherical model singularities. On the other hand, thanks to the consideration of a binary fluid, we can consider in the present analysis two local densities (both local charge *and* total density), described by a two-dimensional interaction matrix with one of its eigenvalues Λ_N, which does not contain the long-range Coulomb behavior, and which describes mainly the density fluctuations as explained in the following. (Note that, similarly to [32], the other eigenvalue Λ_Z is dominated by the $1/k^2$ divergence and would not drive criticality alone.)

When $\mathcal{I}_0 < \mathcal{I}_{\max}$, the function $\mathcal{J}_d(\lambda) \equiv \mathcal{J}_d(\lambda, \lambda^\dagger = 0)$ is well defined for $\lambda \geqslant 0$, and decreasing with λ. The spherical condition (31) may then be rewritten in the compact form

$$1 = k_B T \mathcal{J}_d(\lambda) + \bar{m}^2 \quad \text{where} \quad \bar{m}^2 = \bar{h}^2/4\lambda^2. \tag{45}$$

When $\bar{h} \neq 0$, the right-hand side of (45) is a continuous, decreasing function of λ, diverging at $\lambda = 0$ and going to zero when $\lambda \to \infty$; hence, for every $T \geqslant 0$, there exists one (and only one) non-negative solution of (45) and the system is free of singularity. On the other hand, when $\bar{h} = 0$, the situation depends on dimensionality. Indeed, concerning the behavior of $\mathcal{J}_-$, as $d^d\mathbf{k}/\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$ behaves as $k^{d-1}dk/(\lambda + j_0 R_N^2 k^2)$, we find the following: (i) when $d < 2$, $\mathcal{J}_d(\lambda)$ diverges when λ goes to zero, Eq. (45) can always be satisfied by some non-negative λ and no critical point occurs; (ii) in the case which matters to us, i.e., for $d > 2$, $\mathcal{J}_d(\lambda = 0)$ is finite and, as $\mathcal{J}_d(\lambda) \leqslant \mathcal{J}_d(0)$, the spherical condition (45) can be fulfilled only when $T \geqslant T_c$ where

$$k_B T_c = 1/\mathcal{J}_d(0). \tag{46}$$

When $T = T_c$, the solution of (45) is $\lambda = 0$, while for $T < T_c$, λ sticks to zero but (45) has to be modified. Hence, the critical point is defined as $(T_c, \bar{h} = 0)$ or, equivalently as $(T_c, \bar{m} = 0)$, while in the fluid language, the critical densities are merely

$$a^d \rho_{\pm,c} = 1/2 \quad \text{and} \quad a^d \rho_c = 1. \tag{47}$$

Note that the critical temperature defined in Eq. (46) is given mainly by the contribution of the nonionic interactions, as

$$T_c = T_c^0[1 + O(\mathcal{I}_0)], \tag{48}$$

where $T_c^0 = 1/k_B \mathcal{J}_d^0(0)$ is the critical temperature when $q = 0$. In the general case, $j_0 \mathcal{J}_-^0(0)$ is of order unity, and one can give some specific values in some particular cases: following Joyce's notation [36], we consider nonionic interactions such as

$$\Delta \bar{J}^0(\mathbf{k}) + \Delta J_{+-}^0(\mathbf{k}) = j_0[1 - \lambda_J(\mathbf{k})], \tag{49}$$

where the characteristic functions $\lambda_J(\mathbf{k})$, of the simple-cubic (sc), body-centered-cubic (bcc), or face-centered-cubic (fcc) lattices with nearest-neighbor interactions are

$$\lambda_J(\mathbf{k}) = \frac{1}{3}\sum_\alpha \cos(\mathbf{k}_\alpha a) \quad (\text{sc}) \tag{50}$$

$$= \prod_\alpha \cos(\mathbf{k}_\alpha a) \quad (\text{bcc}) \tag{51}$$

$$= \frac{1}{3}\sum_\alpha \cos(\mathbf{k}_\alpha a)\cos(\mathbf{k}_{\alpha+1} a) \quad (\text{fcc}), \tag{52}$$

with the convention $\mathbf{k}_{d+1} = \mathbf{k}_1$. In these case, one gets the estimates [36]

$$j_0 \mathcal{J}_-(0) = \tfrac{1}{2} K_c + O(\mathcal{I}_0), \tag{53}$$

where $K_c(\text{sc}) \simeq 1.52$, $K_c(\text{bcc}) \simeq 1.39$, and $K_c(\text{fcc}) \simeq 1.34$.

C. Critical vicinity

The vicinity of the critical point is characterized by two small parameters $(t, \bar{h})$ [or $(t, \bar{m})$] with the reduced temperature

$$t \equiv (T - T_c)/T_c. \tag{54}$$

In this vicinity, λ is also a small parameter and one can get the physical properties of the system as perturbations in terms of this Lagrange multiplier. Indeed, when $\lambda \geqslant 0$, because the eigenvalue $\Lambda_+(\mathbf{k};\boldsymbol{\lambda})$ is strictly positive and $1/\Lambda_+(\mathbf{k};\boldsymbol{\lambda})$, as well as its derivative with respect to λ are integrable functions of $\mathbf{k}$, $\mathcal{J}_+$ can be expanded according to a Taylor expansion

$$\mathcal{J}_+(\lambda) = \mathcal{J}_+(0) + O(\lambda). \tag{55}$$

Concerning $\mathcal{J}_-$, the behavior of $d\mathbf{k}/\Lambda_-$ near the origin as $k^{d-1}dk/(\lambda + j_0 R_N^2 k^2)$ leads to the usual spherical model expansion (see [36])

$$\mathcal{J}_-(\lambda) = \mathcal{J}_-(0)[1 - \tilde{p}\lambda^{1/\gamma} + O(\lambda)], \tag{56}$$

where γ is the critical exponent

$$\gamma = \max\{2/(d-2); 1\} \quad \text{when} \quad d > 2, \tag{57}$$

while the positive constant $\tilde{p}$ is given by the universal relation [37]

$$\tilde{p}\mathcal{J}_-(0)\left[j_0 \frac{R_N^2}{a^2}\right]^{1+1/\gamma} = \frac{1}{2^d \pi^{d/2-1}\Gamma(d/2)\sin(\pi/\gamma)}, \tag{58}$$

where Γ is the gamma function. As a whole, $\mathcal{J}_d(\lambda)$ is characterized by the expansion

$$\mathcal{J}_d(\lambda) = \mathcal{J}_d(0)[1 - p\lambda^{1/\gamma} + O(\lambda)], \tag{59}$$

with some given positive constant p, which leads to the usual spherical model universality class as explained in the following.

The equation of state of the system is *implicitly* defined by the spherical condition (45) together with the link (32). Moreover, *explicit* expressions can be obtained when treating perturbatively these equations in the vicinity of a critical point which is defined by the two small parameters t and $\bar{m}$. Considering the difference between (45) and its expression at criticality, together with the expansion (59), we find, at leading order in λ,

$$\lambda = \tfrac{1}{2}\mathcal{A}(t+\bar{m}^2)^{\gamma}\,\{1+O[(t+\bar{m}^2)^{\gamma-1}]\}, \qquad (60)$$

where we define the slow varying function

$$\mathcal{A} = 2p^{-\gamma}(1+t)^{-\gamma}. \qquad (61)$$

Combined with (32), this expansion leads to the equation of state

$$\bar{h} = \mathcal{A}\,\bar{m}\,(t+\bar{m}^2)^{\gamma}\,\{1+O[(t+\bar{m}^2)^{\gamma-1}]\}, \qquad (62)$$

which is the same as in short-range spherical models [36]! Hence, the same universality class compared to nonionic models is realized: the long range of Coulomb interactions do not break the usual critical fluctuations. This conclusion was also derived for a symmetric system in Stell's work [4] and is robust to asymmetry as seen in the following.

Naturally, the physical behavior contained in Eq. (62) is similar to that found in nonionic models: For instance, the divergence near criticality of the susceptibility (or, in fluid language, compressibility) is

$$\left.\frac{\partial\bar{m}}{\partial\bar{h}}\right|_T(T,\bar{h}=0) \sim \frac{1}{t^{\gamma}} \quad \text{when} \quad t\to 0^+, \qquad (63)$$

where γ, defined in Eq. (57), is the usual spherical model critical exponent [36]. Similarly, for T below T_c and for small $\mathbf{k}$, the system exhibits the discontinuity

$$\lim_{\bar{h}\to 0^{\pm}} \bar{m}(\bar{h},T) = m_{\pm} = \pm t^{1/2}, \qquad (64)$$

so that we retrieve the critical exponent $\beta=\frac{1}{2}$. Finally, we note that, contrarily to what happens in binary short-range spherical models I, no demagnetization effect is at stake in the present ionic spherical model [compare (62) to (84) of I]. This is due to the consideration here of systems with the partial symmetry $m^{\dagger}=0$, as enforced by electroneutrality, which happily destroys this unrealistic effect for a fluid model.

D. Density correlations

We now turn to the calculation of the species and density correlation functions, while the analysis of charge correlations is done in the next section. In the present symmetric model, the correlations given in Eq. (3) reduce to

$$G_{\tau\upsilon}(\mathbf{k};\boldsymbol{\lambda}) = \frac{k_BT}{16a^{2d}}\left[\frac{1}{\Lambda_N(\mathbf{k};\boldsymbol{\lambda})} + \frac{(-1)^{\vartheta_{\tau\upsilon}}}{\Lambda_Z(\mathbf{k};\boldsymbol{\lambda})}\right], \qquad (65a)$$

$$G_{XX}(\mathbf{k};\boldsymbol{\lambda}) = \frac{k_BT}{16a^{2d}}\frac{1}{\Lambda_X(\mathbf{k};\boldsymbol{\lambda})}, \qquad (65b)$$

where $\vartheta_{\tau\upsilon}=0$ if $\tau=\upsilon$ and 1 otherwise. Similarly to the binary spherical model (see I), these correlations are linear combinations of the two eigenmodes $1/\Lambda_N$ and $1/\Lambda_Z$. However, in this special symmetric case (where $\Delta J^{\dagger}=m^{\dagger}=0$), G_{NN} and G_{ZZ} involve, respectively, only $1/\Lambda_N$ and $1/\Lambda_Z$. This accidental decoupling is full of consequences as seen in the next section concerning charge correlations and as opposed to realistic asymmetric systems. As seen in Eq. (38), the term $1/\Lambda_Z$ describes a short-range function with the typical length scale R_Z and with a vanishing integral over the whole system. On the other hand, the term $1/\Lambda_N \approx 1/(\lambda + j_0R_N^2k^2)$ [see (35)], which exhibits a singularity when k and λ vanish, is responsible for the critical behavior: Indeed, at the critical point, characterized by $\lambda=0$,

$$G_{NN}(\mathbf{k};T_c,\boldsymbol{\rho}_c) \sim \frac{1}{k^2}, \qquad (66)$$

which means in the r space, $G_{NN}(\mathbf{r})_c \sim 1/r^{d-2}$ when $|\mathbf{r}|\to\infty$ [the same property holds for $G_{\tau\upsilon}$, which also involve $1/\Lambda_N$, see (65a)]. Hence, the species and density correlations exhibit the usual long-range critical fluctuations characterized by a critical exponent $\eta=0$ as in short-range spherical models [36]. Away from criticality, for $\lambda\neq 0$, we also find that the density structure factor can be written at small k as

$$\frac{S_{NN}(\mathbf{k};T,\boldsymbol{\rho})}{S_{NN}(\mathbf{0};T,\boldsymbol{\rho})} = \frac{1}{1+k^2\xi_N^2(T,\boldsymbol{\rho})+O(k^4)}, \qquad (67)$$

with the total fluctuations $S_{NN}(\mathbf{0};T,\boldsymbol{\rho}) = k_BT/4a^d\rho\lambda$ and the density correlation length

$$\xi_N(T,\boldsymbol{\rho}) = R_N\sqrt{j_0/\lambda(T,\boldsymbol{\rho})}. \qquad (68)$$

On approach of the critical point, as $T\to T_c^+$ on the axis $\bar{h}=0$ (i.e., when $\boldsymbol{\rho}=\boldsymbol{\rho}_c$), these quantities diverge as

$$S_{NN}(\mathbf{0};T,\boldsymbol{\rho}_c) \sim \frac{1}{t^{\gamma}} \quad \text{and} \quad \xi_N(T,\boldsymbol{\rho}_c) \sim \frac{1}{t^{\nu}}, \qquad (69)$$

with $\nu=\gamma/2$, which are indeed the expected behavior.

In order to characterize the spatial dependence of correlations, one can also study various characteristic lengths. A choice, relevant for the comparison with simulations, is to consider the moments of the small-k expansion of S_{NN},

$$\frac{S_{NN}(\mathbf{k};T,\boldsymbol{\rho})}{S_{NN}(\mathbf{0};T,\boldsymbol{\rho})} = 1 - \xi_{N,1}^2(T,\boldsymbol{\rho})k^2 + \sum_{p=2}^{\infty}(-1)^p\xi_{N,p}^{2p}(T,\boldsymbol{\rho})k^{2p}. \qquad (70)$$

(We notice that the different coefficient $\xi_{N,p}^{2p}$ does not need to be positive.) In the present model, we find that the first moment is merely $\xi_{N,1}(T,\boldsymbol{\rho})=\xi_N(T,\boldsymbol{\rho})$ while the higher moments are given in the limit $(T,\boldsymbol{\rho})\to(T_c,\boldsymbol{\rho}_c)$ by

$$\xi_{N,p}(T,\boldsymbol{\rho}) \approx \lim_{p\to\infty}\xi_{N,p}(T,\boldsymbol{\rho}) \approx \xi_N(T,\boldsymbol{\rho}). \qquad (71)$$

One can also consider $\xi_{N,\infty}$, the true decay length of the density correlation, given in the complex k plane by the singularity nearest to the real axis: We also find $\xi_{N,\infty}\approx\xi_N$ near criticality [see Appendix (B)].

