Crossover Scales at the Critical Points of Fluids with Electrostatic Interactions

André G. Moreira *, M. M. Telo da Gama
Departamento de Física da Faculdade de Ciências and Centro de Física da Matéria Condensada
Universidade de Lisboa, Avenida Professor Gama Pinto 2, P-1649-003 Lisboa, Portugal

Michael E. Fisher
Institute for Physical Science and Technology,
University of Maryland, College Park, Maryland 20742, U.S.A.

Abstract

Criticality in a fluid of dielectric constant $D$ that exhibits Ising-type behavior is studied as additional electrostatic (i.e., ionic) interactions are turned on. An exploratory perturbative calculation is performed for small ionicity as measured by the ratio of the electrostatic energy $e^2/Da$ (of two univalent charges, $\pm e$, separated by the atomic/ionic diameter $a$) to $k_B T_c^0$ which represents the strength of the short-range nonionic (i.e., van der Waals) interactions in the uncharged fluid. With the aid of distinct transformations for the short-range and for the Coulombic interactions, an effective Hamiltonian with coefficients depending on the ionicity is derived at the Debye-Hückel limiting-law level for a fully symmetric model. The crossover between classical (mean-field) and Ising behavior is then estimated using a Ginzburg criterion.

*Current address: Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Kantstr. 55, 14513 Teltow, Germany.
This indicates that the reduced crossover temperature depends only weakly on the ionicity (and on the range of the nonionic potentials); however, the trends do correlate with the, much stronger, dependence observed experimentally.

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I. INTRODUCTION

Early studies of the liquid-vapor critical point of ionic systems were carried out on molten salts and related systems with relatively poor temperature stability and resolution. Results for ionic critical behavior at low reduced temperatures were first published by Pitzer and co-workers a decade ago. Subsequently other solutions of organic salts, with low critical temperatures, were studied yielding somewhat puzzling results.

One of the systems studied in detail was triethyl-n-hexylammonium triethyl-n-hexylboride (N$_{2226}$–B$_{2226}$) in diphenyl ether. In 1990, Singh and Pitzer reported a coexistence-curve exponent, $\beta \simeq 0.476$, close to the mean field value of $\frac{1}{2}$. Their data are compatible with Ising criticality ($\beta \simeq \frac{1}{3}$) only if the mean field to Ising crossover occurs at a reduced temperature, $t_x \equiv |T - T_c|/T_c \simeq 10^{-4}$. This value of $t_x$ is unusually small—in ordinary fluids $t_x \sim 1$ and the observed critical exponents are clearly of Ising character. In 1992, Zhang et al. confirmed the mean-field critical behavior of this system by reporting a susceptibility exponent, $\gamma \simeq 1.0$.

A different system also studied nearly a decade ago was tetra-n-pentylammonium bromide dissolved in water. Japas and Levelt Sengers reported an Ising-type coexistence curve with $\beta = 0.319$–0.337. Other studies reported Ising or mean-field criticality depending on the particular ionic solution. For reviews of the various experiments, see: Refs.

The presence of the solvent, which lowers the critical temperature of the salts, complicates the situation considerably. The bare Coulomb interaction is reduced by a factor that depends on, $D$, the static dielectric constant of the solvent. Additionally, in polar solvents, solvation shells are formed around each ion and the resulting effective interactions between the ions are not well characterized at present. The mechanisms driving criticality in these various systems are not clear, but there appear to be two classes of critical behaviour: Coulombic systems, where the electrostatic interactions primarily drive the phase transition and solvophobic mixtures in which the phase transition is mainly driven by the short-ranged interactions that favor solvent-solvent and solute-solute contacts.
In Table I we display data on the melting temperature of three salts and their critical temperatures in solution. Clearly, if $T_m$ is lower than $T_c$ the Coulomb interactions are too weak to drive the phase transition, especially in high dielectric-constant solvents. However, there are cases where the ionic interactions are strong enough to play a role at temperatures of the order of $T_c$. In these systems, a crossover from mean-field to Ising criticality was observed, with reduced crossover temperatures $t_x$, that decrease as the relative ionic character or ionicity increases, i.e., the dielectric constant of the solvent decreases. Ising exponents are observed only closer to $T_c$ as the ionicity increases. It is plausible to suppose that the effect of the Coulomb interactions is the reduction of the crossover temperature; this reduction might be so strong that Ising critical behavior could not be observed in practice. Ideal Coulombic electrolyte criticality would then be characterized by classical (mean-field) behavior, while solvophobic electrolyte criticality remained in the 3D Ising universality class.

However, a theoretical description of the dependence of $t_x$ on the Coulombic and other interactions is still lacking. Indeed, previous attempts to study the crossover temperature of model ionic fluids do not seem to predict any reduction, at least for the restrictive primitive model (RPM) consisting of an equal number of equisized positive and negative hard-spheres. Following the suggestion of Fisher and Levin, Leote de Carvalho and Evans and Fisher and Lee employed a Ginzburg criterion which led them to conclude that the reduced crossover temperature of the RPM is similar to that of ordinary fluids.

Although the study of criticality in the RPM has proceeded for half a decade, progress has been slow and no definitive conclusions have yet been reached. Fisher and Levin extended the original Debye-Hückel theory and established the importance of including dipolar Bjerrum pairs and of accounting for the solvation of the neutral, but electrostatically active, pairs in the screening ionic fluid. These authors have obtained the best theoretical estimates of the critical density and temperature of the RPM when compared with the results of computer simulations.

However, the direct Fisher-Levin approach does not address the question of the univer-
sality class of the RPM. On the other hand, computer simulations of the critical behavior of the RPM have been carried out; but these also have not provided clear-cut answers. Calliol et al. have obtained evidence of consistency with Ising exponents, as have Orkoulas and Panagiotopoulos, but Valleau and Torrie claim that no sign of Ising behavior is observed in their simulations above criticality.

