Field-theoretic approach to ionic systems:
Criticality and tricriticality

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A Landau-Ginzburg functional of two order parameters (charge-density ϕ and mass-density deviation η) is developed in order to yield a field theory relevant to ionic lattice gases as well as a family of off-lattice models of ionic fluids that go beyond the restricted primitive model (RPM). In a mean-field (MF) approximation an instability of a uniform phase with respect to charge fluctuations with a wave-number $k \neq 0$ is found. This second-order transition to a charge-ordered phase terminates at a tricritical point (tcp). Beyond MF, a singularity of a mass correlation function for $k \to 0$ occurs at ion concentration lower than that of the MF tcp. An effective functional depending only on η is constructed. For low ion concentration the usual Landau form of the simple-fluid (Ising) functional is obtained; hence in this theory the critical point is in the Ising universality class.

I. Introduction

Over the past few years there has been growing interest in the critical behavior and phase separation of ionic fluids and of the Hamiltonian model that has been most widely used in trying to understand the experimental results, the restricted primitive model (RPM), which we shall discuss below. The interest stems in part from the fact that on the experimental side there has emerged no clear picture of universality in the critical behavior of these fluids of the sort that describes a wide variety of non-ionic fluids. For example, in a series of impressive experiments done on a family of ionic fluids, Narayanan and Pitzer[1] have obtained results consistent with Ising-like behavior. But within the family they studied, they encountered a wide range of reduced temperatures $t = (T - T_c)/T_c$ that mark the crossover from behavior well-described by mean-field theory to behavior that is Ising-like as one approaches the critical temperature T_c from above along the critical isochore. (Some of the crossovers come at much smaller t than encountered in the case of simple non-ionic fluids.) That means that not all members of the family can be well-described by the RPM; whatever the crossover temperature of the RPM, it is given by a single reduced temperature t according to the law of corresponding states.

Theoretical studies have revealed no simple ionic-fluid universality either. For example the most comprehensive simulation [2-4] and theoretical [5-12] studies both suggest that the critical point of the RPM [12-14] is a simple liquid-gas critical point, whereas studies of lattice-gas versions of the RPM [12-14] reveal that on simple cubic and body-centered cubic lattices one should expect tricriticality instead of simple criticality. This is in striking contrast to the situation one finds in non-ionic fluid models, where one has come to expect off-lattice and lattice models to share the same critical behavior. The shape of the phase diagram found in the continuous RPM from recent Monte Carlo simulations [2-4] is shown in Fig.1. The critical behavior revealed by these simulations is consistent with a critical point related to the density fluctuations that represents an instability with respect to

2

fluctuations of wave number $k = 0$. In the case of the RPM with the positions of the ions restricted to the lattice sites, i.e., a lattice RPM, quite different phase behavior has been found, both in simulation and in mean-field results [12-13] as well as in a general theoretical study [14]. From these references, what emerges is an instability of the uniform phase induced by charge fluctuations with wave number $k \neq 0$. The line of the second-order transition to the charge-ordered phase with the period $2\pi/k$ just below the transition (λ-line) appears to terminate at a tricritical point, which lies in a different range of densities and temperatures than the critical point found in the continuum-space RPM studies, as shown in Fig.2.

In order to better understand this question of universality in ionic-systems we have developed a field-theoretic approach for studying the boundary of stability of a uniform phase in such systems. As prototypic microscopic models we consider both the lattice and the continuous versions of the RPM. In our treatment the differences between the lattice and the continuous systems are reflected in different forms of the couplings in the Landau-Ginzburg (LG) functional, which has the same general structure in both cases. With our method we are able to reproduce the essential properties of ionic systems both for the continuous-space and the lattice RPM within one formalism. We can also include the effects of the short-range interactions between various species, i.e. extend our model beyond the RPM.

As in the earlier lattice RPM studies we have cited, an instability of the uniform phase with respect to charge fluctuations with $k \neq 0$ is already found at the mean-field level when we apply our approach to the lattice RPM. We find second-order and first-order transitions to a charge-ordered phase at temperatures above and below that of a tricritical point respectively. The density at the tricritical point is found to be 1/3 on the simplest mean-field level for both the lattice and the continuous versions of our LG functional. The structure of the charge-ordered phase depends on whether the positions of the ions are or

3

are not restricted to the lattice sites.

In addition to the instability induced by the charge-fluctuations with $k \neq 0$, an instability related to the mass-fluctuations with $k = 0$ occurs in a different region of thermodynamic space. This other instability, which has already been investigated on the mean-field level in the context of several standard ionic-fluid approaches applied directly to the continuum-space RPM [5-12] can be detected when the charge-fluctuations are integrated out in our formalism. We find an equation for the critical point consistent with the fluid-theory result found previously by one of us [7]. We also derive the effective functional depending only on density deviations from the average value, i.e. with the charge fluctuations integrated out. Near the critical point this functional has the same form as the "ϕ^4" functional representing the Ising universality-class. Hence in our treatment of the RPM model the critical point induced by the mass fluctuations belongs to the Ising universality class.