E. Charge correlations

When one examines ionic fluids, electrostatic properties are revealed in part by the charge correlations which, in the present *symmetric* model, are *solely* determined by the eigenvalue Λ_Z as explicit in Eq. (65b). The latter being free of the singularities of Λ_N, charge correlations display smooth behavior and, especially, remain short range even near and at criticality. Indeed, the small-k behavior of the charge structure factor can be written as

$$S_{ZZ}(\mathbf{k};T,\boldsymbol{\rho})=\frac{k_BT}{S_dq^2\rho}\frac{k^2}{1+k^2R_Z^2(T,\boldsymbol{\rho},\hat{\mathbf{k}})+O(k^4)},\qquad(72)$$

where $O(k^4)$ contains only even powers of k^2. Consequently, one can check that the system satisfies the electroneutrality sum rule [38] characteristic of internal screening,

$$S_{ZZ}(\mathbf{k}=\mathbf{0};T,\boldsymbol{\rho})=0,\qquad(73)$$

over the entire phase space. Moreover, the structure of (72) implies that $S_{ZZ}(\mathbf{r})$ is a *short-range* function over the screening length R_Z given in Eq. (39). In fact, R_Z is always of order of the Debye length (1), and accordingly stays finite near and at the critical point. Indeed, neglecting the anisotropic contribution $\Sigma_4(\hat{\mathbf{k}})/a^2$ thanks to (12), one has, near criticality,

$$\frac{R_Z^2}{\xi_D^2}(T_c,\boldsymbol{\rho}_c;\hat{\mathbf{k}})\approx 8j_0\mathcal{J}_d(0),\qquad(74)$$

which leads to $R_{Z,c}=O(\xi_{D,c})$ as $j_0\mathcal{J}_d(0)$ is of order unity [see Sec. (III B)]. Note also that, in the low-density limit, the spherical constraint (45) implies $\mathcal{J}_d\approx 1/2\lambda$, so that

$$\lambda\approx\frac{k_BT}{4\rho a^d}\quad\text{when}\quad\rho a^d\to 0.\qquad(75)$$

Consequently, the charge characteristic length R_Z approaches exactly the Debye length at low coupling,

$$R_Z(T,\boldsymbol{\rho},\hat{\mathbf{k}})\approx\xi_D(T,\boldsymbol{\rho}),\qquad(76)$$

which is in accord with Brydges and Federbush's result of [26]. (This result also implies that in the low-density limit, the charge structure factor reduces to

$$S_{ZZ}^{\mathrm{DH}}=\frac{k^2}{\xi_D^{-2}+k^2},\qquad(77)$$

which coincides with the Debye-Hückel result.) As a consequence, the true decay length of the charge correlations, which characterizes the large-r behavior of $S_{ZZ}(\mathbf{r})$ and which is given by

$$\xi_{Z,\infty}(T,\boldsymbol{\rho},\hat{\mathbf{k}})=R_Z(T,\boldsymbol{\rho},\hat{\mathbf{k}})\big[1+O\big(\mathcal{I}_0^2\big)\big]\qquad(78)$$

[see Appendix (B)], remains of the order of the screening length ξ_D, and therefore stays finite in the critical region. We note that the anisotropy present here via $\Sigma_4(\hat{\mathbf{k}})$ in R_Z is an artifact of the anisotropy introduced by the Fourier transforms of the Coulomb potential [see (11)].

We can also analyze S_{ZZ} via its small-k behavior

$$S_{ZZ}(\mathbf{k};T,\boldsymbol{\rho})=\sum_{p=1}^{\infty}(-1)^{p-1}\xi_{Z,p}^{2p}(T,\boldsymbol{\rho},\hat{\mathbf{k}})k^{2p}.\qquad(79)$$

We first find

$$\xi_{Z1}(T,\boldsymbol{\rho})=\xi_D(T,\boldsymbol{\rho}),\qquad(80)$$

which shows that the system always satisfies the Stillinger-Lovett second moment sum rule (2), even near and *at* criticality (a specialization of this sum rule for the present geometry and definitions of the Fourier transforms is presented in Appendix A). In fact, this sum rule characterizes the screening by a charged fluid of any external charge and is the condition for a system to be conducting [38]. However, as seen in the following, its satisfaction at criticality is not automatic and is a consequence here of the special symmetry and universality class of the model. The higher moments of the charge structure factor are given by

$$\xi_{Z,2}(T,\boldsymbol{\rho},\hat{\mathbf{k}})=\xi_D^{1/2}R_Z^{1/2}(T,\boldsymbol{\rho},\hat{\mathbf{k}}),\qquad(81a)$$

$$\xi_{Z,p}^{2p}(T,\boldsymbol{\rho},\hat{\mathbf{k}})=\xi_D^2R_Z^{2(p-1)}(T,\boldsymbol{\rho},\hat{\mathbf{k}})[1+O(\mathcal{I}_0)]\qquad(81b)$$

(see Appendix B) so that $\lim_{p\to\infty}\xi_{Z,p}$ is merely $R_Z(T,\boldsymbol{\rho},\hat{\mathbf{k}})$ $[1+O(\mathcal{I}_0)]$.

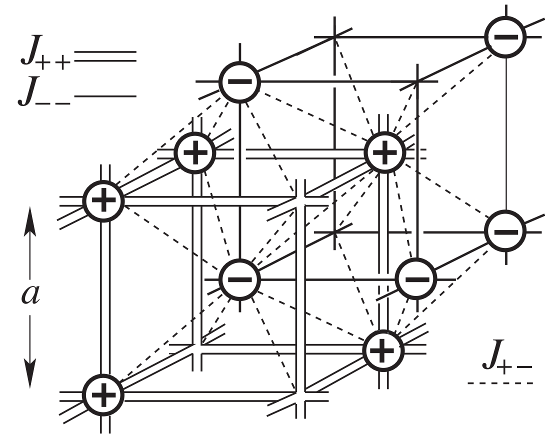

FIG. 1. Two interwoven lattices + and − modeling a binary Coulomb fluid.

F. Simplest model for numerics

In this section, we define a model with precise nonionic interactions in order to get quantitative estimates of the different characteristic lengths and conditions of validity. We consider the basic ionic spherical model (BISM), a particular case of the previous model in dimension 3. The nonionic interactions are taken as the nearest-neighbor interactions

$$J_{+-}^0(\mathbf{R})=J>0\quad\text{if}\quad\mathbf{R}=\left(\pm\frac{a}{2},\pm\frac{a}{2},\pm\frac{a}{2}\right)\qquad(82)$$

$$=0\qquad\text{otherwise},\qquad(83)$$

so that

$$\widehat{J}_{+-}^0(\mathbf{k})=8J\prod_{\alpha}\cos(k_\alpha a/2),\qquad(84)$$

while J_{++}^0 and J_{--}^0 are set equal to zero (the system is indeed symmetric). If the two species were equal, this model would mimic a one component fluid on a bcc lattice, with step $a_0=a\sqrt{3}/2$ (see Fig. 1). In the nonionic case where $q=0$, the critical temperature corresponds to the one component nearest-neighbor bcc spherical model, i.e.,

$$k_BT_c^0=8J/K_c(\mathrm{bcc}),\qquad(85)$$

where $K_c(\mathrm{bcc})$ was introduced in Eq. (53). The nonionic interactions are characterized by

$$j_0=4J\quad\text{and}\quad R_0^2=\tfrac{1}{8}a^2.\qquad(86)$$

When Coulomb interactions are present ($q \neq 0$), the conditions of validity can be made explicit. First, the positiveness of j_0' requires the condition $\mathcal{I}_0 < \mathcal{I}_i$ [see (40)]. Second, the amplitude of the k^2 term in the small-k expansion of Λ_N [see (35)] is merely

$$j_0 R_N^2 = \tfrac{1}{2} a^2 J[1 - \mathcal{I}_0/\mathcal{I}_{ii}], \quad (87)$$

with $\mathcal{I}_{ii} = 18/\pi \simeq 5.72$, so that $\mathcal{I}_0 < \mathcal{I}_{ii}$ is required to ensure the convexity of $\Lambda_-(\mathbf{k})$ near the origin. Finally, we check numerically that $\mathbf{k} = \mathbf{0}$ is the absolute minimum of $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$ over the entire Brillouin zone as long as

$$\mathcal{I}_0 < 12/\pi \simeq 3.8. \quad (88)$$

In fact, this condition is a necessary condition as can be shown analytically considering the corner of the Brillouin zone $\mathbf{k} = (\pi/a, \pi/a, \pi/a)$. As a whole, as soon as $\mathcal{I}_0 < \mathcal{I}_i$, the hypothesis made in Sec. III B is satisfied and the resulting properties apply.

We can then give some estimates of the characteristic lengths of density and charge correlations. As regards density correlations, the true decay length ξ_N involves the parameter p introduced in Eq. (56). Its value can be given in the low-ionicity limit, noting that, when $q = 0$,

$$\mathcal{J}_d^0(\lambda) = \frac{1}{2\lambda} P\left(\frac{4J}{\lambda}\right), \quad (89)$$

where P is the Green function associated with the bcc lattice with nearest-neighbor interaction, which expansion is given in (3.19) of [36]. The latter expansion leads to

$$p = \frac{\sqrt{2}}{\pi K_c(\text{bcc})\sqrt{J}} [1 + O(\mathcal{I}_0)]. \quad (90)$$

Hence, the density correlation length diverges near criticality as

$$\xi_N \approx a \frac{1}{\pi K_c(\text{bcc})} \frac{1}{t^\nu} [1 + O(\mathcal{I}_0)], \quad (91)$$

where $1/\pi K_c(\text{bcc}) \simeq 0.229$. Normalized by the step of the bcc lattice a_0, this divergence is $\xi_N/(a_0/t^\nu) \approx 2/\sqrt{3}\pi K_c(\text{bcc}) \simeq 0.264$ which is close to its value in the Ising model [39].

Finally, concerning charge correlations, the characteristic length R_Z behaves near criticality as

$$R_Z^2 \approx \frac{a^2}{\pi \mathcal{I}_0}(1 - \mathcal{I}_0/\mathcal{I}_i). \quad (92)$$

Its ratio to the Debye length approaches near the critical point

$$\frac{R_Z}{\xi_D} \approx \left[\frac{32J(1 - \mathcal{I}_0/\mathcal{I}_i)}{k_B T_c}\right]^{1/2}, \quad (93)$$

which is well of order unity and equals $2\sqrt{K_c(\text{bcc})} \simeq 2.4$ in the low-ionicity limit. Similarly, in the low-density limit, this ratio is well of order unity and tends again toward $2\sqrt{K_c(\text{bcc})}$.

IV. ASYMMETRIC CLASSICAL SYSTEMS

A. General properties

In the previous section, the symmetry of the system had crucial consequences concerning, e.g., the finiteness of the charge correlation lengths or the validity of the SL sum rule. However, even if convenient for theory, symmetry is a charming lure which has to be treated with care in any realistic description of Coulomb fluids. Hence, we deal in this section with asymmetric systems. As the present model is built so as to satisfy charge symmetry ($q_+ = -q_- = q$), we consider the asymmetry which originates from the short-range interactions, describing, e.g., hard-core mismatch or different nonionic attractions. Hence, we deal with the model defined in Sec. II where we suppose $J_{++}^0 \neq J_{--}^0$. Even if electroneutrality still requires $m^\dagger = 0$, $\lambda^\dagger$ does not vanish in the general case and satisfies the spherical condition (50b) of I, which reduces here to

$$\lambda^\dagger = -\int_{\mathbf{k}} \frac{\Delta J^\dagger(\mathbf{k})}{\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})} \Big/ \int_{\mathbf{k}} \frac{1}{\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})}. \quad (94)$$

In addition to this equation, any state of the system is defined by the spherical condition (45) and the link between external and internal fields

$$\bar{h} = 2\bar{m}\lambda \quad \text{and} \quad h^\dagger = 2\bar{m}\lambda^\dagger. \quad (95)$$

In fact, the eigenvalues $\Lambda_\pm$ display similar behavior at small k compared to the symmetric case. Indeed, we find for small (but nonzero) vectors

$$\Lambda_N(\mathbf{k};\boldsymbol{\lambda}) = \lambda + j_0 R_N^2(\boldsymbol{\lambda})k^2 + O(k^4), \quad (96)$$

where the length R_N now depends on $\boldsymbol{\lambda}$ via

$$R_N^2(\boldsymbol{\lambda}) = R_0^2 - \frac{1}{576} S_d a^2 \mathcal{I}_0 - \frac{2a^2}{S_d \mathcal{I}_0} \frac{\lambda^{\dagger 2}}{j_0^2}, \quad (97)$$

with R_0^2 defined in Eq. (37). (We note that the notation R_N^2 does not presuppose the *a priori* positiveness of this coefficient.) Similarly, $\Lambda_Z(\mathbf{k};\boldsymbol{\lambda})$ has the same expression (38) at order $1/k^2$ and 1 as in the symmetric case.

B. Singularities

To quantify the asymmetry introduced by the difference $J_{++}^0 - J_{--}^0 \neq 0$, we define the asymmetry parameter δ_J,

$$\delta_J = \frac{\max_{\mathbf{k}\in\mathcal{B}} |\Delta J^\dagger(\mathbf{k})|}{j_0}, \quad (98)$$

which also measures the asymmetric Lagrange multiplier $\lambda^\dagger$. Indeed, as $\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})$ is always positive, the constraint (94) leads to the bond

$$|\lambda^\dagger| \leqslant j_0 \delta_J. \quad (99)$$

We can then show that for ionicities $\mathcal{I}_0$ and asymmetries δ_J not too large, the singularities of the system occur similarly to in the symmetric systems. In fact, they occur when Λ_- vanishes as it signals a singular behavior of $\mathcal{J}_d(\lambda)$ involved in the spherical constraint (45). However, in the thermodynamic limit where $\mathcal{J}_d$ is given by an integration over $\mathbf{k}$, an isolated annulation of $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$ does not enforce a thermodynamic singularity; hence, in this asymmetric case where $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$ might be discontinuous at $\mathbf{k} = \mathbf{0}$, we do not consider the contribution from the isolated point $\mathbf{k} = \mathbf{0}$.