Nevertheless, it is instructive to pose a more modest question, namely: “How does the introduction of weak electrostatic interactions affect the near-critical behavior of a fluid that, when uncharged, displays Ising criticality?” While one cannot discard the possibility that the long-range Coulomb interactions discontinuously change the universality class, the Debye screening of the ions at any non-zero ionic strength can be regarded as giving rise to an effective short-ranged interaction and thus — at least in a perturbative sense — we may suppose that weak electrostatic couplings will not change the character of the transition. They must, nonetheless, affect all the non-universal critical properties: and many of these are of independent interest.

Accordingly, in this article, we address this last issue. Specifically, we consider an ordinary fluid of dielectric constant $D$ with only short-range, or van der Waals interactions, that exhibits criticality of Ising character at a temperature $T^0_c$. For simplicity in this essentially exploratory study, we focus on a fully symmetric model in which the particles of the original, uncharged fluid are all identical having repulsive cores of diameter $a$ and fixed attractive pair interactions, the strength of which is measured by $k_B T^0_c$.

Then we ask how the reduced crossover temperature, $t$, changes when electrostatic interactions are switched on so that half the particles become positive ions of charge $+e$ and the rest negative ions carrying charge $-e$. The strength of the Coulomb forces may be measured by the “contact energy” $e^2 / Da$, so that one can imagine either increasing $e$ from zero or, for fixed charges, decreasing the dielectric constant $D$ from very high values. Naturally, the critical temperature of the system will change and it is thus reasonable to
define the ionicity of the critical charged system by
\[ I \equiv \frac{e^2}{D a k_B T_c} = \frac{1}{T_c^*}, \] (1)

where \( T^* = \frac{D a k_B T}{e^2} \) is the standard definition of reduced temperature in primitive model electrolytes.\( \equiv \) The ionicity will constitute our perturbative parameter.

To treat the model, we first consider, in Section II, the purely ionic limit (where \( k_B T_0^c = 0 \)) and, using a lattice cutoff, reformulate the Coulomb interactions via a quadratically truncated sine-Gordon transformation.\( \equiv \) This corresponds to a Debye-Hückel limiting-law level of analysis although the expansion could be carried to higher order.\( \equiv \) Then, in Section III, we introduce (charge independent) short-range interactions with the aid of a Kac-Hubbard-Stratonovich (KHS) transformation. In the resulting (approximate) Hamiltonian we integrate out the sine-Gordon charge field \( \psi(\mathbf{r}) \), perturbatively to obtain an effective Landau-Ginzburg-Wilson (LGW) Hamiltonian in terms of a spin (or density) field, \( s(\mathbf{r}) \), but with coefficients depending on the ionicity, \( I \). Finally, effectively truncating at the \( s^4 \) level, we estimate the crossover temperature with the aid of a Ginzburg criterion in Section IV. This treatment indicates that, in general, the reduced crossover temperature decreases by an amount of order 25%. Such a weak change is far too small to describe the experimental observations although the overall trends seem to correlate: see Table II and the discussion and conclusions in Section V.

II. LATTICE CUTOFF MODEL FOR THE IONIC FLUID

Consider a system of unit-valence positive and negative ions with repulsive cores but otherwise interacting only through Coulomb forces. To account approximately for the ionic cores we may suppose the ions reside on the sites of a lattice of spacing \( a \) equal to the atomic diameter. Alternatively, in momentum space, we can employ a cutoff on a corresponding Brillouin zone or, for convenience, approximate this by a sphere of radius \( \pi/a \). The grand
partition function for the lattice system with sites labelled $i, j$, etc., is

$$Z = \sum_{n_+, n_-} \exp\left\{ -\mu_+ n_+ - \mu_- n_- \right\} \times \sum_{\{\rho_+, \rho_-\}} \exp\left\{ -\frac{1}{2} \sum_{i,j} [\rho_+(i) - \rho_-(i)] \varphi_c(i, j) [\rho_+(j) - \rho_-(j)] \right\},$$  \hspace{1cm} (2)

where the first sum runs over $n_+$ and $n_-$, the total numbers of positive and negative ions, subject to $n_+ + n_- \leq N$, the number of lattice sites, while the second sum runs over different lattice configurations, for given numbers, $n_+$ and $n_-$. The occupation variable $\rho_+(i)$, is 1 if a positive ion is at site $i$, but 0 otherwise, with a similar definition of $\rho_-$. We omit the possibility of ionic pairing (molecule formation)\footnote{ } so that a lattice site cannot be occupied by more than a single ion. The remaining symbols have their usual meanings: $\mu_+$ and $\mu_-$ being the chemical potentials (divided by $k_B T$) for the positive and negative ions, respectively.

Since this is a first approach and we are interested in real fluids (rather than details induced by the lattice structure) we do not take the Coulomb interaction proportional to the lattice Green’s function but simply use the reduced three-dimensional isotropic Coulomb potential so that in (2) we have

$$\varphi_c(i, j) = \frac{e^2}{k_B T D r_{ij}},$$  \hspace{1cm} (3)

where $r_{ij}$ is the distance separating sites $i$ and $j$.