Since we find the tricritical point observed previously only in the lattice RPM as well as the liquid-gas type critical point found previously only in the continuous RPM our approach enables us to give a unified description of the continuum-model and lattice-model behavior of ionic systems. Moreover, it sharply reveals two distict transitions that can be driven by the Coulombic forces in such models. One is a transition from a charge-disordered to a charge-ordered phase. The other is a liquid-gas type transition that does not involve charge ordering at all. In the continuum-space version one expects at least two solid phases associated with different charge ordering [15] as well as the fluid phase, and it may be that the locus of charge-ordering transitions we find in our field theoretic versions of the RPM will occur in the continuum-space RPM as a solid-solid transition, or when one passes from a fluid to solid state. A reliable description of transitions involving solid phases of the continuum-space RPM that can be used to give a global-description of both its fluid and solid phases requires going beyond the treatment we have given here.

4

In lattice-gas versions of the RPM, the details of the charge ordering that can occur will surely depend sensitively upon the lattice geometry and upon the extent of the core of the interparticle potential excluding multiple occupancy of neighboring sites as well as a central site as they do in non-ionic lattice-gas models [16]. It seems likely that in some extended-core models, one will find both the liquid-gas-like criticality and phase separation characteristic of the continuum RPM as well as charge-ordering at higher densities involving phases that are also density ordered and hence solid-like. The lattice-gas version of the RPM and its extended-core generalization may well prove valuable in modelling the transitions one finds in the continuum-space RPM solid.

Beyond the RPM we find evidence that the position of the tcp is extremely sensitive to the strength of the additional, short-range interactions, as for example the interactions between the ions and the particles of the solvent. For reasonable values of the parameter describing the effect of these interactions in a simple extension of the RPM we find within our formalism that the tcp lies in the immediate vicinity of the cp found in the recent simulations, either slightly above or slightly below the cp in temperature, with its location depending very sensitively on the values of the parameter describing the effect of the short-range interactions. This raises the possibility that in some real ionic fluids in which there are substantial short-range interaction involving the solvent, one might find a tcp realizable in the liquid state or incipient as a tcp involving metastable liquid phases.

II. The functional in the case of RPM (no ion-solvent interactions)

Our choice is designed to be relevant to a lattice-gas version of the RPM as well as variants thereof, such as the standard off-lattice RPM and an extension that includes the effect of ion-solvent interactions.

In order to study criticality in ionic systems within a field-theoretic framework, we first construct an appropriate Landau-Ginzburg (LG) functional. We start the construction by calculating the grand thermodynamical potential Ω^{MF} in the MF approximation. For the

mixture Ω^{MF} has the form

$$\beta\Omega^{MF} = \beta F^h[\rho_\alpha(\mathbf{r})] + \beta\Big(U^{MF}[\rho_\alpha(\mathbf{r})] - \int d\mathbf{r}\mu_\alpha\rho_\alpha(\mathbf{r})\Big). \tag{1}$$

In the lattice case the integration in (1) should be replaced by a summation over the lattice sites, with the lattice constant a equal to the diameter of the ions. ρ_α and μ_α are the density and the chemical potential of the component α respectively and the summation convention for the repeated Greek indices is used. U^{MF} is the energy in the MF approximation. F^h is the Helmholtz free energy of the hard-core reference system, in the lattice (and ideal) case given by

$$\beta F^h = \sum_{\mathbf{x}} \rho_\alpha(\mathbf{x}) \log \rho_\alpha(\mathbf{x}). \tag{2}$$

In continuous models

$$F^h = \int d\mathbf{r} f^h[\{\rho_\alpha(\mathbf{r})\}] \tag{3a}$$

with

$$\beta\frac{\partial^2 f^h}{\partial\rho_\alpha\partial\rho_\beta} = \frac{\delta^{Kr}_{\alpha,\beta}}{\rho_\alpha} - c^h(\rho). \tag{3b}$$

Here we will limit ourselves to F^h given by (2). More accurate forms of F^h in the continuous models will affect the explicit expressions for the coupling constants of the final LG functional, but not its general structure.