Thanks to these considerations, one can check that the singularity of the model happens when $\mathbf{k} \to \mathbf{0}$ and $\lambda = 0$. To prove this result, we impose three conditions similar to those in symmetric systems. First, we suppose that the total interactions are globally attractive so that $j_0' > 0$, which requires the condition (40). Second, we enforce the small-k expansion (96) to be convex, i.e., $R_N^2 > 0$, which is fulfilled in the interior of an ellipsoid, which in $d = 3$ reduces to

$$\left[\frac{1}{72}\pi\mathcal{I}_0 - \frac{R_0^2}{a^2}\right]^2 + \frac{1}{72}\delta_J^2 < \frac{R_0^4}{a^4}. \tag{100}$$

This condition concerns the interval of validity of (96) made of vectors of the Brillouin zone such as $|\mathbf{k}_\alpha| \leqslant k_-$ for all α. Finally, in the close complementary part $\mathcal{B}'$ of the Brillouin zone (made of vectors with one $|\mathbf{k}_\alpha| \geqslant k_-$), $\Lambda_-(\mathbf{k};\boldsymbol{\lambda}) - \lambda$ can be proved to be strictly positive by comparing its value to the associated symmetric system (referred to with superscripts SYM) defined as having the same J_{+-} and $\Delta\bar{J}$ interactions but with $\Delta J^\dagger = 0$. Indeed, we suppose the associated symmetric system to fulfill the conditions of Sec. III B, which requires $\mathcal{I}_0 < \mathcal{I}_{\max}$ and implies that the minimum of $\Lambda_-^{\mathrm{SYM}}(\mathbf{k};\boldsymbol{\lambda}) - \lambda$ is zero and is reached only when $\mathbf{k}$ vanishes. Accordingly, the minimum

$$\delta\Lambda_-^{\mathrm{SYM}} \equiv \min_{\mathbf{k}\in\mathcal{B}'}\{\Lambda_-^{\mathrm{SYM}}(\mathbf{k};\boldsymbol{\lambda}) - \lambda\}, \tag{101}$$

which is attained for some $\mathbf{k}$ in $\mathcal{B}'$ [because of the continuity of $\Lambda_-^{\mathrm{SYM}}(\mathbf{k};\boldsymbol{\lambda})$] is strictly positive and independent of asymmetry by construction. Then, performing the decomposition

$$\Lambda_-(\mathbf{k};\boldsymbol{\lambda}) - \lambda = \Lambda_-^{\mathrm{SYM}}(\mathbf{k};\boldsymbol{\lambda}) - \lambda - \big[D(\mathbf{k};\boldsymbol{\lambda}) - \tfrac{1}{2}|\widehat{\mathcal{J}}_{+-}(\mathbf{k})|\big], \tag{102}$$

and noticing that thanks to the bound $\sqrt{x^2 + y^2} \leqslant |x| + |y|$, the second brackets of (102) are smaller than $2j_0\delta_J$, we find that for asymmetries not too large, $\delta_J < \delta_J^{\max}$, with, e.g.,

$$\delta_J^{\max} = \delta\Lambda_-^{\mathrm{SYM}}/2j_0, \tag{103}$$

$\Lambda_-(\mathbf{k};\boldsymbol{\lambda}) - \lambda$ is larger than some strictly positive value. As a conclusion, for $\mathcal{I}_0 < \mathcal{I}_{\max}$, $(\mathcal{I}_0, \delta_J)$ in the ellipsoid (100) and $\delta_J < \delta_J^{\max}$, the minimum of $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$ is λ and is reached only when $\mathbf{k} \to \mathbf{0}$.

As regards the behavior of $\lambda^\dagger$ near criticality, we first note that, as the integrand of $\int_{\mathbf{k}} 1/\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})$ in Eq. (94) behaves as $d^d\mathbf{k}\,k^2/[\lambda + O(k^2)]$, this integral is well defined when λ vanishes, as well as its derivatives with respect to λ and $\lambda^\dagger$. [The same argument is true for $\int_{\mathbf{k}} \Delta J^\dagger(\mathbf{k})/\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})$.] Let us note $\lambda_c^\dagger$ the critical value of $\lambda^\dagger$ and $\mathfrak{J}_d^\dagger(\lambda, \lambda^\dagger)$ the right-hand side of (94). The derivatives of $\mathfrak{J}_d^\dagger$ with respect to λ and $\lambda^\dagger$ are continuous for every $\lambda \geqslant 0$ and $\lambda^\dagger$, and, for δ_J not too large, $\partial(\lambda^\dagger - \mathfrak{J}_d^\dagger)/\partial\lambda^\dagger|_\lambda \neq 0$ when $\lambda = 0$ and $\lambda^\dagger = \lambda_c^\dagger$. Thanks to the implicit functions theorem, one concludes that when δ_J is not too large, $\lambda^\dagger$ solution of (94) is a $\mathcal{C}^1$ function of λ,

$$\lambda^\dagger = \lambda_c^\dagger + O(\lambda). \tag{104}$$

Moreover, we are interested in truly asymmetric system where $\lambda_c^\dagger \neq 0$. This condition is achieved in many examples: for instance, it is met in systems where symmetric nonionic interactions are supplemented with nearest-neighbor interactions with different amplitudes. The condition that $\Delta J^\dagger(\mathbf{k})$ has a constant sign over the Brillouin zone is also a sufficient condition for $\lambda_c^\dagger$ not to vanish. Finally, one can expect that the vanishing of the integral $\int_{\mathbf{k}} \Delta J^\dagger(\mathbf{k})/\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})$ at criticality is only accidental for some very particular interactions, with no robustness with respect to the addition of small asymmetric perturbations. If the interactions are such as $\lambda_c^\dagger = 0$, the system would recover some special accidental symmetry at the critical point.

Finally, the singularities of the system appear to be linked to the function $\mathcal{J}_d(\boldsymbol{\lambda})$ defined in Eq. (33) and involved in the spherical constraint (45). First, let us define the shorthand notation $\mathcal{J}_d(\lambda) = \mathcal{J}_d[\lambda, \lambda^\dagger(\lambda)]$. Because the small-$k$ behavior of $\Lambda_\pm(\mathbf{k};\boldsymbol{\lambda})$ is similar to its counterparts in the symmetric case, $\mathcal{J}_d(\lambda)$ displays a small-λ expansion similar to (59). Moreover, $\mathcal{J}_d(\lambda)$ is continuous for $\lambda \geqslant 0$, finite at $\lambda = 0$, and its monotonicity requires an extra bound on δ_J. Indeed, let us call λ_m the domain of validity of (59) in the asymmetric case, meaning that the latter equation is valid in the interval $0 \leqslant \lambda \leqslant \lambda_m$ where $\mathcal{J}_d(\lambda)$ is decreasing. For $\lambda \geqslant \lambda_m$, we consider Λ_m the minimum of $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$ for all $\mathbf{k}$, i.e., $\Lambda_\pm(\mathbf{k};\boldsymbol{\lambda}) \geqslant \Lambda_m > 0$. As there is no singularity in the link between $\lambda^\dagger$ and λ, as $d\lambda^\dagger/d\lambda$ is bounded for $\lambda \geqslant \lambda_m > 0$, and as

$$\frac{d\mathcal{J}_d(\lambda)}{d\lambda} = \frac{1}{4}\int_{\mathbf{k}}\left\{-\frac{1}{\Lambda_+(\mathbf{k};\boldsymbol{\lambda})^2} - \frac{1}{\Lambda_-(\mathbf{k};\boldsymbol{\lambda})^2} + \frac{4[\bar{\lambda} + \Delta\bar{J}(\mathbf{k})][\lambda^\dagger + \Delta J^\dagger(\mathbf{k})]\,d\lambda^\dagger/d\lambda}{[\Lambda_-\Lambda_+(\mathbf{k};\boldsymbol{\lambda})]^2}\right\}, \tag{105}$$

one can show that for low enough asymmetry, i.e., for

$$\delta_J \leqslant \frac{\Lambda_m}{8j_0 \max_{\lambda\geqslant\lambda_m}\{|d\lambda^\dagger/d\lambda|\}}, \tag{106}$$

the function $\mathcal{J}_d(\lambda)$ is also decreasing for $\lambda \geqslant \lambda_m$.

C. Phase diagram

We are now in a position to show that criticality in this asymmetric ionic model is mainly driven by the nonionic interactions in the usual universality class of spherical models. Thanks to the spherical condition (45) and to the monotonicity of $\mathcal{J}_d(\lambda)$, one realizes that, when $d_< < d < d_>$ with $d_< = \frac{1}{2}d_> = 2$, (i) for $\bar{h} \neq 0$ and $T > 0$, the model is free of singularity; (ii) for $\bar{h} = 0$, the system is singular for $T \leqslant T_c$ where the critical temperature is given by (46) while $h_c^\dagger = \bar{m}_c = 0$, so that (47) still applies. [Note that for $T < T_c$, λ sticks to 0 but (45) has to be modified.] At this point, it is worth analyzing the influence of asymmetry on the critical temperature. To do so, we compare an asymmetric system with its associated symmetric system defined above. We first notice that $T_c \leqslant T_c^{\mathrm{SYM}}$. More precisely, in the case where $\Delta J^\dagger(\mathbf{k};\delta_J) = \delta_J\Delta\tilde{J}^\dagger(\mathbf{k})$, we find that T_c is a decreasing function of δ_J, with the small-δ_J behavior

$$T_c = T_c^{\mathrm{SYM}}\big[1 - s\delta_J^2 + o(\delta_J^2)\big], \tag{107}$$

defined with some positive constant s. We note that the decreasing trend of T_c with asymmetry is in accord with recent simulations of hard-core continuum electrolyte models [40], but it contradicts with various approximate theories [41,42].

In the general case, the state of the system is given by the two spherical conditions (45) and (94), and by the link (95). As stated above, the implicit relation (94) may be solved implicitly, giving $\lambda^\dagger$ as a function of λ and the resulting equation (45) displays the same structure as in symmetric models provided one considers $\mathcal{J}_d(\lambda)=\mathcal{J}_d[\lambda,\lambda^\dagger(\lambda)]$. Moreover, as the latter function displays the typical small-λ expansion (59), the expansion (60) still applies so that the equation of state is similar to the symmetric one [see Eq. (62)], but with now in addition

$$h^\dagger = 2\bar{m}\lambda_c^\dagger\{1+O[(t+m^2)^\gamma]\}. \tag{108}$$

The equation of state (62) enforces the system to display the same critical exponents β, γ, etc. (see next section for the correlation length exponents) as in the symmetric ionic model, which coincide with the nonionic spherical model exponents. Hence, even in asymmetric systems, the long range of Coulomb interactions does not change the universality class which is driven mainly by the strong enough nonionic interactions. The origin of this property lies again in the eigenvalue Λ_N, in which the $1/k^2$ Coulomb divergence is exactly canceled thanks to electroneutrality and which therefore displays the usual singularities of nonionic systems. Note finally that the singularities for $T<T_c$ occur when $\bar{m}^2=-t$, and are localized on the parabola $(\bar{h}=0, h^{\dagger 2}=4\lambda_c^{\dagger 2}|t|, t)$ for $T\lesssim T_c$.

D. Infection of correlations

As regards the different correlation functions, on the one side, the species and density correlations display the same singularities as in symmetric systems, so that their characteristic lengths diverge with the same exponents; on the other side, charge correlations display drastically different behavior as they become infected by the density divergences. The origin of these properties lies in the decomposition of all the correlations on the two eigenmodes $1/\Lambda_N$ and $1/\Lambda_Z$, as explicit in Eq. (3), where the mixing amplitude B behaves here at small k as

$$B(\mathbf{k};\boldsymbol{\lambda}) = 1-\frac{16}{v_d^2}\frac{\lambda^{\dagger 2}}{q^4}k^4+O(k^6), \tag{109}$$

so that $1-B\neq 0$ *a priori*.

Concerning the density correlations, the term B/Λ_N behaves as $[1+O(k^4)]/[\lambda+j_0R_N^2k^2+O(k^4)]$ [see (96)], while the term $(1-B)/\Lambda_Z$ describes a short-range function [see (38)]. Hence, at the critical point, S_{NN} behaves as $1/k^2$ and the critical exponent η is zero. Away from the critical point, when $\lambda\neq 0$,

$$\frac{S_{NN}(\mathbf{k};T,\boldsymbol{\rho})}{S_{NN}(\mathbf{0};T,\boldsymbol{\rho})} = \frac{1}{1+k^2\xi_N^2(T,\boldsymbol{\rho})+O(k^4)}+O(k^4), \tag{110}$$

where $S_{NN}(\mathbf{0};T,\boldsymbol{\rho})=k_BT/4\rho a^d\lambda$ diverges near criticality with the usual $1/t^\gamma$ form at $\boldsymbol{\rho}_c$ while the density correlation length

$$\xi_N(T,\boldsymbol{\rho}) = R_N[\lambda(T,\boldsymbol{\rho})]\sqrt{j_0/\lambda(T,\boldsymbol{\rho})} \tag{111}$$

diverges as $1/t^\nu$ with $\nu=\gamma/2$, the usual spherical model exponent. Because the structure of the calculation is similar to Sec. III D, we also find $\xi_{N,1}=\xi_N$ and the property that the moments $\xi_{N,p}$, $\lim_{p\to\infty}\xi_{N,p}$, and the true decay length $\xi_{N,\infty}$ all approach ξ_N in the vicinity of the critical point (see Appendix B). (Note that we need to impose some extra conditions on the nonionic interactions in order to compute $\xi_{N,\infty}$ in this case.) The critical behavior of density correlations is therefore the same as in symmetric system.

Concerning charge correlations, we find that S_{ZZ} has an analytic small-k behavior similar to (79). Its first moment ξ_{Z1} coincides with the Debye length ξ_D *when* the system is *not* critical, indicating that the fluid satisfies the Stillinger-Lovett sum rule and is therefore in a conducting state. However, contrarily to in the symmetric systems, the singularities of $1/\Lambda_N(\mathbf{k};\boldsymbol{\lambda})$ appear to infect G_{ZZ} because the amplitude $1-B(\mathbf{k};\boldsymbol{\lambda})$ in Eq. (3) does not vanish in the general case for asymmetric systems [see (109)]. Hence, *at* the critical point, we find

$$\xi_{Z1}(T_c,\boldsymbol{\rho}_c) = \xi_{D,c}\big[1+w_c^2\lambda_c^{\dagger 2}\big]^{1/2},$$

with

$$w^2 = 2a^2/S_d\mathcal{I}_0 j_0^2R_N^2, \tag{112}$$

so that $\xi_{Z,1,c}\neq\xi_{D,c}$ when $\lambda_c^\dagger\neq 0$ which is indeed supposed in the general case. Hence, the Stillinger-Lovett sum rule is violated at criticality in this asymmetric model, showing that the system can no longer be conducting because asymmetry, which couples charge and density correlations, leads to singular charge fluctuations.