Given a positive definite matrix $A_{ij}$, the identity

$$\exp\left\{ -\frac{1}{2} \sum_{i,j} y_i A_{ij} y_j \right\} = \sqrt{\det[A_{ij}]} \int_{-\infty}^{+\infty} \left( \prod_{i} dx_i \right) \exp\left\{ -\frac{1}{2} \sum_{i,j} x_i A^{-1}_{ij} x_j - i \sum_{i} x_i y_i \right\},$$  \hspace{1cm} (4)

(where $i = \sqrt{-1}$) may be used to rewrite the grand partition function of a repulsive system with discrete variables in terms of the partition function of a system with continuous variables: this constitutes the well known sine-Gordon transformation\footnote{ } that may be regarded as a modified form of the Kac-Hubbard-Stratonovich transformation used for attractive interactions\footnote{ }\footnote{ }. These transformations are standard and need not be discussed in further detail here.
The diagonal elements of the electrostatic interaction matrix, $\varphi_c(i, i)$, are chosen to guarantee that $\varphi_c(i, j)$ is positive definite but are otherwise arbitrary since a lattice site cannot be occupied by more than a single ion. Thus (4) may be used to write (2) as,

$$Z = \int \frac{D\psi}{Z_0} \exp\left\{-\frac{1}{2} \sum_{i,j} \psi(i) \varphi_c^{-1}(i, j) \psi(j)\right\} W_0,$$

where the weight function is given by

$$W_0 = \sum_{n_+, n_-} \sum_{\{\rho_+, \rho_-\}} \exp\left\{-i \sum_j [\rho_+(j) - \rho_-(j)] \psi(j) - \mu_+ n_+ - \mu_- n_-\right\}.\quad (6)$$

The continuous field $\psi(j)$, ranging from $-\infty$ to $+\infty$, is conjugate to the (reduced) discrete charge density

$$q(j) = \rho_+(j) - \rho_-(j).\quad (7)$$

On the lattice one has $D\psi = \prod_j d\psi(j)$, while $Z_0$ is an unimportant constant given by

$$Z_0 = \int D\psi \exp\left\{-\frac{1}{2} \sum_{i,j} \psi(i) \varphi_c^{-1}(i, j) \psi(j)\right\} = \sqrt{(2\pi)^N \det[\varphi_c(i, j)]}.\quad (8)$$

Defining the thermodynamic fields $\mu \equiv (\mu_+ + \mu_-)/2$ and $\gamma \equiv (\mu_+ - \mu_-)/2$, and noting that the total ionic density may be written as

$$\rho(j) = \rho_+(j) + \rho_-(j) = q^2(j),\quad (9)$$

the weight function takes the more convenient form

$$W_0 = \sum_{q=-1,0,1} \exp\left\{-i \sum_j q(j) [\psi(j) + i \gamma] - \sum_j q^2(j) \mu\right\}.\quad (10)$$

Carrying out the sum over $q$ here, leads to

$$W_0 = \prod_j \left(1 + \exp\{i[\psi(j) + i \gamma] - \mu\} + \exp\{-i[\psi(j) + i \gamma] - \mu\}\right)$$

$$= \exp\left\{\sum_j \ln[1 + 2 \exp(-\mu) \cos(\psi(j) + i \gamma)]\right\}.\quad (11)$$
It may now be checked, using (5) and (11), that global charge neutrality, namely \( \langle q \rangle = 0 \), is obtained if \( \gamma = 0 \), i.e., when the chemical potentials of the positive and negative ions are the same. From hereon we assume this to be so and set \( \gamma = 0 \).

Provided \( z \equiv e^{-\mu} < \frac{1}{2} \), we may expand the logarithm in the weight function \( W_0 \) with respect to \( \psi(j) \). By truncating the expansion at second order we find

\[
\left( \frac{Z}{Z_{LL}} \right)^{1/N} \approx 1 + 2z + \cdots ,
\]

(12)

where we have defined the Debye-Hückel limiting-law partition function as,

\[
Z_{LL} = \int \frac{D\psi}{Z_0} \exp \left\{ -\frac{1}{2} \sum_{i,j} \psi(i) \left[ \varphi^{-1}_c(i,j) + \frac{2z}{(1+2z)} \delta(i,j) \right] \psi(j) \right\} = \int \frac{D\psi}{Z_0} \exp \left\{ -\frac{1}{2} \sum_{i,j} \psi(i) \varphi^{-1}_{LL}(i,j) \psi(j) \right\},
\]

(13)

where \( \delta(i,j) \) is the Kronecker delta and \( \varphi_{LL}(i,j) \) is the Debye-Hückel limiting-law (DHLL) reduced effective potential as we will demonstrate.

Now, Fourier transformation of the electrostatic potential (3) on the lattice leads to

\[
\hat{\varphi}_c(k) = 4\pi \ell_B \left[ 1 + O(k^2a^2) \right],
\]

(14)

where \( \ell_B = e^2/Dk_BT = a/T^* \) is the Bjerrum length (the distance at which two elementary charges interact with an energy \( k_BT \)). The \( O(k^2a^2) \) terms here arise from the lattice structure or, equivalently within our approximation, from the repulsive core of the ion-ion interactions. Since our subsequent analysis will utilize only the leading \( k \to 0 \) behavior, the effects of the lattice structure entering this way, \textit{via} the Coulombic potential, should not be significant; thus we will neglect the \( O(k^2a^2) \) term in (14). Alternatively, one may regard the pure \( 1/k^2 \) behavior to be retained in (14) as defining (via inverse Fourier transformation) the Coulomb potential as viewed on the lattice in real space: this would mean that \( \varphi_c(i,j) \) as stated in (3) should be modified slightly on distance scales of order \( a \). However, in a fuller, more precise treatment, of the lattice primitive model it is possible that such contributions could play a more crucial role, but that issue lies outside the scope of our present analysis.
It follows from (13) and (14) that the DHLL effective potential in Fourier space is given by

\[ \hat{\varphi}_{LL}(k) = \frac{1}{4\pi \ell_B(T)} \left( \frac{k^2}{k^2 + 4\pi \ell_B \eta} \right), \]

where \( \eta = \frac{2z}{1+2z} \) with \( z \equiv e^{-\mu} \) and, for convenience here and in most places below, we express \( k, \ell_B, \) etc., using length units for which \( a \equiv 1. \) By differentiating the grand partition function (3) with respect to \( \mu \) and expanding the result in powers of \( \psi, \) we find the total density of ions is given by

\[ \rho \equiv \langle q^2(j) \rangle = \frac{2z}{1+2z} - \frac{z(1+2z+2z^2)}{(1+z)(1+2z)^2} \langle \psi_j^2 \rangle + \cdots. \]