For the RPM model $\alpha = +, -, 0$ correspond to a cation, an anion or a solvent particle (a 'hole') respectively, and Ω^{MF} can be expressed in terms of the local charge $\phi(\mathbf{r}) = \rho_+ - \rho_-$ and ion-mass $\rho(\mathbf{r}) = \rho_+ + \rho_- = 1 - \rho_0$ densities. The energy contributions to Ω^{MF} read:

in a continuum

$$U^{MF} - \mu_\alpha \int d\mathbf{r}\rho_\alpha(\mathbf{r}) = \frac{1}{2}\int d\mathbf{r} \int_{|\mathbf{r}-\mathbf{r}'|>a} d\mathbf{r}' V_c(\mathbf{r}-\mathbf{r}')\phi(\mathbf{r})\phi(\mathbf{r}') - \mu \int d\mathbf{r}\rho(\mathbf{r}) \tag{4a}$$

6

on a lattice

$$U^{MF} - \mu_\alpha \sum_{\mathbf{x}} \rho_\alpha(\mathbf{x}) = \frac{1}{2} \sum_{\mathbf{x}} \sum_{\mathbf{x}' \neq \mathbf{x}} V_c(\mathbf{x} - \mathbf{x}') \phi(\mathbf{x}) \phi(\mathbf{x}') - \mu \sum_{\mathbf{x}} \rho(\mathbf{x}), \tag{4b}$$

where $\mu = \mu_+ - \mu_0 = \mu_- - \mu_0$. $V_c(r) = q^2/(Dr)$, with q being the charge and D the dielectric constant, is the Coulomb potential. Note the restrictions on the integration in (4a) and the summation in (4b), which are necessary to avoid the self-energy contributions. These restrictions have a strong effect on the form of U^{MF} in the Fourier representation. It is convenient to introduce

$$V(r) = V_c(r)\theta(r - a). \tag{5}$$

Then, with V_c replaced by V, the integration in (4a) and the summation in (4b) are over the whole space, with no restrictions, and

$$U^{MF} = \int \frac{d\mathbf{k}}{(2\pi)^d} \tilde{V}(k) \tilde{\phi}(\mathbf{k}) \tilde{\phi}(-\mathbf{k}). \tag{6}$$

The tilde refers to the Fourier transform of the corresponding function. In the continuum version, an upper cutoff $\sim 2\pi/a$ is assumed as in standard theories, and in the lattice case the integral is strictly restricted to $\mathbf{k} = (k_1, k_2, k_3)$ such that $-\pi \leq k_i \leq \pi$ (k_i measured in units a^{-1}). The explicit forms of $\tilde{V}(k)$ are

in the continuum

$$\tilde{V}(\mathbf{k}) = 4\pi \frac{\cos k}{k^2}. \tag{7}$$

The restriction on integration in (4a), $|\mathbf{r} - \mathbf{r}'| > a$, results in the factor $\cos k$ multiplying the Fourier transform of the Coulomb potential.

on the lattice

$$\tilde{V}(\mathbf{k}) = 2\pi \left[\frac{1}{3(1 - f(\mathbf{k}))} - V_0 \right] \tag{8a}$$

$$V_0 = \int_{-\pi}^{\pi} \frac{dk_1}{2\pi} \cdots \int_{-\pi}^{\pi} \frac{dk_3}{2\pi} \frac{1}{3(1 - f(\mathbf{k}))} \tag{8b}$$

7

with

$$f(\mathbf{k}) = \frac{1}{3} \sum_{i=1}^{3} \cos k_i. \tag{8c}$$

The first term in (8a) is the Fourier transform of the Coulomb potential V_c and the second term results from the fact that the summation in (4b) is restricted to $\mathbf{x} \neq \mathbf{x}'$.

The Ω^{MF} assumes a minimum for the charge density $\phi = 0$ and the mass density $\rho = \rho_0^*$, and is next expanded in a power series in ϕ and $\eta = \rho - \rho_0^*$. Assuming that ϕ and η are both of small magnitude and vary slowly on the length scale of the lattice constant or particle core diameter a, we truncate the expansion and in the lattice case use a continuous approximation for Ω^{MF}.

The above procedure, described in more detail in [17], leads to a functional of the two-order parameter (OP) fields, ϕ and η, of the following form:

$$\Omega = \Omega_g + \Omega_{int} \tag{9a}$$

with the Gaussian part given by

$$\beta\Omega_g = \frac{1}{2!} \int d\mathbf{r} \left[a_2 \phi^2(\mathbf{r}) + A_2 \eta^2(\mathbf{r}) \right]$$
$$+ \frac{1}{2!} \int d\mathbf{r} \int d\mathbf{r}' \phi(\mathbf{r}) \beta V(|\mathbf{r} - \mathbf{r}'|) \phi(\mathbf{r}') \tag{9b}$$

and with

$$\beta\Omega_{int} = \int d\mathbf{r} \left[\frac{1}{3!} b_3 \phi^2(\mathbf{r}) \eta(\mathbf{r}) + \frac{1}{4!} a_4 \phi^4(\mathbf{r}) + h.o.t. \right] \tag{9c}$$

In the above r is a dimensionless distance, such that $a \equiv 1$; $h.o.t.$ stands for 'higher order terms'. In [17] we obtain for F^h given by (2):

$$a_2 = \rho_0^{*-1} \tag{10a}$$

$$A_2 = [\rho_0^*(1 - \rho_0^*)]^{-1} \tag{10b}$$

$$b_3 = -3\rho_0^{*-2} \tag{10c}$$

8

$$a_4 = 2\rho_0^{*-3} \tag{10d}$$

where we use the standard notation in which ρ_0^* is the dimensionless density ρa^3 and

$$\beta V(r) = \beta^* r^{-1}\theta(r - 1) \tag{10e}$$

with $\beta^* = T^{*-1} = \beta q^2/Da$. Higher-order couplings can also be expressed in terms of ρ_0^*.