Singularities also appear in the second-moment length ξ_{Z2}. Indeed, when $\lambda\neq 0$, it satisfies

$$\xi_{Z2}^4(T,\boldsymbol{\rho}) = -\xi_D^2(T,\boldsymbol{\rho})\big[w^2\lambda^{\dagger 2}\xi_N^2-R_Z^2\big](T,\boldsymbol{\rho},\hat{\mathbf{k}}), \tag{113}$$

and, on approach of the critical point on the axis $\bar{h}=h^\dagger=0$, it diverges as

$$\xi_{Z2}(T,\boldsymbol{\rho}_c)\sim 1/t^{\nu/2} \quad \text{when} \quad t\to 0^+, \tag{114}$$

introducing a new length which diverges less rapidly than the $1/t^\nu$ density correlation length. We also note the change of sign of ξ_{Z2}^4 which tends to $-\infty$ near criticality, whereas in the low-density limit it remains positive (as is always the case in symmetric systems). However, using (11), a Taylor expansion of $(\widehat{\varphi}_{\tau\tau}^C-\widehat{\varphi}_{+-}^C)(\mathbf{k})$ near the origin, and the expansion

$$\widehat{J}_{\tau\upsilon}^0(\mathbf{k}) = \widehat{J}_{\tau\upsilon}^0(\mathbf{0})\big[1-k^2R_{\tau\upsilon}^2+k^4R_{\tau\upsilon,4}^4+O(k^6)\big], \tag{115}$$

with some given coefficients $R_{\tau\upsilon,4}$, one can perform an expansion of $\Lambda_N(\mathbf{k};\boldsymbol{\lambda})$ at the order k^4 included and a straightforward calculation shows that ξ_{Z2} is well defined *at* the critical point. Concerning the other correlation lengths, using a decomposition similar to (B2), we isolate the more divergent contribution to $\xi_{Z,p}$ with the result

$$\xi_{Z,p}^{2p}(T,\boldsymbol{\rho}) \approx -w^2\lambda^{\dagger 2}\xi_D^2\xi_N^{2(p-1)}(T,\boldsymbol{\rho}), \tag{116}$$

when $(T,\boldsymbol{\rho})\to(T_c,\boldsymbol{\rho}_c)$. If we redefine $\widehat{\xi}_{Z,p}^{2p}=-\xi_{Z,p}^{2p}$ in the expansion (79), we find

$$\lim_{p\to\infty}\widehat{\xi}_{Z,p}(T,\boldsymbol{\rho}) \approx \xi_N(T,\boldsymbol{\rho}), \tag{117}$$

when $(T,\boldsymbol{\rho})\to(T_c,\boldsymbol{\rho}_c)$. Finally, thanks to the decomposition (3) one realizes that the singularities of G_{NN} and G_{ZZ} in the complex k plane are the same, and are given by the vanishing of either $\Lambda_N(\mathbf{k};\boldsymbol{\lambda})$, $\Lambda_Z(\mathbf{k};\boldsymbol{\lambda})$, or of the square root

TABLE I. Charge correlation lengths near criticality [the symbol $\approx$ stands for the limit $(T,\boldsymbol{\rho})\to(T_c,\boldsymbol{\rho}_c)$]. The density correlation length ξ_N diverges as $1/t^\nu$, whereas R_Z, of order of the Debye length ξ_D, stays finite.

S_{ZZ}	Symmetric fluids	Asymmetric fluids
$\xi_{Z,1}$	ξ_D	ξ_D if $\lambda\neq 0$; $>\xi_{D,c}$ at $(T_c,\boldsymbol{\rho}_c)$
$\xi_{Z,2}^4$	$\xi_D^2 R_Z^2$	$-\xi_D^2[w^2\lambda^{\dagger 2}\xi_N^2-R_Z^2]$
$\xi_{Z,p}^{2p}$	$\xi_D^2 R_Z^{2(p-1)}[1+O(\mathcal{I}_0)]$	$\approx -w^2\lambda^{\dagger 2}\xi_D^2\xi_N^{2(p-1)}$
$\xi_{Z\infty}$	$R_Z[1+O(\mathcal{I}_0^2)]$	$\approx\xi_N$

D [see (28)]. As shown in Appendix B, thanks to some extra hypothesis on the nonionic interactions, we get

$$\xi_{Z,\infty}(T,\boldsymbol{\rho})\approx\xi_N(T,\boldsymbol{\rho})\quad\text{when}\quad(T,\boldsymbol{\rho})\to(T_c,\boldsymbol{\rho}_c).\tag{118}$$

This is a singular consequence of asymmetry: it enforces charge correlations to display similar singularities and the same divergent characteristic length as density correlations near criticality! The critical density fluctuations have therefore infected charge fluctuations and screening clouds fluctuate in part on the critical density length scale. (A glossary of the previous results is displayed in Table I.)

Note, however, that, *at* the critical point, charge correlations still display an exponential decay at large separations so that exponential screening is still at stake (even if the Stillinger-Lovett sum rule is not fulfilled). Indeed, at large separations in $d=3$, we find near but not at criticality

$$G_{ZZ}(\mathbf{r})\approx 2\frac{\delta_J^2 c_\delta T_0}{j_0^2 T_c}\frac{\xi_D^4}{R_N^2}\frac{e^{-r/\xi_N}}{\xi_N^4 r}-\frac{\xi_D^4}{R_Z^4}\frac{e^{-r/\xi_Z}}{r}\tag{119}$$

(where $c_\delta=\lambda_c^\dagger/\delta_J$ is *a priori* of order unity) while only the second term survives at criticality. The first term in Eq. (119), which spatially depends on the density correlation length, vanishes as $1/\xi_N^4\propto t^{4\nu}$ which is in fact the maximum amplitude allowed by the satisfaction of the Stillinger-Lovett sum rule for $T>T_c$.

At this point, it is worth having a comparison with the results of the theory developed by Stell [4]. Indeed, some *a priori* similar structure of charge correlations was found in asymmetric systems, typically as

$$S_{ZZ}^S\approx\Gamma^4 e^{-\Gamma r}/\mathcal{I}r,\tag{120}$$

where Γ is the inverse of a length diverging near criticality. However, one must first note that, contrarily to the result (119), the form (120) does not vanish when asymmetry goes to zero which is certainly an undesired feature. Moreover, (120) does predict $\xi_{Z,\infty}\neq\xi_{N,\infty}$ when $\eta\neq 0$ which is also a difference with our analysis. We first believe that in the analysis of [4], the large-r behavior (120) should not be derived by the small-k expansion of $S_{ZZ}(\mathbf{k})$ when the latter is analytic. On the contrary, in our study, we did perform a rigorous analysis looking for the pole of $S_{ZZ}(\mathbf{k})$ in the complex k plane which leads to the exact form of $S_{ZZ}(r)$. With this correction, the second remark could then be corrected by assuming that $X(k)$ as defined in Ref. [4] could be given by the scaling form $a_0(\kappa^2+k^2)^{t/2}x(k)$.

E. Charge-density correlations

In an asymmetric system, we can also study the charge-density correlations which, as seen in Eq. (3), are given by combinations of the two eigenmodes $1/\Lambda_N$ and $1/\Lambda_Z$ and are therefore infected by the singularities of density fluctuations. Their small-k expansion is always analytic, with the form

$$S_{NZ}(\mathbf{k};T,\boldsymbol{\rho})=S_{NZ}(\mathbf{0};T,\rho)+\sum_{p=1}^{\infty}(-1)^{p-1}\xi_{NZ,p}^{2p}(T,\boldsymbol{\rho},\hat{\mathbf{k}})k^{2p},\tag{121}$$

and they remain short range even at criticality. Their spatial integral $S_{NZ}(\mathbf{0};T,\boldsymbol{\rho})$ is always zero *except at* the critical point where it reduces to

$$S_{NZ}(\mathbf{0};T_c,\boldsymbol{\rho}_c)=\frac{\lambda_c^\dagger}{j_0}\frac{\xi_{D,c}^2}{R_{N,c}^2}\neq 0,\tag{122}$$

as $\lambda_c^\dagger$ is nonzero in the general case. The first moment of (121) is also singular: it is given when $\lambda\neq 0$ by

$$\xi_{NZ,1}(T,\boldsymbol{\rho})=\xi_D\lambda^\dagger\xi_N^2/j_0R_N^2,\tag{123}$$

which diverges as $1/t^{2\nu}$ near criticality. At the critical point, however, it has a well-defined expression

$$\xi_{NZ,1}^2(T_c,\boldsymbol{\rho}_c)=-\frac{4j_0'}{q^2v_d}-a^2\Sigma_4(\hat{\mathbf{k}})-\frac{R_{N,2}^4}{R_N^2}+\frac{j_0}{\lambda_c^\dagger}R^{\dagger 2},\tag{124}$$

where

$$j_0R^{\dagger 2}\equiv\tfrac{1}{4}(\widehat{J}_{++}(\mathbf{0})R_{++}^2-\widehat{J}_{--}(\mathbf{0})R_{--}^2),\tag{125}$$

while $R_{N,2}^4$ is the amplitude of the k^4 term in the expansion (96). Finally, noticing that $[\lambda^\dagger+\Delta J^\dagger]/\widehat{J}_{+-}\sqrt{1+4(\lambda^\dagger+\Delta J^\dagger)/\widehat{J}_{+-}^2}$ has an expansion in powers of k^2 with no singularity when $\lambda\to 0$, and using the same analysis as in Eq. (B1), we find that the higher moments diverge near criticality as

$$\xi_{NZ,p}^{2p}(T,\boldsymbol{\rho})\approx\big(\lambda^\dagger\xi_D^2/j_0R_N^2\big)\xi_N^{2p},\tag{126}$$

so that

$$\lim_{p\to\infty}\xi_{NZ,p}(T,\boldsymbol{\rho})\approx\xi_N(T,\boldsymbol{\rho})\quad\text{when}\quad(T,\boldsymbol{\rho})\to(T_c,\boldsymbol{\rho}_c).\tag{127}$$

Hence, the true decay length of density fluctuations characterizes also the charge-density fluctuations as a consequence of asymmetry which couples all the different correlations.

F. Simplest model for numerics

In order to get some quantitative predictions, we consider again the model described in Sec. III F where we introduce asymmetry by adding different next-nearest-neighbor interactions

$$J_{++}(\mathbf{R}) = -J_{--}(\mathbf{R}) = \tfrac{2}{3}\delta_J J \quad \text{if } \mathbf{R}=(\pm a, 0, 0) \text{ and permutations} \tag{128}$$

$$= 0 \quad \text{otherwise.} \tag{129}$$

The asymmetry function $\Delta J^{\dagger}$ is then merely

$$\Delta J^{\dagger}(\mathbf{k};\delta_J) = \frac{2}{3}\delta_J J\left[3 - \sum_{\alpha}\cos(\mathbf{k}_{\alpha}a)\right]. \tag{130}$$

For convenience, we suppose $\delta_J > 0$ which means that $\lambda^{\dagger}$ is nonpositive [see (94)]. The positiveness of j_0' and R_N^2 still requires, respectively, the conditions (40) and (100), which involve the definitions of (86). Moreover, we check numerically that the absolute minimum of $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$ occurs when $\mathbf{k}\to\mathbf{0}$, as long as

$$\delta_J < 1 - \pi\mathcal{I}_0/12, \tag{131}$$

which is in fact a necessary condition to avoid the competition with the corner of the Brillouin zone, $\mathbf{k}=(\pi/a,\pi/a,\pi/a)$, as can be proved analytically.

When these conditions are met, the critical temperature is given by (46) where $\mathcal{J}_d(0)\propto\int_{\mathbf{k}}[1/\Lambda_N + 1/\Lambda_Z]_c$. We find numerically that T_c is a decreasing function of asymmetry, while its dependence on ionicity is subtle: For δ_J small enough, T_c is a decreasing function of $\mathcal{I}_0$, while for δ_J large enough, T_c is first increasing at small ionicities and then decreasing for larger ionicities. To understand this behavior, we note that because Λ_N behaves as $j_0R_N^2k^2$ at criticality, where R_N^2 is given by (97), the critical temperature can be expected to behave as $1 + O(\delta_J^2/\mathcal{I}_0) + O(\mathcal{I}_0)$, while additional $O(\delta_J^2)$ terms might be present because of higher-order contributions. Hence, we fitted the results for the critical temperatures as

$$T_c(\mathcal{I}_0,\delta_J) = T_c(0,0)\left[1 - \left(\varsigma_0 + \frac{\varsigma_1}{\mathcal{I}_0}\right)\delta_J^2 + \varsigma_2\mathcal{I}_0 + O\left(\delta_J^4, \mathcal{I}_0^{3/2}\right)\right]. \tag{132}$$

We find good comparisons with numerical calculations with the choices $\varsigma_0=0.095$, $\varsigma_1=0.047$, and $\varsigma_2=-0.082$, while $T_c(0,0)$ is $1.44\times(4J/k_B)$. The nonmonotonic dependence of T_c on ionicity is therefore a consequence of the competition between the two terms $\delta_J^2/\mathcal{I}_0$ and $\mathcal{I}_0$.

Concerning the different correlation lengths, we find estimates of R_Z and ξ_N similar to their values in symmetric systems with corrections of order $[1+O(\delta_J)]$ [see (92) and (91)]. Moreover, the length R_N can be bounded as

$$0 \leqslant \frac{1}{16}a^2\left[1 - \frac{1}{18}\pi\mathcal{I}_0 - \frac{4}{\pi}\frac{\delta_J^2}{\mathcal{I}_0}\right] \leqslant R_N^2 \leqslant \frac{1}{8}a^2\left[1 - \frac{1}{18}\pi\mathcal{I}_0\right]. \tag{133}$$

Finally, concerning the length ξ_{Z2}, we define t_X the crossover temperature at which ξ_{Z2}^4 [see (113)] changes its sign, which is given by

$$t_X = \frac{2}{\pi K_c(\text{bcc})}\frac{|\lambda_c^{\dagger}|}{j_0}. \tag{134}$$

At leading order in asymmetry, one can neglect the δ_J dependance of the integrands in the right-hand side of (94), leading to the estimate

$$\frac{\lambda_c^{\dagger}}{4J} \simeq -0.579\,\delta_J, \tag{135}$$

so that the crossover temperature is approximately

$$t_X \simeq 0.265\,\delta_J. \tag{136}$$

V. SEMICLASSICAL IONIC SPHERICAL MODELS

In the present section, we consider a model of charged fluids where quantum effects are dealt with semiclassically by taking into account algebraic $1/r^{d+\sigma}$ interactions, with $\sigma>0$, which encompass induced, permanent dipole-dipole or van der Waals forces. Hence, the typical small-k behavior of the nonionic interactions now contains nonanalytical terms that we note

$$\widehat{J}^0_{\tau\upsilon}(\mathbf{k}) = \widehat{J}^0_{\tau\upsilon}(\mathbf{0})\left[1 - k^{\sigma}\left(R^0_{\mathcal{L},\tau\upsilon}\right)^{\sigma} - k^2R^2_{\tau\upsilon} + \mathcal{O}_{\sigma,4}\right], \tag{137}$$

for either $\sigma<2$ or $\sigma>2$, but $\sigma/2$ not an integer and with the new length scale $R^0_{\mathcal{L},\tau\upsilon}$. The subscript $\mathcal{L}$ will be used to label quantities deriving from the long-range nonionic interactions and for brevity here and below, we let $\mathcal{O}_{x,n}$ denote a function which is the combination of nonanalytic terms *negligible* compared to k^x, and analytic terms *of order* k^n. These nonionic interactions are supposed to be attractive enough for the conditions (15) and (16) to be met, so that they suffice to drive criticality in absence of Coulomb forces. We define the characteristic ranges $R^0_{\mathcal{L},N}$, $R^0_{\mathcal{L},Z}$, R^0_N, and R^0_Z with the small-k expansions

$$\Delta\bar{J}^0(\mathbf{k}) + (-)^{\vartheta_X}\Delta J^0_{+-}(\mathbf{k}) = j_0k^{\sigma}\left(R^0_{\mathcal{L},X}\right)^{\sigma} + j_0k^2\left(R^0_X\right)^2 + \mathcal{O}_{\sigma,4}, \tag{138}$$

where $\vartheta_N=0=1-\vartheta_Z$. We note that the coefficients of these expansions are not necessarily positive but, thanks to (16), $(R^0_{\mathcal{L},N})^{\sigma}>0$ when $\sigma<2$, while $(R^0_N)^2>0$ when $\sigma>2$. Finally, the leading nonanalytic term of $\Delta J^{\dagger}$ is measured by $R^{\dagger}_{\mathcal{L}}$ defined via

$$\Delta J^{\dagger}(\mathbf{k}) = j_0k^{\sigma}R^{\dagger\,\sigma}_{\mathcal{L}} + \mathcal{O}_{\sigma,2}, \quad \text{when } \mathbf{k}\to\mathbf{0}. \tag{139}$$