(16)

Retaining only the first term in this series, which implies \( \eta \approx \rho, \) and transforming (15) back into real space, we obtain

\[ \varphi_{LL}(r) \propto \exp\left(-\frac{r}{\xi_D}\right), \]

(17)

where \( \xi_D = \frac{1}{\sqrt{4\pi \ell_B \rho}}, \) is the standard Debye screening length\(^3\) thus demonstrating that the correct DHLL effective potential for ionic systems may be obtained from a quadratic expansion of the sine-Gordon weight function, in \( \psi \) — a well known result.\(^2\,^8\)

In the next section we derive, using similar techniques, a field-theoretic description of a system with additional short-range forces. As explained, we will focus on the situation where these forces drive the critical behavior. Then by integrating out the electrostatic interactions at the DHLL level we obtain corrections to the nonuniversal critical parameters, including an estimate of the crossover temperature, \( t_x. \)

**III. SYMMETRIC IONIC MODEL WITH SHORT-RANGE ATTRACTIONS**

By adding to the lattice-cutoff model an attractive symmetric short-range pairwise potential identical for all ionic pairs, so that \( \varphi_{++}^s(i,j) = \varphi_{--}^s(i,j) = \varphi_{+-}^s(i,j) = \varphi_s(i,j), \) the grand partition function becomes
\[ Z = \sum_{\{q\}} \exp \left\{ - \sum_i q^2(i) \mu - \frac{1}{2} \sum_{i,j} \left[ q(i) \varphi_c(i, j) q(j) + q^2(i) \varphi_s(i, j) q^2(j) \right] \right\}, \]  

(18)

where we have set \( \gamma \equiv (\mu_+ - \mu_-)/2 = 0 \), to ensure global charge neutrality. The sum on \( \{q\} \) runs over all possible configurations of ions on the lattice.

The sine-Gordon transformation may be used as before on the electrostatic interactions in (18) to obtain a description in terms of the field, \( \psi \). In general, the short-range interaction matrix has positive and negative eigenvalues\(^\text{35}\) and thus the KHS transformation cannot be applied directly.\(^\text{30}\) Here, we assume that \( -\varphi_s(i, j) \) is positive definite and use the identity

\[ \exp \left\{ \frac{1}{2} \sum_{i,j} y_i A_{ij} y_j \right\} = \sqrt{\frac{\det[A_{ij}]}{(2\pi)^N}} \int_{-\infty}^\infty \left( \prod_i dx_i \right) \exp \left\{ -\frac{1}{2} \sum_{i,j} x_i A_{ij}^{-1} x_j - \sum_i x_i y_i \right\} \]  

(19)

to transform the short-range attractive interactions. After these transformations the grand partition function (18) reads

\[ Z = \int \frac{D\psi Ds}{Z_1} \exp \left\{ -\frac{1}{2} \sum_{i,j} \left[ \psi(i) \varphi_c^{-1}(i, j) \psi(j) + s(i) \varphi_s^{-1}(i, j) s(j) \right] \right\} \mathcal{W}_1, \]  

(20)

where the field \( s(j) \) is conjugate to the total ionic density \( q^2(j) \): see (9). The normalizing factor is now

\[ Z_1 = \frac{(2\pi)^N}{\sqrt{\det[\varphi_c(i, j)] \det[\varphi_s(i, j)]}}, \]  

(21)

and the new weight function is

\[ \mathcal{W}_1 = \exp \left\{ \sum_j \ln [1 + 2 \exp[-s(j) - \mu] \cos \psi(j)] \right\}. \]  

(22)

Now let us shift (and rescale) the \( s \) field by putting

\[ \tilde{s}_j = \frac{1}{2}(s_j + \mu - \ln 2), \]  

(23)

and expand the logarithm in (22) in powers of \( \psi \) and \( \tilde{s} \). For \( \psi = 0 \) this shift eliminates the odd powers of \( \tilde{s} \) (of order higher than unity) from the expansion, thereby simplifying subsequent calculations. We will truncate the expansion at second order in \( \psi \), thus treating
the electrostatic interactions only at the DH limiting-law level. The expansion in \( \tilde{s} \) will be retained to fourth order: we assume \( \tilde{s}(r) \) to be the basic order-parameter field and, as in the usual LGW formulation,\(^{30,31}\) this is the minimum number of terms required to study simple critical points. The grand partition function then reads

\[
Z \approx \int \frac{D\psi Ds}{Z_1} \exp \left\{ -\frac{1}{2} \sum_{i,j} \psi(i) \left[ \varphi^{-1}(i,j) + \frac{\delta(i,j)}{2} \right] \psi(j) + \frac{1}{4} \sum_j (\tilde{s}_j - \frac{1}{3} \tilde{s}_3^3) \psi^2_j \\
- \bar{\mu} \sum_j \tilde{s}(j) - \frac{1}{2} \sum_{i,j} \tilde{s}(i) \left[ 4 \varphi^{-1}(i,j) - \delta(i,j) \right] \tilde{s}(j) - \frac{1}{12} \sum_j \tilde{s}_4^4 \right\},
\]

(24)

where we have put \( \bar{\mu} = 1 + 2 (\ln 2 - \mu) \sum_j \varphi^{-1}(0,j) \).