A. Criticality

In the absence of charge ($q=\mathcal{I}_0=0$) and asymmetry ($\delta_J=0$), the nonionic interactions generate the usual criticality of spherical models with power-law forces [36]. Indeed, in this symmetric case where $\lambda^{\dagger}=0$ (in order to enforce electroneutrality), criticality occurs when $\lambda=0$ and the small-λ expansion of $\mathcal{J}_d$ displays the usual structure [see (59)]

$$\mathcal{J}_d(\lambda) = \mathcal{J}_d(0)[1 - p\lambda^{1/\gamma} + O(\lambda)], \tag{140}$$

with now

$$\gamma = \max\{\sigma_m/(d-\sigma_m); 1\} \quad \text{where} \quad \sigma_m = \min\{\sigma, 2\}, \tag{141}$$

and with some positive constant p. Again, we consider only nonclassical regimes where $d_< < d < d_>$ with $d_< = d_>/2 = \sigma_m$.

When charges and possibly asymmetry are present, the same criticality prevails provided $\mathcal{I}_0$ and δ_J are not too large. Indeed, the eigenvalues Λ_N and Λ_Z behave when $\mathbf{k} \to \mathbf{0}$ as

$$\Lambda_N(\mathbf{k};\boldsymbol{\lambda}) = \lambda + j_0 k^\sigma \left(R_N^{\mathcal{L}}\right)^\sigma + j_0 k^2 R_N^2(\boldsymbol{\lambda}) + \mathcal{O}_{\sigma,4}, \tag{142}$$

$$\Lambda_Z(\mathbf{k};\boldsymbol{\lambda}) = \frac{S_d q^2}{4a^d}\,\frac{1}{k^2}\big[1 + k^2 R_Z^2(\boldsymbol{\lambda};\hat{\mathbf{k}}) + k^{2+\sigma}\left(R_Z^{\mathcal{L}}\right)^{2+\sigma} + \mathcal{O}_{2+\sigma,4}\big], \tag{143}$$

where the ranges R_N and R_Z are still defined with (97) and (39), respectively, while $R_N^{\mathcal{L}} = R_{\mathcal{L},N}^0$, and

$$\left(R_Z^{\mathcal{L}}\right)^{2+\sigma} = 2a^2\left(R_{\mathcal{L},Z}^0\right)^\sigma/\mathcal{I}_0 S_d. \tag{144}$$

Once again, the structure of Λ_N leads to the exact cancellation of the $1/k^2$ Coulomb divergence in Eq. (142), so that the same criticality as when $\mathcal{I}_0 = \delta_J = 0$ is at stake provided some conditions which ensure that $\mathbf{k} \to \mathbf{0}$ is the absolute minimum of $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})$. When $\sigma > 2$, these conditions are the same as in Sec. IV B. However, when $\sigma < 2$, the condition (100) can be released because the leading behavior of Λ_N, which is now of order k^σ, has a positive coefficient thanks to (16).

When these conditions are fulfilled, criticality occurs in symmetric or asymmetric systems similarly to the previous Coulomb+short-range spherical model (with, however, a different universality class), when $k_B T_c = 1/\mathcal{J}_d(0)$ and $\bar{h} = 0$ so that the critical density is merely $\rho_c a^d = 1$. Near criticality, the equation of state displays the usual structure

$$\bar{h} = \mathcal{A}\bar{m}(t+\bar{m}^2)^\gamma \,\{1 + O[(t+\bar{m}^2)^{\gamma-1}]\} = 2\bar{m}\lambda, \tag{145}$$

where γ is defined in Eq. (140) and $\mathcal{A}$ in Eq. (61). Moreover, we also check that the next corrections to scaling in the brackets of the right-hand side of (145) are merely of order $O[(t+\bar{m}^2)^{\theta_\sigma}]$ where $\theta_\sigma = |2-\sigma|\gamma/\sigma_m$. The phase separation singularities occur when $t + \bar{m}^2 = 0$, and the critical exponent β is still $\frac{1}{2}$. As regards density correlations, except *at* the critical point, we find the small-k expansion

$$\frac{S_{NN}(\mathbf{k};T,\boldsymbol{\rho})}{S_{NN}(\mathbf{0};T,\boldsymbol{\rho})} = \frac{1}{1 + k^\sigma \xi_{N,\sigma}^\sigma + k^2 \xi_{N,1}^2 + \mathcal{O}_{\sigma,4}} + \mathcal{O}_{\sigma+4,4}. \tag{146}$$

The spatial integral $S_{NN}(\mathbf{0};T,\rho)$, proportional to the isothermal compressibility, is $k_B T/4\rho a^d \lambda(T,\boldsymbol{\rho})$, and, thanks to (145), diverges as $1/t^\gamma$ near criticality when $\boldsymbol{\rho} = \boldsymbol{\rho}_c$. The two characteristic lengths in Eq. (146) are

$$\xi_{N,\sigma}(T,\boldsymbol{\rho}) = R_N^{\mathcal{L}}[\boldsymbol{\lambda}(T,\boldsymbol{\rho})][j_0/\lambda(T,\boldsymbol{\rho})]^{1/\sigma}, \tag{147a}$$

$$\xi_{N,1}(T,\boldsymbol{\rho}) = R_N^0[\boldsymbol{\lambda}(T,\boldsymbol{\rho})]\,[j_0/\lambda(T,\boldsymbol{\rho})]^{1/2}. \tag{147b}$$

When $\boldsymbol{\rho} = \boldsymbol{\rho}_c$, $\xi_{N,\sigma}$ diverges as $1/t^{\gamma/\sigma}$ while $\xi_{N,1}$, as $1/t^{\gamma/2}$, with $\xi_{N,\sigma}^\sigma/(R_N^{\mathcal{L}})^\sigma = \xi_{N,1}^2/R_N^2$. We identify ξ_N the density correlation length, as the most divergent characteristic length, i.e., $\xi_N = \xi_{N,\sigma}$ when $\sigma < 2$ and $\xi_N = \xi_{N,1}$ when $\sigma > 2$, which diverges near criticality as $1/t^\nu$ with the critical exponent $\nu = \gamma/\sigma_m$. With this definition, one may write the density correlations in the scaling form $S_{NN}(\mathbf{k}) = (1/t^\gamma)D^{<(>)}(\xi_N k; t^{\theta_\sigma}, \ldots)$, where $<$ ($>$) refers to $\sigma < 2$ ($\sigma > 2$), and where the exponent θ_σ describes corrections to scaling defined above. In real space, it is well known [43] that the first nonanalyticity in k of the small-k expansion of $S_{NN}(\mathbf{k})$ rules the large-r behavior of $G_{NN}(\mathbf{r})$. Hence, when $\mathbf{r}$ goes to infinity, we find the scaling expressions

$$G_{NN}(\mathbf{r};T,\rho) \approx \frac{D_N^<}{r^{d-2+\eta}}\left(\frac{\xi_N}{r}\right)^{2\sigma} \quad \text{when } \sigma < 2, \tag{148}$$

while

$$G_{NN}(\mathbf{r};T,\rho) \approx \frac{D_N^>}{r^{d-2+\eta}}\left(\frac{\xi_N}{r}\right)^2\left(\frac{\xi_{N,\sigma}}{r}\right)^\sigma \quad \text{when } \sigma > 2, \tag{149}$$

with the critical exponent $\eta = 2 - \sigma_m$ which satisfies the usual scaling relation $\gamma = (2-\eta)\nu$. The amplitudes in Eqs. (148) and (149) are $D_N^< = \Gamma^*(\sigma)S_d T/2a^d T_0 (R_N^{\mathcal{L}})^\sigma = D_N^> R_N^2/(R_N^{\mathcal{L}})^\sigma$ where we define

$$\Gamma^*(x) = -2^{d-1}\Gamma(d/2)\Gamma[(d+x)/2]/\pi^d\Gamma(-x/2). \tag{150}$$

We notice that Eq. (149) involves both ξ_N and $\xi_{N,\sigma}$ because, in the case $\sigma > 2$, the t^{θ_σ} corrections to scaling in $S_{NN}(\mathbf{k})$ are linked to the asymptotic behavior of $G_{NN}(\mathbf{r})$. Finally, we check that at criticality $G_{NN}(\mathbf{r})_c \sim 1/r^{d-2+\eta}$ as must be.

B. Charge correlations

As regards charge correlations, the question we address is what kind of interplay occurs with (i) Coulomb $1/r^{d-2}$ interactions, (ii) nonionic $1/r^{d+\sigma}$ quantum effects, and, possibly (iii) near critical $1/r^{d-2+\eta}$ density fluctuations. This information is in fact included in the small-k expansion of S_{ZZ}. We first find that when $(T,\boldsymbol{\rho}) \neq (T_c,\boldsymbol{\rho}_c)$, $S_{ZZ}(\mathbf{k})$ can be expanded according to

$$S_{ZZ}(\mathbf{k};T,\boldsymbol{\rho}) = k^2\xi_D^2\left(1 - k^2\tilde{\xi}_{Z,2}^2 - k^{2+\sigma}\xi_{Z,2+\sigma}^{2+\sigma} + \mathcal{O}_{2+\sigma,4}\right). \tag{151}$$

The first correction in Eq. (151) is defined by

$$\tilde{\xi}_{Z,2}^2(\hat{\mathbf{k}};T,\boldsymbol{\rho}) = \left[R_Z^2 - \xi_{N,\sigma}^\sigma w^2 \lambda^{\dagger 2}\right](\hat{\mathbf{k}};T,\boldsymbol{\rho}), \tag{152}$$

with

$$w^2(T,\boldsymbol{\rho}) = 2a^2/S_d\mathcal{I}_0 j_0{}^2\left(R_N^{\mathcal{L}}\right)^\sigma(T,\boldsymbol{\rho}), \tag{153}$$

while the nonanalytic correction of order $k^{4+\sigma}$ involves

$$\xi_{Z,2+\sigma}^{2+\sigma}(T,\boldsymbol{\rho}) = \left(R_Z^{\mathcal{L}}\right)^{2+\sigma} - 2w^2 j_0 \lambda^\dagger R_{\mathcal{L}}^{\dagger\,\sigma}\xi_{N,\sigma}^\sigma + w^2\lambda^{\dagger 2}\xi_{N,\sigma}^{2\sigma}. \tag{154}$$

The structure of (151) is in fact drastically different from what is found in Coulomb+short-range binary spherical model. Indeed, in the entire phase space, the term $k^{4+\sigma}$ is nonanalytic (recall that $\sigma/2$ is not an integer) so that G_{ZZ} is *always algebraic at large distances*. More precisely, we find that the large-r behavior of charge correlations is

$$G_{ZZ}(\mathbf{r};T,\rho) \approx \frac{1}{r^{d+4+\sigma}} k_B T \xi_{Z,4+\sigma}^{2+\sigma}\Gamma^*(4+\sigma), \tag{155}$$

except *at* criticality. [We note that the sign of (155) is not determined and depends on the interactions.] Hence, independently of any criticality, we find that long-range quantum effects added to Coulomb forces destroy the usual picture of the exponential Debye screening, *even* in the low-density limit and lead to algebraic screening. By way of comparison, we recall that for classical fluids with only $1/r^{d+\sigma}$ interactions where $-d < \sigma < 0$, only the Coulomb fluids with $\sigma = -2$ exhibit perfect exponential screening (as a consequence of Poisson's equation), whereas other potentials lead to algebraic decays of $G_{ZZ}(r)$ [44]. Moreover, we note that the algebraic decay (155) is not in contradiction with Brydges and Federbush's article [26] where exponential screening in Coulomb fluids is rigorously proven in the low-density limit: Indeed, only Coulomb in addition to *short*-range interactions were taken into account in Ref. [26], whereas the quantum effects enforce here long-range $1/r^{d+\sigma}$ nonionic interactions. In addition, it is satisfactory to note that, when one considers $d = 3$ systems with $\sigma = 3$ (i.e., with typically van der Waals $1/r^6$ interactions) our analysis reproduces the exact $1/r^{10}$ decay proven in point-charge fluids with fully quantum dynamics [45,46]. Finally, we signal that such an algebraic decay was also found in a recent study of Coulomb fluids with dispersion interactions, based on an Ornstein-Zernicke analysis [28].

Nevertheless, charge correlations in the present model do still exhibit a kind of screening, but which is only *algebraic*: namely, the $1/r^{d-2}$ Coulomb potential is multiplied by an algebraic factor $1/r^{\sigma+6}$ in the resulting charge correlations (155). Moreover, whether symmetric or asymmetric but not critical, the system satisfies the Stillinger-Lovett sum rule, as clear in Eq. (151), even though the screening is only algebraic. In fact, this algebraic screening arises from two different mechanisms: In a symmetric system, according to the decomposition (65b), S_{ZZ} is governed by $1/\Lambda_Z$, which behaves typically as $(1/k^2)[1 + O(k^2) + O(k^{2+\sigma})]$, after the factorization of the long-range $1/k^2$ Coulomb potential [cf. (143)], giving a first nonanalytic term of order $k^{4+\sigma}$. Moreover, in an asymmetric system, because of the expansion

$$B^N_{ZZ} = k^4\big(4a^4/S_d^2\mathcal{I}_0^2\, j_0'^2\big)\big(\lambda^{\dagger 2} + 2\lambda^\dagger j_0' R_{\mathcal{L}}^{\dagger\,\sigma}\, k^\sigma + \mathcal{O}_{\sigma,2}\big), \tag{156}$$

the contribution of B^N_{ZZ}/Λ_N [see (3)] also leads to a $k^{4+\sigma}$ term in G_{ZZ}. These two mechanisms reveal how long-range integrable forces can destroy exponential screening thanks (i) to the decomposition of every correlation on only two eigenmodes, and (ii) to the structure of these eigenmodes which involve the two kinds of interactions (algebraic and Coulombic). This property appears in fact to be a consequence of the external screening as explained in the diagrammatic analysis of Appendix C.

Back to criticality, one may now ask the following: "How is this algebraic screening modified when long-range critical density fluctuations occur?" The answer depends in fact crucially on symmetry. Indeed, in a symmetric system, the amplitudes $\breve{\xi}^2_{Z,2}$ in Eq. (152) and $\xi^{2+\sigma}_{Z,2+\sigma}$ in Eq. (154) are always finite because the contributions involving the diverging length $\xi_{N,\sigma}$ exactly vanish with $\lambda^\dagger \propto \delta_J$; charge correlations then display a regular behavior near criticality. Similarly, *at* criticality, (151) is valid and well defined so that the system still satisfies the Stillinger-Lovett sum rule (2). Hence, as enforced by the decomposition (3), charge and density correlations are disentangled and characterized by two different eigenmodes, as in models with Coulomb+short-range interactions.

TABLE II. Large-distance behavior of charge correlations in semiclassical ionic spherical symmetric or asymmetric models. The density correlation length ξ_N diverges as $1/t^\nu$. By way of comparison, the density correlations $G_{NN}(\mathbf{r})$ behave as $1/r^{d+\sigma}$ away from criticality, and as $1/r^{d-2+\eta}$ *at* criticality.

$G_{ZZ}(\mathbf{r})$	Symmetric	Asymmetric
(T_c, ρ_c),	$\sim 1/r^{d+4+\sigma}$	$\sim 1/r^{d+\sigma+2\eta}$
$(T, \boldsymbol{\rho}) \neq (T_c, \rho_c)$	$\sim 1/r^{d+4+\sigma}$	$\sim (\xi_N/r)^{4-2\eta}/r^{d+\sigma+2\eta}$

On the other hand, for *asymmetric* systems, the amplitudes $\breve{\xi}^2_{Z,2}$ and $\xi^{2+\sigma}_{Z,2+\sigma}$ diverge respectively as $1/t^\gamma$ and $1/t^{2\gamma}$, so that the large-r behavior (155) of G_{ZZ} becomes divergent near criticality, and can be written in the scaling form

$$G_{ZZ}(\mathbf{r}; T, \rho) \approx \frac{D^<_Z}{r^{d+4-\sigma}}\left(\frac{\xi_N}{r}\right)^{2\sigma} \quad \text{when } \sigma < 2 \tag{157}$$

$$\approx \frac{D^>_Z}{r^{d+\sigma}}\left(\frac{\xi_N}{r}\right)^{4} \quad \text{when } \sigma > 2, \tag{158}$$

where $D^<_Z = k_B T\, w^2 \lambda^{\dagger 2}\Gamma^*(4+\sigma) = D^>_Z R^4_N/(R^{\mathcal{L}}_N)^{2\sigma}$. Naturally, as enforced by (3), the density singularities infect the charge correlations. Moreover, *at* criticality, the consequences of the charge-density mixing depends on the long-range behavior of density fluctuations, i.e., on η. Indeed, we find

$$S_{ZZ}(\mathbf{k})_c = k^2\xi^2_{D,c}\big[1 + k^{2-\sigma}\xi^{2-\sigma}_{Z,2-\sigma} + \mathcal{O}_{2-\sigma,2}\big], \tag{159}$$

for $\eta = 2 - \sigma > 0$, while

$$S_{ZZ}(\mathbf{k})_c = k^2\xi^2_{D,c}\big[\mathcal{E}_c - k^{\sigma-2}\xi^{\sigma-2}_{Z,\sigma,c} + \mathcal{O}_{\sigma-2,2}\big] \tag{160}$$

for $\eta = 0 < \sigma - 2$, with $\xi^{2-\sigma}_{Z,2-\sigma} = (w^2\lambda^{\dagger 2})_c = \xi^{\sigma-2}_{Z,\sigma}[R^4_N/(R^{\mathcal{L}}_N)^{2\sigma}]$ and $\mathcal{E}_c = 1 + [w^2\lambda^{\dagger 2}(R^{\mathcal{L}}_N)^\sigma/R^2_N]_c$. At large separations, the scaling behavior (157) reduces to

$$G_{ZZ}(\mathbf{r})_c \approx \frac{1}{r^{d+4-\sigma}}\,(-)k_B T_c\, \xi^{2-\sigma}_{Z,2-\sigma,c}\,\Gamma^*(4-\sigma) \tag{161}$$

for $\eta = 2 - \sigma > 0$, while

$$G_{ZZ}(\mathbf{r})_c \approx \frac{1}{r^{d+\sigma}}\, k_B T_c\, \xi^{\sigma-2}_{Z,\sigma,c}\,\Gamma^*(\sigma) \tag{162}$$

for $\eta = 0 < \sigma - 2$. The critical density fluctuations therefore infect charge fluctuations and weaken the algebraic screening of the system by a factor $r^{4-2\eta}$ compared to the noncritical state (157) (see also Table II). This effect is stronger when $\sigma > 2$ since $\eta = 0$ characterizes a longer range of the $1/r^{d-2+\eta}$ critical density fluctuations compared to the case $\eta > 0$ when $\sigma < 2$. Similarly, the validity of the Stillinger-Lovett sum rule (2) *at* the critical point also depends on η: When $\eta > 0$, and according to (159), the system still satisfies the Stillinger-Lovett sum rule at criticality, and may well be regarded as conductor even though with a weak algebraic screening. On the contrary, when $\eta = 0$, the Stillinger-Lovett sum rule is violated *at* criticality as $\mathcal{E}_c \neq 1$ in Eq. (160) and the system is nonconducting. This result is similar to the Coulomb+short-range ionic spherical model (see previous sections), where the value $\eta = 0$ is always at stake. Moreover, we note that this interplay between critical density fluctuations and screening, enforced by asymmetry and *ruled* by the value of η, can in fact be also derived from the analysis of [4].

Finally, similar conclusions can be drawn about charge-density fluctuations in asymmetric fluids. Except at criticality, their behavior at small k is

$$S_{NZ}(\mathbf{k};T,\boldsymbol{\rho}) = k^2\xi^2_{NZ,1} - k^{2+\sigma}\xi^{2+\sigma}_{NZ,2+\sigma} + \mathcal{O}_{\sigma+2;4}, \qquad (163)$$

where $\xi^2_{NZ,1}(T,\boldsymbol{\rho}) = \xi^2_D\lambda^\dagger\xi^\sigma_{N,\sigma}/j_0(R^{\mathcal{L}}_N)^\sigma$ and $\xi^{2+\sigma}_{NZ,2+\sigma}(T,\boldsymbol{\rho}) = \xi^2_D\,[\xi^\sigma_{N,\sigma}/(R^{\mathcal{L}}_N)^\sigma][\lambda^\dagger\xi^\sigma_{N,\sigma}/j_0 - R^{\dagger\,\sigma}_{\mathcal{L}}]$, so that

$$G_{NZ}(\mathbf{r};T,\boldsymbol{\rho}) \approx \frac{D_{NZ}}{r^{d+2+\sigma}}$$

with

$$D_{NZ} = S_d\rho q\Gamma^*(2+\sigma)\xi^{2+\sigma}_{NZ,2+\sigma}(T,\boldsymbol{\rho}). \qquad (164)$$

Near criticality, these correlations are singular as $\xi^2_{NZ,1}$ and $\xi^{2+\sigma}_{NZ,2+\sigma}$ diverge, respectively, as $1/t^{\gamma/\sigma}$ and $1/t^{2\gamma/\sigma}$, and, in the r space, their algebraic behavior is

$$G_{NZ}(\mathbf{r};T,\rho) \approx \frac{D^{<(>)}_{NZ}}{r^{d+|2-\sigma|}}\left(\frac{\xi_N}{r}\right)^{4-2\eta} \quad \text{when} \quad \sigma < (>)\, 2, \qquad (165)$$

where $D^<_{NZ} = S_d\rho q\xi^2_D\lambda^\dagger\Gamma^*(\sigma+2)/j_0(R^{\mathcal{L}}_N)^\sigma = D^>_{NZ}R^4_N/(R^{\mathcal{L}}_N)^{2\sigma}$. Hence, these correlations are also infected by the density correlations as a consequence of the general decomposition (3). However, compared to the $1/r^{d-2}$ Coulomb interactions, some algebraic screening is still at stake as G_{NZ} is multiplied by a decay $1/r^{4+\sigma}$. *At* the critical point, differences arise depending on η: When $\eta > 0$, $S_{NZ}(\mathbf{0})_c = 0$, whereas, when $\eta = 0$, $S_{NZ}(\mathbf{0})_c = (\xi^2_D\lambda^\dagger/j_0R^2_N)_c \neq 0$ as in the short-range case. Moreover, at criticality and for large r, we find $G_{NZ}(\mathbf{r})_c \approx D^{<(>)}_{NZ,c}/r^{d+|2-\sigma|}$, where $D^<_{NZ,c} = D^>_{NZ,c}(R^{\mathcal{L}}_N)^{2\sigma}/R^4_N = -S_d\rho_c q\xi^2_D\lambda^\dagger\Gamma^*(|2-\sigma|)/j_0(R^{\mathcal{L}}_N)^\sigma$ when $\sigma < (>) 2$. Hence, compared to the scaling form (165), the screening of the cross charge-density correlations is weakened by a factor $r^{4-2\eta}$, i.e., all the more effectively as $\eta = 0$ (compared to $\eta > 0$), as a consequence of the coupling with the critical density fluctuations.

VI. CONCLUSION

Our aim has been to shed some light on ionic criticality. Indeed, many debates and speculations left the universality class of Coulomb fluids unsettled theoretically: For instance, it has been both proposed via approximate approaches that the long-range Coulomb interactions could or could not lead to a mean-field behavior [3,4]. In order to exhibit some basic mechanisms at stake in critical ionic fluids, we devised an exactly solvable spherical model which accounts for both charge and density fluctuations.

We first find that the universality class of the model is left unchanged when nonionic forces are implemented with Coulomb interactions provided the latter are not too strong. This result is not contradicting recent Monte Carlo simulations which establish an Ising behavior in the restricted primitive model. Its origin lies in our model in the fact that the system is characterized by two eigenmodes Λ_N and Λ_Z of the matrix describing the interactions in a binary fluid: in the mode Λ_N, the long-range $1/k^2$ Coulomb singularity is exactly canceled thanks to electroneutrality so that its vanishing, which rules criticality, drives the usual spherical model universality class.

We also find that charge and density correlations are decoupled in fully symmetric systems, and characterized, *respectively*, by the eigenmodes Λ_Z and Λ_N. As a consequence, they exhibit different behavior: while G_{NN} displays usual critical divergence, G_{ZZ} varies smoothly and stays short range over a screening length $\xi_{Z,\infty}$ which remains finite near criticality. However, in the realistic case where some asymmetry is present (e.g., in hard core diameters or in short-range features), we find that both charge and density correlations are coupled via similar decompositions on *both* $1/\Lambda_N$ and $1/\Lambda_Z$ [see (3)]. Accordingly, the charge correlation length $\xi_{Z,\infty}$ *diverges* near criticality exactly as the density correlation length $\xi_{N,\infty}$. Similarly, the validity of the Stillinger-Lovett sum rule, which discriminates between conducting and nonconducting fluids, depends on symmetry: satisfied in symmetric systems, this sum rule is violated in asymmetric fluids if and only if $\eta = 0$, which describes longer-range $1/r^{d-2+\eta}$ density fluctuations compared to the case $\eta > 0$. This conclusion is consistent with what can be deduced in part from the formulation of [4]. Hence, even if sensible only in short-range characteristics, the asymmetry of a fluid can have dramatic consequences on the overall screening effect, as a consequence of its coupling with the Coulomb interactions.

As a by-product, we also investigate the influence on the previous model of $1/r^{d+\sigma}$ interactions (with $\sigma > 0$), mimicking quantum effects in a semiclassical way. We find that, contrarily to the usual picture of the exponential Debye screening, charge correlations decay only algebraically as $1/r^{d+\sigma+4}$. Compared to the $1/r^{d-2}$ Coulomb interactions, one concludes that some screening is still at stake, but only algebraic. This result is consistent with some exact results in quantum plasmas [45,46] and with Ornstein-Zernicke approaches [28].

APPENDIX A: STILLINGER-LOVETT SECOND MOMENT SUM RULE

The Stillinger-Lovett second moment sum rule distinguishes between conducting and nonconducting media. It describes in fact the screening of an external charge by a conducting system and can be derived by the linear response theory (one can refer to [38] for a general review of sum rules in charged fluids and their demonstrations based on the Born-Green-Yvon (BGY) hierarchy). We present in this Appendix its generalization to the geometry of the model. Hence, we consider an external charge spread on one sublattice, e.g., the lattice +, with a charge density $\delta\rho^{\text{ext}}$ such as

$$\delta\rho^{\text{ext}}(\mathbf{R}_+) = \int_{\mathbf{k}} e^{i\mathbf{k}\cdot\,\mathbf{R}_+}\delta\rho^{\text{ext}}(\mathbf{k}), \qquad (\text{A1})$$

where the Fourier transform is associated with the reference sublattice. We define $\delta\phi^{\text{ext}}_\tau(\mathbf{R}_\tau)$ the electrostatic potential created on the sublattice τ by the external charge. It is given by the Poisson equation as

$$\delta\phi_\tau^{\rm ext}(\mathbf{k}) = \delta\rho^{\rm ext}(\mathbf{k})\widehat{\varphi}_{+\tau}^{C}(\mathbf{k}), \tag{A2}$$

where the Coulomb potential is given by (9) and (10). In the linear response theory, this external potential induces a change in density given by

$$\delta\rho_\tau(\mathbf{k}) = -\beta\sum_\upsilon q_\upsilon \delta\phi_\upsilon^{\rm ext}(\mathbf{k})G_{\tau\upsilon}(\mathbf{k};\boldsymbol{\lambda}), \tag{A3}$$

so that the induced charge density is merely

$$\delta\rho_Z(\mathbf{k}) = -\beta\sum_{\tau,\upsilon} q_\tau q_\upsilon \delta\phi_\upsilon^{\rm ext}(\mathbf{k})\, G_{\tau\upsilon}(\mathbf{k};\boldsymbol{\lambda}). \tag{A4}$$

Then, one characterizes a conducting system such as it shields every external charge, which can be written as

$$\lim_{\mathbf{k}\to\mathbf{0}}\{\delta\rho_Z(\mathbf{k}) + \delta\rho^{\rm ext}(\mathbf{k})\} = 0. \tag{A5}$$

The combination of (A2), (A4), and (A5) leads to the sum rule

$$\lim_{\mathbf{k}\to\mathbf{0}}\beta\sum_{\tau,\upsilon} q_\tau q_\upsilon G_{\tau\upsilon}(\mathbf{k};\boldsymbol{\lambda})\frac{v_d}{k^2} = 1, \tag{A6}$$

where v_d/k^2 is the singularity of the Coulomb potential at the origin, which is equivalent to the equality $\xi_{Z,1}=\xi_D$ in Eq. (2).