In order to perform the integration over the non-critical field \( \psi \), we rewrite the partition function in reciprocal space, replacing lattice sums by integrals, using

\[
\frac{1}{N} \sum_k \approx \int_\Omega \frac{d^3k}{(2\pi)^3} \equiv \int_k (N \to \infty),
\]

(25)

where \( \Omega \) is the first Brillouin zone of the reciprocal lattice.\(^{27,31}\) We further suppose that the Fourier transformed short-range potential is of the form\(^{24}\)

\[
\hat{\varphi}_s(k) \approx 4 J_0 (1 - R_0^2 k^2),
\]

(26)

where \( J_0 \) is related to the strength of the interaction (divided by \( k_B T \) and \( R_0 \) to the interaction range, both of which can be determined for a given model. The values of \( J_0 \) and \( R_0 \) affect the nonuniversal critical parameters (temperature, chemical potential and crossover temperature) but, as we will see below, estimates of the crossover temperature, \( t_\times \), may be obtained by examining various typical values for \( R_0 \). As in the discussion following (14), we have neglected in (26) higher order lattice terms, etc., of the form \( k^4 a^4 \), etc.

Finally, in terms of the ionicity \( I \), defined in (1) it is convenient to introduce the small perturbation parameter \( y \) and to rescale the \( \psi \) field in reciprocal space according to

\[
y^2 = 4 \pi I \equiv \frac{4 \pi}{T_\times}, \quad \tilde{\psi}(k) = \frac{\hat{\psi}(k)}{y}.
\]

(27)

[Since we are interested only in the critical region, we may, here, neglect the difference between \( T^* \) and \( T^*_c \), as used in (1).] The reduced Hamiltonian, \(-\hat{H}/k_B T\), in (24) then
becomes

\[
\mathcal{H} = -\frac{1}{2} \int \left( \frac{y^2}{2} + k^2 \right) |\tilde{\psi}(k)|^2 + \frac{y^2}{4} \int \int \hat{s}(k_1) \tilde{\psi}(k_2) \tilde{\psi}(-k_1 - k_2) \\
- \frac{y^2}{12} \int \int \int \hat{s}(k_1) \hat{s}(k_2) \hat{s}(k_3) \tilde{\psi}(-k_1 - k_2 - k_3 - k_4) - \Delta \mu_{sr} \tilde{\psi}(0) \\
- \frac{1}{2} \int \left( r_{sr} + \tau_{sr}^2 k^2 \right) |\hat{s}(k)|^2 - u_{sr} \int \int \hat{s}(k_1) \hat{s}(k_2) \hat{s}(k_3) \hat{s}(-k_1 - k_2 - k_3),
\]

(28)

where \(\Delta \mu_{sr} = 1 + (\ln 2 - \mu)/2 J_0\) while

\[
r_{sr} = \frac{1}{J_0} - 1, \quad \tau_{sr}^2 = \frac{R_0^2}{J_0}, \quad u_{sr} = \frac{1}{12},
\]

(29)

are the coefficients of the reduced Hamiltonian of the short-range uncharged fluid.

Now on integrating over \(\tilde{\psi}\) in the partition function (24), the coefficients of \(\hat{s}^n\) in \(\mathcal{H}\) become renormalized because the fields are coupled through the cubic and fifth order terms, \(\hat{s} \tilde{\psi}^2\) and \(\hat{s}^3 \tilde{\psi}^2\). This integration over \(\tilde{\psi}\) as a simple Gaussian field could be carried out exactly but it involves a nontrivial diagonalization of \(\mathcal{H}\) which is not required, since the resulting Hamiltonian is to be expanded only to fourth order in \(\hat{s}\), for consistency with the previous truncation. (However, the study of Brilliantov\textsuperscript{24} is instructive in this respect.) In fact, the simplest way to calculate the electrostatic corrections to the coefficients of \(\hat{s}^n\), is via perturbation theory using Feynman diagrams. To this end we write the partial reduced Hamiltonian

\[
\mathcal{H}_\psi = -\frac{1}{2} \int \left( \frac{y^2}{2} + k^2 \right) |\tilde{\psi}(k)|^2 + \frac{y^2}{4} \int \int \hat{s}(k_1) \tilde{\psi}(k_2) \tilde{\psi}(-k_1 - k_2) \\
- \frac{y^2}{12} \int \int \int \hat{s}(k_1) \hat{s}(k_2) \hat{s}(k_3) \tilde{\psi}(-k_1 - k_2 - k_3 - k_4),
\]

(30)

where the first term is simply Gaussian while we regard the second and third as the “interaction”.

A standard cumulant expansion\textsuperscript{30,31} yields the \(n\)-point correlation functions generated by the Gaussian propagator. By carrying the expansion out to fourth order, we obtain a
Hamiltonian for a single fluctuating field in the form
\[ H_0 = -\frac{1}{2} \int \left( r_0 + \tau_0^2 k^2 \right) |\hat{s}|^2 - v_0 \int \int \hat{s} \hat{s} \hat{s} - u_0 \int \int \int \hat{s} \hat{s} \hat{s} - \Delta \mu_0 \hat{s}_0. \]  

(31)

where the coefficients, renormalized by the electrostatic interactions, are given to leading orders by

\[ r_0 = r_{sr} - \frac{1}{8} y^4 I_2(y), \]

(32)

\[ \tau_0^2 = \tau_{sr}^2 + \frac{1}{8} y^4 I_{3,4}(y), \]

(33)

\[ v_0 = \frac{1}{12} y^2 I_1(y) - \frac{1}{48} y^6 I_3(y), \]

(34)

\[ u_0 = \frac{1}{12} [1 + \frac{1}{2} y^4 I_2(y) - \frac{3}{32} y^8 I_4(y)], \]

(35)

\[ \Delta \mu_0 = \Delta \mu_{sr} - \frac{1}{4} y^2 I_1(y). \]

(36)

If the first Brillouin zone of the reciprocal lattice is approximated by a sphere of radius \( \pi/a \) the propagator integrals, \( I_n(y) \), are given by

\[ I_n \approx \frac{1}{2 \pi^2} \int_0^\pi dx \frac{x^2}{(x^2 + y^2/2)^n}, \]

(37)

\[ I_{3,4} \approx \frac{1}{2 \pi^2} \int_0^\pi dx \left\{ \frac{x^2}{(x^2 + y^2/2)^3} - \frac{4 x^4}{3 (x^2 + y^2/2)^4} \right\}. \]

(38)

Clearly, when the ionicity vanishes, \( y \to 0 \), the coefficients \( r, \tau, \cdots \) reduce to those of the short-range, uncharged fluid.