APPENDIX B: DIFFERENT CORRELATION LENGTHS

In this Appendix we exhibit some values of the characteristic lengths involved in the Coulomb+*short*-range interaction models.

1. Density moments $\xi_{N,p}$

First, we write the small-k expansion of Λ_N as

$$\Lambda_N(\mathbf{k};\boldsymbol{\lambda}) = \lambda\left[1+\sum_{p=1}^{\infty}\frac{j_0}{\lambda}R_{N,p}^{2p}k^{2p}\right], \tag{B1}$$

where the coefficients $R_{N,p}$ remain bounded when λ goes to zero, leading to

$$\frac{1}{\Lambda_N(\mathbf{k})} = \frac{1}{\lambda}\left\{1+\sum_{p=1}^{\infty}\left(-\frac{j_0}{\lambda}R_N^2\right)^p k^{2p}\left[\sum_{q=0}^{\infty}\left(\frac{R_{N,q+1}}{R_N}\right)^{2q}k^{2q}\right]^p\right\}. \tag{B2}$$

The ratios $R_{N,q+1}/R_N$ are bounded when λ vanishes so that the brackets in Eq. (B2) can be expanded in powers of k^2 with bounded coefficients. Hence, when $\lambda\to 0$, the coefficients of k^{2p} in Eq. (B2) behave as $(-j_0R_N^2/\lambda)^p[1+O(\lambda)]$. On the other hand, we know that $\Lambda_Z(\mathbf{k};\boldsymbol{\lambda})$ and $B(\mathbf{k};\boldsymbol{\lambda})$ can be expanded in powers of k^2:

$$\Lambda_Z(\mathbf{k};\boldsymbol{\lambda}) = \frac{v_d q^2}{4k^2}\left[1+\sum_{p=1}^{\infty}R_{Z,p}^{2p}k^{2p}\right], \tag{B3}$$

$$B(\mathbf{k};\boldsymbol{\lambda}) = 1-\sum_{p=2}^{\infty}B_{2p}k^{2p}, \tag{B4}$$

with $R_{Z,1}=R_Z$ and where the coefficients $R_{Z,p}$ and B_{2p} remain bounded when $\lambda\to 0$. As a conclusion, one can see that in symmetric and asymmetric models,

$$\xi_{N,p}^{2p} \approx \left(\frac{j_0}{\lambda}R_N^2\right)^p. \tag{B5}$$

2. True length $\xi_{N,\infty}$ in the symmetric case

The large-r behavior of G_{NN} is given by the singularity of $G_{NN}(\mathbf{k})$ nearest to the real axis. In the symmetric case, one has

$$4\beta a^{2d}G_{NN}(\mathbf{k}) = 1/[\lambda + \Delta J_\Sigma(\mathbf{k})], \tag{B6}$$

where $\Delta J_\Sigma(\mathbf{k})\equiv\frac{1}{2}(\widehat{J}_{+-}+\widehat{J}_{\tau\tau})(\mathbf{0}) - \frac{1}{2}(\widehat{J}_{+-}+\widehat{J}_{\tau\tau})(\mathbf{k})$ is independent of λ. In the complex k plane, ΔJ_Σ does not have any singularity and the singularity of G_{NN} arises from the vanishing of the denominator of (B6). We define k_Σ such as for k with both $|\mathrm{Re}(k)|$ and $|\mathrm{Im}(k)|$ smaller than k_Σ, the small-k expansion of ΔJ_Σ is valid. When $|\mathrm{Re}(k)|\leqslant k_\Sigma$ and $0\leqslant \mathrm{Im}(k)\leqslant k_\Sigma$, the vanishing of Λ_N given in Eq. (B1) has a unique solution $k=i\kappa$ where $\kappa\to 0$ as $\kappa R_N=(\lambda/j_0)^{1/2}[1+O(\lambda)]$. As seen in Sec. III B, when some conditions on $\mathcal{I}_0$ are imposed, $\mathbf{k}=\mathbf{0}$ is the only solution of $\Delta J_\Sigma(\mathbf{k})=0$ so that $\Delta J_\Sigma(\mathbf{k})>0$ for $\mathbf{k}\neq\mathbf{0}$ in the Brillouin zone.

Proposition 1. For a function f continuous on a compact $\mathcal{K}$ of the $\mathbb{C}$ plane, such as $f[\mathrm{Re}(k)]\neq 0$ in $\mathcal{K}$, then

$$\exists\,\eta,\quad \exists\,k_f\ /\ \forall\,k\in\mathcal{B},\quad |\mathrm{Im}(k)|\leqslant k_f \Rightarrow |f(k)|>\eta. \tag{B7}$$

Indeed, if not true, for all η, there would exist a suite k_n such as $|\mathrm{Im}(k_n)|<1/n$ and $|f(k_n)|<\eta$. In the compact $\mathcal{K}$, we could then extract a convergent partial suite of $\mathrm{Re}(k_n)$ converging toward k_∞ such as $|f(k_\infty)|<\eta$ which is in contradiction with $f[\mathrm{Re}(k)]\neq 0$ on the compact $\mathcal{K}$.

Then, if we consider the compact $\mathcal{B}_\Sigma$ made of the complex numbers such as $|\mathrm{Re}(k)|\geqslant k_\Sigma$ and $0\leqslant\mathrm{Im}(k)\leqslant k_\Sigma$, one knows that there exist some η and k'_Σ such as $|\Delta J_\Sigma(k)|>\eta$ when $0\leqslant\mathrm{Im}(k)\leqslant k'_\Sigma$, *independently* of λ so that $\lambda+\Delta J_\Sigma(k)\neq 0$ for $\lambda<\eta$. As a conclusion, when $\lambda\to 0$, $i\kappa$ is the only singularity of $G_{NN}(k)$ nearest to the real axis and it therefore rules $\xi_{N,\infty}$ as $\xi_{N,\infty}\approx R_N(j_0/\lambda)^{1/2}$.

3. Charge correlation lengths in symmetric systems

In order to compute the small-k expansion of S_{ZZ} in a symmetric model, we first notice that Λ_Z can be expanded according to

$$\Lambda_Z(\mathbf{k};\boldsymbol{\lambda}) = \frac{v_d q^2}{4k^2}\left[1+\sum_{p=1}^{\infty}\frac{\tilde{R}_{Z,p}^{2p}}{q^2}k^{2p}\right], \tag{B8}$$

with some given $\tilde{R}_{Z,p}$ which remain bounded when $\lambda\to 0$ and/or when $q\to 0$. Thanks to the decomposition (65b), this expansion leads to

$$S_{ZZ}(\mathbf{k}) = k^2\xi_D^2\sum_{p=0}^{\infty}\left(-R_Z^2k^2\right)^p\left(1+\sum_{q=2}^{\infty}\frac{\tilde{R}_{Z,q}^{2q}}{\tilde{R}_{Z,1}^{2}}k^{2(q-1)}\right)^p. \tag{B9}$$

Considering that the ratios $\tilde{R}_{Zq}^{2q}/\tilde{R}_{Z1}^{2}$ are bounded when $q\to 0$, one gets at leading order in q^2, $\xi_{Z,p}^{2p}\approx \xi_D^2 R_Z^{2(p-1)}$ in a symmetric system.

When q is small enough, we can compute the large-distance characteristic length $\xi_{Z,\infty}$ more precisely. Let us write

$$\Lambda_Z(\mathbf{k};\boldsymbol{\lambda}) = \lambda + 2j_0' + \frac{q^2 v_d}{4k^2}[1+k^2\Sigma_4(\hat{\mathbf{k}})] + \Delta J_Z(\mathbf{k};q), \tag{B10}$$

where we isolate the leading $1/k^2$ and $O(1)$ terms of the Coulomb potential with

$$2\Delta J_Z(\mathbf{k};q) \equiv \left\{\widehat{J}_{+-}(\mathbf{k}) - \frac{q^2 v_d}{4k^2}[1+k^2\Sigma_4(\hat{\mathbf{k}})]\right\} - \left\{\widehat{J}_{\tau\tau}(\mathbf{k}) + \frac{q^2 v_d}{4k^2}[1+k^2\Sigma_4(\hat{\mathbf{k}})]\right\} + (\widehat{J}_{\tau\tau}-\widehat{J}_{+-})(\mathbf{0}). \tag{B11}$$

When $q=0$, $\Delta J_Z^0(\mathbf{k})$ is an analytic function of the short-range interactions without singularity, and, as $|\Delta J_Z(\mathbf{k};q)-\Delta J_Z^0(\mathbf{k})| = q^2 O(k^2)$ when $\mathbf{k}\to\mathbf{0}$,

$$\left|\Delta J_Z(\mathbf{k};q)-\Delta J_Z^0(\mathbf{k})\right| \leqslant M q^2, \tag{B12}$$

for some given M. If the conditions of validity of the model are satisfied, we know that $\Lambda_Z^0(\mathbf{k},\boldsymbol{\lambda})-\lambda$, which is independent of λ, never vanishes in $\mathcal{B}$. Hence, thanks to Proposition 1, we know that there exists η and k_Z such as

$$|\mathrm{Re}(k)| \leqslant \pi/a \text{ and } 0\leqslant \mathrm{Im}(k)\leqslant k_Z \Rightarrow \left|2j_0' + \Delta J_Z^0(k)\right| > \eta. \tag{B13}$$

When q is nonzero, Λ_Z vanishes when

$$-\frac{q^2 v_d}{4k^2} = \left[2j_0' + \Delta J_Z^0(\mathbf{k})\right] + \lambda + \frac{1}{4}q^2 v_d \Sigma_4(\hat{\mathbf{k}}) + \Delta J_Z(\mathbf{k};q) - \Delta J_Z^0(\mathbf{k}). \tag{B14}$$

Using (B12) and (B13), one can show that for q small enough, the modulus of the right-hand side of (B14) is greater than $\eta/2$ for k satisfying (B14). Hence, the vanishing of Λ_Z occurs for $|k^2| < q^2 v_d/2\eta$, so that $\Delta J_Z(\mathbf{k};q)-\Delta J_Z^0(\mathbf{k}) = O(q^4)$. Hence, in the region $|\mathrm{Re}(k)|\leqslant \pi/a$ and $0\leqslant \mathrm{Im}(k)\leqslant k_Z$, (B14) has a unique solution, which is $k=(i/R_Z)[1+O(\mathcal{I}_0^2)]$, leading to (78).

4. True correlation lengths in asymmetric systems

For this analysis we need to make an extra hypothesis on the interactions in order to ensure that $D(\mathbf{k};\boldsymbol{\lambda})$ defined in Eq. (28) does not have spurious singularity in the complex k plane. We suppose

$$\text{(i)}\quad \widehat{J}_{+-}(\mathbf{k})\neq 0 \quad\text{in}\quad \mathcal{B}-\delta\mathcal{B}, \tag{B15}$$

where $\delta\mathcal{B}$ is the frontier of the Brillouin zone which is fulfilled for example when J_{+-}^0 describes a nearest-neighbor interaction [see (84)]. We also suppose

$$\text{(ii)}\quad \Delta J^{\dagger}(\mathbf{k}) = 0 \quad\text{on}\quad \delta\mathcal{B}. \tag{B16}$$

With these conditions, one can check that $D(\mathbf{k};\boldsymbol{\lambda})\neq 0$ in the Brillouin zone when $\lambda^{\dagger}\neq 0$, which is indeed an hypothesis of the model. Thanks to (3), one knows that the singularity in the complex k plane of G_{NN} and G_{ZZ} arises either from the vanishing of $\Lambda_{\pm}$ or of D.

a. Vanishing of $\Lambda_-(\mathbf{k})$

With the notation of Sec. IV B, we write

$$\Lambda_-(\mathbf{k},\boldsymbol{\lambda};\delta_J) - \lambda = [\Lambda_-^{\mathrm{SYM}}(\mathbf{k};\boldsymbol{\lambda})-\lambda] + \tfrac{1}{2}|\widehat{J}_{+-}(\mathbf{k})| - D(\mathbf{k};\boldsymbol{\lambda}), \tag{B17}$$

where the first brackets in the right-hand side of (B17) are merely $\Delta\bar{J}(\mathbf{k}) + j_0' - \frac{1}{2}|\widehat{J}_{+-}(\mathbf{k})|$. As seen in Sec. IV B, for $\mathcal{I}_0 < \mathcal{I}_{\max}$, there exists some positive bound $\delta\Lambda_-^{\mathrm{SYM}}$ such as for $\mathbf{k}$ in $\mathcal{B}$ with one $|\mathbf{k}_\alpha|\geqslant k_-$,

$$\Lambda_-^{\mathrm{SYM}}(\mathbf{k};\boldsymbol{\lambda}) - \lambda \geqslant \delta\Lambda_-^{\mathrm{SYM}} > 0. \tag{B18}$$

Thanks to Proposition 1, one can check that there exist $\delta\Lambda_-'$ and k_-', such as

$$|\mathrm{Re}(k)|\geqslant k_- \quad\text{and}\quad 0\leqslant \mathrm{Im}(k)\leqslant k_-' \tag{B19}$$

so that

$$|\Lambda_-^{\mathrm{SYM}}(k,\boldsymbol{\lambda})-\lambda| \geqslant \delta\Lambda_-' > 0, \tag{B20}$$

independently of λ. In order to bound $D(\mathbf{k};\boldsymbol{\lambda}) - \frac{1}{2}|\widehat{J}_{+-}(\mathbf{k})|$, we first establish the following property.

Proposition 2. For a continuous function f on a compact $\mathcal{K}$ such as $|f[\mathrm{Re}(k)]| < j$, there exists k_f such as

$$k \text{ in } \mathcal{K} \text{ and } |\mathrm{Im}(k)|\leqslant k_f \Rightarrow |f(k)|\leqslant 2j. \tag{B21}$$

Indeed, if the proposition was not true, we could build a converging suite of complex k_n such as $|f(k_n)|\geqslant 2j$, $\mathrm{Im}(k_n)\to 0$ and $\mathrm{Re}(k_n)\to k_\infty$, where k_∞ is in $\mathcal{K}$, and such as $|f(k_\infty)|\geqslant 2j$ which is not possible.