Finally, the third order term in (31) may be eliminated in the usual way, \( \hat{s} \mapsto \hat{s} + v_0/4 u_0 \), yielding a standard short-range LGW Hamiltonian, namely,

\[ H_s = -\frac{1}{2} \int \left( r + \tau^2 k^2 \right) |\hat{s}|^2 - u \int \int \int \hat{s} \hat{s} \hat{s} - \Delta \mu \hat{s}_0. \]  

(39)

14
with coefficients,

\[ r = r_0 - \frac{3v_0^2}{4u_0}, \quad \tau^2 = \tau_0^2, \quad u = u_0, \quad \Delta \mu = \Delta \mu_0 - \frac{v_0 r_0}{4u_0} + \frac{v_0^3}{8u_0^3}. \]  \tag{40}

Accepting the limitations imposed and the approximations made, we are now in a position to study the effects of the electrostatic interactions on the critical behavior of a simple fluid. The easiest way to proceed, as indicated above, is to use the Ginzburg criterion to estimate the crossover temperature, \( t_x \), as a function of the ionicity \( \mathcal{I} \propto y^2 \). This criterion indicates the size of the temperature interval around the critical point outside which a mean-field description is self-consistent. For temperatures inside that interval the mean-field description breaks down and Ising behavior (in this case) should manifest itself. The temperature scale so set has become known as the Ginzburg temperature, \( t_G \), and it is reasonable to take it as an estimate of the crossover temperature, \( t_x \), although the presence of significant higher-order terms in (28) could undermine the practical validity of the criterion. In the next section we compare the Ginzburg temperatures of systems with finite ionicity (\( \mathcal{I} \propto y^2 > 0 \)) and without electrostatic interactions (\( y = 0 \)).

**IV. APPLICATION OF THE GINZBURG CRITERION**

The condition for a self-consistent mean-field description is that fluctuations of the field (calculated using the mean field) are much smaller than the typical or average mean field. For the \( s^4 \) Hamiltonian (39) studied below \( T_c \), this condition may be expressed conveniently as

\[ \frac{3\sqrt{2}}{\pi} \frac{u}{|r|^{1/2} \tau^3} \ll 1. \]  \tag{41}

Naturally, in deriving this, we have set \( \Delta \mu = 0 \), so that the critical point is approached along an axis of asymptotic symmetry. It is then appropriate to note that the short-range coefficient, \( r_{sr} \), can normally be written as

\[ r_{sr} = \frac{T - T_{c,0}}{T_{c,0}}, \]  \tag{42}

15
where $T_{c,0}^0$ is the mean-field critical temperature of the uncharged system. For a system with electrostatic interactions the mean-field critical temperature, $T_{c,0}(y)$, increases by an amount which follows from (32) and (40) as

$$ t_0(y) = \frac{T_{c,0}(y)}{T_{c,0}^0} - 1 = \frac{1}{8} y^4 I_2(y) + \frac{3 y_0^2}{4 u_0}, $$

(43)

We may use this result to rewrite the coefficient $r$ in (41) as

$$ r = \frac{T - T_{c,0}(y)}{T_{c,0}^0} = [1 + t_0(y)] t, $$

(44)

where $t = (T - T_{c,0})/T_{c,0}$ is the (mean-field) reduced temperature of the charged system. The Ginzburg criterion then becomes

$$ t_G(\mathcal{I}) \sim \frac{18}{\pi^2} \frac{u^2(y)}{[1 + t_0(y)] \tau(y)} \ll |t|, $$

(45)

which defines the reduced Ginzburg temperature, $t_G$. At this point the value of $t_G$ depends on the ionicity $\mathcal{I} = y^2/4\pi$ through $\tau(y)$, $u(y)$ and $t_0(y)$, as given in (33), (35), (40) and (43), respectively, and on the range, $R_0$ through $\tau_{sr}$. The dependence of $t_G$ on $J_0$ has dropped out since, using (29), one finds $\tau_{sr}^2 = [1 + t_0(y)] R_0^2$.

For the short-range uncharged system the Ginzburg temperature reduces to

$$ t_G(0) = \frac{1}{8\pi^2} \frac{a^6}{R_0^6}. $$

(46)

If, as a convenient and not unreasonable value, one adopts $R_0/a \simeq 0.4828$, one obtains $t_G(0) = 1$. For this particular short-range model, we have calculated the parameters of the reduced Hamiltonian (39) of the system with electrostatic interactions, as a function of the ionicity, $\mathcal{I}$. The results for $\tau$, $u$ and the shift in the mean field critical temperature of the system are plotted in Fig. 1, as functions of $\mathcal{I}$. The corresponding Ginzburg temperature, $t_G(\mathcal{I})$, is displayed in Fig. 2. The effective interaction range, $\tau$ increases monotonically with ionicity while the coefficient, $u$, of the fourth order term exhibits a maximum at $\mathcal{I} \simeq 3$ and decreases slowly at higher ionicities. However, within our Debye-Hückel limiting-law approximation, $u$ remains positive for all ionicities with, in fact, $u \rightarrow \frac{1}{12} (1 + \frac{1}{12} \pi) \simeq 0.105$ as
$y \to \infty$. As a result the Ginzburg temperature, $t_G$, varies nonmonotonically with ionicity, $\mathcal{I}$: see Fig. 2. A maximum, $t_G \simeq 1.03$, occurs at $\mathcal{I} \simeq 0.7$ indicating that, in general, the electrostatic interactions reduce (by up to $\simeq 30\%$) the interval around $T_c$ in which Ising critical exponents may be observed. Closer inspection of the behavior of $t_G$ with $\mathcal{I}$ reveals an initial drop off of $t_G$, as shown in the inset.

In order to check the robustness of these results, we have calculated the ratio of reduced Ginzburg temperatures, $t_G(y)/t_G(0)$, for other values of $R_0/a$ in the range 0.1 to 10 (corresponding to uncharged Ginzburg temperatures, $t_G(0)$, spanning 12 orders of magnitude). The results are plotted in Fig. 3. The behavior of the ratio of Ginzburg temperatures, $t_G(y)/t_G(0)$, varies with the particular value of $R_0$ but at ionicities $\mathcal{I} \geq 2$, a reduction of $t_G$ is found for all the systems. At low ionicities, however, the behavior of $t_G$ depends on the range of the nonionic interactions. The initial drop off is more rapid for low values of $R_0/a$. For the system with $R_0/a = 0.1$ a minimum value of $t_G$ is clearly visible.

In assessing the results shown in Figs. 1–3, the perturbative nature of our calculations must be borne in mind. The scale of probable validity in $\mathcal{I}$ may be guaged by noting that Monte Carlo results for the RPM\cite{22, 25, 27} the extreme limit of “complete ionicity,” indicate $\mathcal{I} \simeq 20.4$. Clearly our results are, at best, of qualitative validity when $\mathcal{I}$ exceeds, say, 5.

Finally, some contact with experimental results may be made by estimating the values of $\mathcal{I}$ using the observed reduced critical temperatures and other data: see Table I which presents the Ginzburg temperatures calculated for various experimental systems (assuming, for simplicity, $R_0/a = 0.4828$) and the corresponding, experimentally assessed\cite{14} crossover temperatures, $t_\times$. Realistic values of $\mathcal{I}$ lead to the prediction of reductions of the reduced Ginzburg temperature that correlate with the experimental data. However, our theoretical results for $t_G$ grossly underestimate the reductions in $t_\times$ observed in the real ionic systems listed.
V. DISCUSSION AND CONCLUSIONS

Starting with a Hamiltonian with attractive short-range as well as long-range Coulomb interactions, we have derived a field-theoretic description for a symmetric model with two coupled fluctuating fields, $\psi$ (conjugate to the charge density) and $s$ (conjugate to the number density). This lays a foundation on which to study explicitly the influence on critical properties of the ionicity, that is the strength of the Coulomb coupling relative to the short-range interactions. In an exploratory approach we expanded the weight function to second order in $\psi$, corresponding to a Debye-Hückel limiting-law level, and to fourth order in $s$, the usual LGW level. Finally, we integrated out the $\psi$ field so generating electrostatic corrections to the coefficients of $s^n$ in the final effective Hamiltonian, $\mathcal{H}_s$ — see (39) — in a systematic way.

We examined the perturbative effects of the electrostatic interactions on the near-critical behavior of a simple fluid by using the Ginzburg criterion to estimate the crossover temperature, $t_x$, as a function of the ionicity, defined more explicitly by $I = e^2/D a k_B T$: see (11). The calculations indicate that as $I$ increases, the effective range of interaction, $\tau$, increases slowly while the coupling of the fourth order term in $\mathcal{H}_s$, namely $u$, decreases for realistic values of $I$ and $R_0$ after an initial, relatively rapid transient. As a result, the relative Ginzburg scale, $t_G(I)/t_G(0)$, [see (17)] decreases with increasing $I$, by up to $20 - 30\%$ (within the approximations): see Fig. 3. This suggests that the expected domain of Ising-type behavior around $T_c$ should, likewise, be reduced by the presence of Coulombic forces.

Although we believe these results are interesting, one must certainly be cautious in applying them to real ionic systems. First, it is not certain that the Ginzburg criterion provides a sufficiently reliable measure of $t_x$. Indeed, despite the correct trend of $t_G$ with the ionicity $I$ seen in Table II, the predicted magnitudes of the reductions of $t_x$ are vastly smaller than observed in the real systems studied.

Second, in our perturbative treatment of the model the critical behavior is always driven by the short-range interactions, and only nonuniversal critical parameters are affected by
the electrostatic interactions. It is unlikely that such a mechanism describes satisfactorily the criticality of all real ionic systems. In fact, as argued by Pitzer\textsuperscript{13} there are chemical systems in which the ionic interactions are almost surely the principal determinants of the critical behavior. And, of course, in the restricted primitive model (RPM) only Coulombic forces act but a critical point is surely realized.\textsuperscript{14} Such systems clearly lie outside the range of validity of our truncated, perturbative treatment. Furthermore, as suggested both theoretically\textsuperscript{7,16–27} and by the experiments of Pitzer and Narayanan,\textsuperscript{15} Coulombic electrolytes of high ionicity may lie on a different global thermodynamic locus than do solvophobic systems such as we have sought to describe in our present approach.