Hence, as $|\Delta J^{\dagger}(\mathbf{k})| < j_0\delta_J$, one knows that there exists $k^{\dagger}$ such as, for $|\mathrm{Re}(k)|\leqslant \pi/a$ and $|\mathrm{Im}(k)|\leqslant k^{\dagger}$, $\Delta J^{\dagger}$ is bounded as $|\Delta J^{\dagger}(k)|\leqslant 2j_0\delta_J$, so that

$$|D(k;\boldsymbol{\lambda}) - \tfrac{1}{2}|\widehat{J}_{+-}(k)|| \leqslant |\lambda^{\dagger}| + |\Delta J^{\dagger}(k)| \leqslant 3j_0\delta_J. \tag{B22}$$

Combining (B17), (B20), and (B22), and defining $k_-'' \equiv \inf(k_-,k_-',k^{\dagger})$, one finds that for low-enough asymmetries, e.g. for $\delta_J < \delta\Lambda_-'/3j_0$, $\Lambda_-(\mathbf{k};\boldsymbol{\lambda})\neq 0$ in the region $|\mathrm{Re}(k)|\geqslant k_-$ and $0\leqslant \mathrm{Im}(k)\leqslant k_-''$. Finally, for k such as $|\mathrm{Re}(k)|\leqslant k_-$ and $0\leqslant \mathrm{Im}(k)\leqslant k_-''$, the same analysis as in Eq. (B2) shows that $k = i\xi_N^{-1}$ is the unique zero of Λ_-, which tends to the real axis when $\lambda\to 0$.

b. Nonvanishing of Λ_+ *and* D

We show that Λ_+ can not vanish in a given strip near the real axis. Indeed, let us write

$$\Lambda_+(\mathbf{k};\boldsymbol{\lambda}) - \lambda = [\Lambda_+^{\mathrm{SYM}}(\mathbf{k};\boldsymbol{\lambda})-\lambda] + D(\mathbf{k};\boldsymbol{\lambda}) - \tfrac{1}{2}|\widehat{J}_{+-}(\mathbf{k})|, \tag{B23}$$

where the first brackets of the right-hand side are merely $\Delta\bar{J}(\mathbf{k}) + j_0' + \frac{1}{2}|\widehat{J}_{+-}(\mathbf{k})|$. In the Brillouin zone, $\Lambda_+^{\mathrm{SYM}}(\mathbf{k};\boldsymbol{\lambda})-\lambda$ never vanishes so that, thanks to Proposition 1, there exist some η and k_+ such as, for $|\mathrm{Re}(k)|\leqslant \pi/a$ and $0\leqslant \mathrm{Im}(k)\leqslant k_+$, one has $|\Lambda_+^{\mathrm{SYM}}(\mathbf{k};\boldsymbol{\lambda})-\lambda| > \eta$, independently of λ. Moreover, thanks to (B22), the bound $\delta_J < \eta/3j_0$ implies that $|\Lambda_+(\mathbf{k};\boldsymbol{\lambda})-\lambda|$ never vanishes in the strip

$0 \leqslant \mathrm{Im}(k) \leqslant k'_+$, with $k'_+ = \inf(k_+, k^\dagger)$, and so is the case also for $\Lambda_+(\mathbf{k};\boldsymbol{\lambda})$ when $\lambda \to 0$.

Concerning $D(\mathbf{k};\boldsymbol{\lambda})$ and thanks to the extra condition (B15) and (B16), one knows that $D_c(\mathbf{k}) \equiv D(\mathbf{k}; \lambda = 0, \lambda_c^\dagger)$ never vanishes in the Brillouin zone, so that thanks to Proposition 1, there exist some η and k_D such as $|D_c(k)| > \eta$ when $|\mathrm{Re}(k)| \leqslant \pi/a$ and $0 \leqslant \mathrm{Im}(k) \leqslant k_D$. Writing $D - D_c = (\lambda^\dagger - \lambda_c^\dagger)[\lambda^\dagger + \lambda_c^\dagger + 2\Delta J^\dagger(\mathbf{k})]$, one can deduce

$$|D(\mathbf{k};\boldsymbol{\lambda})| \geqslant \eta - 6 j_0 \delta_J (\lambda^\dagger - \lambda_c^\dagger), \tag{B24}$$

valid for $|\mathrm{Re}(k)| \leqslant \pi/a$ and $0 \leqslant \mathrm{Im}(k) \leqslant k'_D$ with $k'_D \equiv \inf(k_D, k^\dagger)$; consequently, close enough from criticality, $D(\mathbf{k};\boldsymbol{\lambda})$ can not vanish in this region.

c. Behavior of G_{NN} and G_{ZZ}

As a conclusion, when λ vanishes, the only singularity of both G_{NN} and G_{ZZ} in the strip $|\mathrm{Re}(k)| \leqslant \pi/a$ and $0 \leqslant \mathrm{Im}(k) \leqslant \inf(k''_-, k'_+, k'_D)$ is linked to the vanishing of Λ_- which occurs for $k = i\xi_N^{-1}$. Hence, in the asymmetric case, $\xi_{Z\infty} = \xi_{N,\infty} = \xi_N$.

APPENDIX C: ALGEBRAIC SCREENING

In this Appendix, we use a diagrammatic analysis in order to establish the algebraic screening present in a charged fluid when at least one species correlation $G_{\tau\upsilon}$ behaves as $1/r^{d+\sigma}$ (being supposed that it is the leading algebraic decay among all the $G_{\tau\upsilon}$ correlations). According to [46], we consider the general decomposition

$$G_{\tau\upsilon}(\mathbf{r}) = G^{\mathrm{DH}}_{\tau\upsilon}(\mathbf{r}) + \sum_{\tau',\upsilon'} \Sigma^{\mathrm{DH}}_{\tau\tau'}(\mathbf{r}) * G^{nn}_{\tau'\upsilon'}(\mathbf{r}) * \Sigma^{\mathrm{DH}}_{\upsilon\upsilon'}(\mathbf{r}), \tag{C1}$$

where $G^{\mathrm{DH}}_{\tau\upsilon}(\mathbf{r}) = -\beta q_\tau q_\upsilon \rho_\tau \rho_\upsilon \phi^{\mathrm{DH}}(\mathbf{r})$, with $\hat\phi^{\mathrm{DH}}(\mathbf{k}) = 4\pi/(k^2 + \xi_D^{-2})$, and where

$$\Sigma^{\mathrm{DH}}_{\tau\tau'}(\mathbf{r}) = \delta_{\tau\tau'}\delta(\mathbf{r}) + G^{\mathrm{DH}}_{\tau\tau'}(\mathbf{r})/\rho_{\tau'}. \tag{C2}$$

The relation (C1) is proven thanks to a reorganization of diagrams in such a way that the root points are attached or not to a G^{DH} bond. Hence, G^{nn} stands for the sum of all the diagrams where the root points are not attached to a G^{DH} bond, while Σ^{DH} is the charge density formed in the Debye-Hückel approximation, by an external charge and its surrounding screening cloud. We check the relation

$$\sum_\tau q_\tau \Sigma^{\mathrm{DH}}_{\tau\tau'}(\mathbf{k}) = q_{\tau'} S^{\mathrm{DH}}_{ZZ}(\mathbf{k}), \tag{C3}$$

where S^{DH}_{ZZ} is given in Eq. (77), which states that in the Debye-Hückel approximation, the total induced charge around an external charge *exactly* compensates for it, as a consequence of the external screening. Using (C3) in Eq. (C1), we find

$$G_{ZZ}(\mathbf{k}) = G^{\mathrm{DH}}_{ZZ}(\mathbf{k}) + \frac{k^4}{\left(k^2 + \xi_D^{-2}\right)^2} \sum_{\tau,\upsilon} q_\tau q_\upsilon G^{nn}_{\tau\upsilon}(\mathbf{k}). \tag{C4}$$

We suppose that one $G_{\tau\upsilon}(\mathbf{k})$ contains a nonanalyticity of order k^σ, which is the leading singularity present in all the correlations. This is indeed the case in the spherical model with $1/r^{d+\sigma}$ interactions. Considering the Ursell functions $h_{\tau\upsilon} = G_{\tau\upsilon}/\rho_\tau\rho_\upsilon$, one can deduce the decomposition (see [46])

$$h_{\tau\upsilon} = h^{\mathrm{DH}}_{\tau\upsilon} + h^{\mathrm{DH}}_{\tau\tau'}\rho_{\tau'} * h^{n-}_{\tau'\upsilon} + h^{n-}_{\tau\upsilon}, \tag{C5}$$

$$h^{n-}_{\tau\upsilon} = h^{nn}_{\tau\tau'} * \Sigma^{\mathrm{DH}}_{\tau'\upsilon}, \tag{C6}$$

thanks to which h^{n-} can be obtained in terms of h and h^{nn} in terms of h^{n-}. We can then show that one $G^{nn}_{\tau\upsilon}$ must contain a nonanalyticity of leading order k^σ. Considering (C4) where every $G^{nn}_{\tau\upsilon}$ is multiplied by k^4, one concludes that $G_{ZZ}(\mathbf{r})$ behaves as $1/r^{d+\sigma+4}$ if no spurious extra cancellation happens, while it decreases even faster if such an accidental cancellation arises. The increase of +4 in the power law of charge correlations compared to density correlations is therefore a consequence of the external screening at stake in both the system and in the Debye-Hückel limit.

[1] M. E. Fisher, Rep. Progr. Phys. **30**, 615 (1967).
[2] M. E. Fisher, S.-K. Ma, and B. G. Nickel, Phys. Rev. Lett. **29**, 917 (1972).
[3] M. E. Fisher, J. Stat. Phys. **75**, 1 (1994): J. Phys.: Condens. Matter **8**, 9103 (1996).
[4] G. Stell, J. Stat. Phys. **78**, 197 (1995).
[5] A. G. Moreira, M. M. Telo da Gama, and M. E. Fisher, J. Chem. Phys. **110**, 10058 (1999).
[6] A. Ciach, Phys. Rev. E. **73**, 066110 (2006).
[7] R. Singh and K. S. Pitzer, J. Am. Chem. Soc. **110**, 8723 (1988).
[8] M. L. Japas and M. Levelt Sengers, J. Phys. Chem **94**, 5361 (1990).
[9] H. Weingärtner and W. Schröer, Adv. Chem. Phys. **116**, 1 (2001).
[10] E. Luijten, M. E. Fisher, and A. Z. Panagiotopoulos, Phys. Rev. Lett. **88**, 185701 (2002); Y. C. Kim *et al.*, *ibid.* **91**, 065701 (2003).
[11] O. Patsahan, I. Mryglod, and J.-M. Caillol, J. Phys.: Condens. Matter **17**, L251 (2005).
[12] A. Ciach, W. T. Góźdź, and G. Stell, Phys. Rev. E **75**, 051505 (2007).
[13] Y. C. Kim and M. E. Fisher, Phys. Rev. E **77**, 051502 (2008).
[14] S. K. Das, Y. C. Kim, and M. E. Fisher, Phys. Rev. Lett. **107**, 215701 (2011); J. Chem. Phys. **137**, 074902 (2012).
[15] A. Alastuey and R. Fantoni, J. Stat. Phys. **163**, 887 (2016).
[16] M. E. Fisher and Y. Levin, Phys. Rev. Lett. **71**, 3826 (1993).
[17] R. J. F. Leote de Carvalho and R. Evans, J. Phys.: Condens. Matter **7**, L575 (1995).
[18] M. E. Fisher and B. P. Lee, Phys. Rev. Lett. **77**, 3561 (1996).
[19] V. C. Weiss and W. Schröer, J. Chem. Phys. **106**, 1930 (1997).
[20] W. Schröer and V. C. Weiss, J. Chem. Phys. **109**, 8504 (1998).
[21] O. Patsahan, Phys. Rev. E **88**, 022102 (2013).
[22] J.-N. Aqua and M. E. Fisher, Phys. Rev. Lett. **92**, 135702 (2004).
[23] J.-N. Aqua and M. E. Fisher, J. Phys. A: Math. Gen. **37**, L241 (2004).

[24] M. E. Fisher, in *Current Topics in Physics*, edited by R. A. Barrio and K. K. Kaski (Imperial College Press, London, 2005), Chap. 1, p. 1.
[25] J.-N. Aqua and M. E. Fisher, Phys. Rev. E **79**, 011118 (2009).
[26] D. C. Brydges and P. Federbush, Commun. Math. Phys. **73**, 197 (1980).
[27] F. Stillinger and R. Lovett, J. Chem. Phys. **48**, 3858 (1968).
[28] R. Kjellander and B. Forsberg, J. Phys. A: Math. Gen. **38**, 5405 (2005).
[29] T. H. Berlin and M. Kac, Phys. Rev. **86**, 821 (1952).
[30] H. E. Stanley, Phys. Rev. **176**, 718 (1968).
[31] E. R. Smith, J. Stat. Phys. **50**, 813 (1988).
[32] E. R. Smith, J. Stat. Phys. (to be published).
[33] E. Lieb and J. L. Lebowitz, Adv. Math. **9**, 316 (1972).
[34] B. Jancovici, J. Phys. (Paris) **47**, 389 (1986).
[35] J.-N. Aqua and F. Cornu, J. Stat. Phys. **105**, 211 (2001).
[36] G. S. Joyce, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. Green (Academic, New York, 1972), Vol. 2, p. 375.
[37] M. C. Barbosa and M. E. Fisher, Phys. Rev. B. **43**, 10635 (1991).
[38] P.-A. Martin, Rev. Mod. Phys. **60**, 1075 (1988).
[39] M. E. Fisher and R. J. Burford, Phys. Rev. **156**, 583 (1967).
[40] J. M. Romero-Enrique, G. Orkoulas, A. Z. Panagiotopoulos, and M. E. Fisher, Phys. Rev. Lett. **85**, 4558 (2000).
[41] E. Gonzalez-Tovar, Mol. Phys. **97**, 1203 (1999).
[42] F. O. Raineri, J. P. Routh, and G. Stell, J. Phys. IV **10**, 99 (2000).
[43] M. J. Lighthill, *Introduction to Fourier Analysis and Generalised Functions* (Cambridge University Press, Cambridge, 1958).
[44] A. Alastuey and P.-A. Martin, J. Stat. Phys. **39**, 405 (1984).
[45] A. Alastuey and P.-A. Martin, Phys. Rev. A **40**, 6485 (1989).
[46] F. Cornu, Phys. Rev. E **53**, 4595 (1996).