Within the approximation presented, \( u \) never vanishes; however, it is possible that carrying the calculations to higher order\textsuperscript{24} would lead to negative \( u \) for sufficiently large ionicity. At a mean-field level in a simple lattice system that would suggest tricriticality\textsuperscript{38} and the presence of an “antiferromagnetic” or crystal phase. But, by any measure, one would then need to retain sixth and, possibly, higher order terms in the effective Hamiltonian\textsuperscript{38} and, in that case, a renormalization group treatment would seem necessary to elucidate the nature of the resulting transition(s)\textsuperscript{24,38} It should be forcibly stressed, however,\textsuperscript{7} that a tricritical point \textit{per se} cannot arise in a normal one- or two-component fluid system except by some special, nongeneric accident! (In a three-component system a tricritical point can occur but is characterized by a particular temperature, \( T_t \), and three fixed densities, say, \( \rho^t_A \), \( \rho^t_B \) and \( \rho^t_C \).)

The present approach has been extended\textsuperscript{39} to \textit{asymmetric} models with distinct short-range interactions, \( \varphi^{s+}_+(r) \), \( \varphi^{s+}_-(r) \) and \( \varphi^{s-}_-(r) \). The calculations yield an effective Hamiltonian very similar to that obtained by Nelson and Fisher\textsuperscript{38} in their study of metamagnets in the presence of an external magnetic field (which, when large enough, induces tricriticality). A renormalization group calculation employing the \( \epsilon \)-expansion has been performed\textsuperscript{39} it yields an unstable Gaussian fixed point, a symmetric Ising-type (Fisher-Wilson \( n=1 \)),\textsuperscript{30,31} fixed point, and two further \textit{asymmetric} Ising fixed points. In addition, a separatrix appears, at the \( s^4 \) level of approximation, that delimits a region of “runaway” flows: such behavior
requires proper study of the Hamiltonian with higher order terms retained. However, as hinted above, the significance of such flows within the context of fluid systems is unclear at this stage.

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Notice that estimates of the ionicity \( I \) based on experimental data are not very accurate since there are difficulties in measuring the effective ionic radius \( a \) that is needed in Eq.(1). The values of \( D, T_c \) and \( a \) for system (a) were taken from Refs. 12 and 37, for (b) and (c) from Refs. 12 and 15, and for (d) from Refs. 2 and 12. For system (e) we used the \( D \) and \( T_c \) from Ref. 10 and \( a \simeq 0.62 \text{ nm} \) from J. M. H. Levelt Sengers (private communication, dated November 1996).
### TABLE I. Experimental melting and critical temperatures, $T_m$ and $T_c$, in various solvents for three organic salts: (a) tetra-$n$-pentylammonium bromide; (b) triethyl $n$-hexyl ammonium triethyl $n$-hexyl boride; (c) tetra-$n$-butylammonium picrate.

| Salt                                      | $T_m$ (K)  | Solvent       | $T_c$ (K) |
|-------------------------------------------|------------|---------------|-----------|
| (a)                                       | $\sim 374.05$ | water         | 404.90    |
| (b)                                       | $\sim 251$ | diphenyl ether | 309–312   |
| (c)                                       | 364–365    | 1-choloroheptane | 404.4     |
|                                           |            | 1-tridecanol   | 342       |
|                                           |            | 1-dodecanol    | $\sim 332$ |
|                                           |            | 1,4-butanediol | $\sim 333$ |

### TABLE II. Experimentally assessed crossover temperatures, $t_x$, and reduced Ginzburg temperatures, $t_G$, calculated assuming an uncharged model with $R_0/a = 0.4828$ [or $t_G(0) = 1$] for (a) tetra-$n$-butylammonium picrate (TBAP) in 1-tridecanol (b) TBAP in 1-dodecanol (c) TBAP in 75% 1-dodecanol plus 25% 1,4-butanediol (d) Na in NH$_3$ (e) tetra-$n$-pentylammonium bromide in water.

| System                      | ionicity, $I$ | $t_x$        | $t_G$       |
|-----------------------------|---------------|--------------|-------------|
| uncharged fluid             | 0             | $O(1)$       | 1           |
| (a)                         | 17.9          | $\sim 10^{-3}$ | $\sim 0.712$ |
| (b)                         | 16.8          | $\sim 0.9 \times 10^{-2}$ | $\sim 0.717$ |
| (c)                         | 8.9           | $\sim 3 \times 10^{-2}$ | $\sim 0.777$ |
| (d)                         | 6.97          | $0.6 \times 10^{-2}$ | $\sim 0.807$ |
| (e)                         | $\sim 1.4$   | $O(1)$       | $\sim 1$   |
FIGURES

FIG. 1. (a) The effective interaction range, $\tau$, in the Hamiltonian as a function of the ionicity, $I$, for a system with $R_0/a = 0.4828$; (b) the fourth order coupling constant, $u$, in (39) as a function of the ionicity; (c) the reduced shift of the mean-field critical temperature, $t_0$. Notice that both $u$ and $t_0$ are independent of the value of $R_0/a$.

FIG. 2. The reduced Ginzburg temperature $t_G$ as a function of ionicity, $I$, for the short-range model of Fig. 1, which is described by $t_G(0) = 1$. The inset shows the behavior of $t_G$ close to the origin.

FIG. 3. Ratio of the Ginzburg temperatures calculated for a system of given ionicity to those for the corresponding short-range models $t_G(I)/t_G(0)$ for the cases $R_0/a = 0.1$ (dashed line), $= 0.2$ (dashed-dotted line), $= 0.4828$ (full line), and $= 10$ (dotted line).
Moreira, Telo da Gama and Fisher, Fig. 3

\[ \frac{t_G(I)}{t_G(0)} \]

\[ \begin{align*}
  & \text{1.0} \\
  & \text{0.8} \\
  & \text{0.6} \\
  & \text{0.4} \\
\end{align*} \]
Moreira, Telo da Gama and Fisher,
Fig. 1c
Moreira, Telo da Gama and Fisher,
Fig. 1a
Moreira, Telo da Gama and Fisher, Fig. 2
Moreira, Telo da Gama and Fisher,
Fig. 1b