The functional defined in Eqs. 9-10 is of lowest order in ϕ and η, allowing for studying boundary of stability of the uniform phase in ionic fluids within bifurcation analysis. Without the *h.o.t.*, however, Ω becomes unstable for $\phi, \eta \to \infty$. ¿From (9) one can easily see that the instability occurs if $\Delta = (b_3^2/3 - a_4 A_2)/12 \geq 0$ (or explicitly $\rho_0^* < 1/3$) and corresponds to $\phi, \eta \to \infty$ in such a way that $\eta = b\phi^2$ with $(-b_3/6 - \sqrt{\Delta})/A_2 \leq b \leq (-b_3/6 + \sqrt{\Delta})/A_2$. For one of the OP fixed, Ω remains finite for the other OP going to infinity. When the *h.o.t.* up to $O(\eta^4)$ are included, Ω becomes stable. Therefore at the later stage of our study (sec.V) we will also include the *h.o.t.* up to $O(\eta^4)$, which stabilize the functional.

In the Fourier space Ω_g has the representation

$$\beta\Omega_g = \frac{1}{2}\int d\mathbf{k}\left(\tilde{C}_{\phi\phi}^0(k)|\tilde{\phi}(\mathbf{k})|^2 + A_2|\tilde{\eta}(\mathbf{k})|^2\right) \tag{11a}$$

where

in the continuum

$$\tilde{C}_{\phi\phi}^0(k) = \rho_0^{*-1}\left(1 + 4\pi\beta^*\rho_0^*\frac{\cos k}{k^2}\right) \tag{11b}$$

on the lattice

$$\tilde{C}_{\phi\phi}^{0latt}(k) = \rho_0^{*-1}\left[1 + 2\pi\rho_0^*\beta^*\left(\frac{1}{3(1 - f(\mathbf{k}))} - V_0\right)\right]. \tag{11c}$$

As already discussed, in the lattice case the integral in (11a) is restricted to $-\pi < k_i < \pi$.

In simple fluids the short-wavelength fluctuations are irrelevant in the critical region, and the long-wavelength fluctuations occur with the same probability in the continuous and in the lattice systems. This is basically the reason of the universality of critical phenomena.

9

For $k \to 0$ i.e. for distances much larger than the lattice constant, both (11b) and (11c) are of the same form: $Ak^{-2} + B$. For the long-wavelength charge fluctuations both the lattice and the continuous systems behave in a similar way, as in the case of the simple fluids. Note, however that the long - wavelength fluctuations are strongly suppressed. The Boltzmann factor $\sim exp(-\beta\Omega[\phi, \eta])$, measuring the probability of fluctuations (ϕ, η), approaches zero for charge fluctuations $\tilde{\phi}(k \to 0)$ (see (11)). For a fluctuation $\tilde{\phi}(k)$ the charge neutrality is violated within regions of linear size $2\pi/k$ and the long-wavelength fluctuations are very rare. The relevant charge fluctuations are of finite wavelengths. A probability of a fluctuation $\tilde{\phi}(k)$ with k finite is different in the continuous and in the lattice case (compare (11b) and (11c)). In the RPM model the critical phenomena correspond to long-wavelength mass fluctuations, which are, however induced by the charge-fluctuations. Since the relevant charge-fluctuations are of short-wavelengths, and the probabilities of the short-wavelength fluctuations in continuum and on the lattice are different, one may expect differences between the lattice and the continuous systems.

III. MF results

Within the MF there is no ordinary critical point of a liquid-gas type, because the OP-s are decoupled in the Gaussian part Ω_g, and A_2 never vanishes. Rather, an instability of the uniform phase with respect to **charge** fluctuations $\tilde{\phi}(k)$ with $k \neq 0$ occurs when $\tilde{C}^0_{\phi\phi}(k) = 0$. The boundary of stability of the uniform phase corresponds to the highest temperature for which $\tilde{C}^0_{\phi\phi}(k)$ vanishes. The bifurcation lines are

in the continuum

$$T_b^*(\rho_0^*) = \frac{2\pi \sin k_b}{k_b} \rho_0^*. \tag{12a}$$

where the wave number corresponding to bifurcation is given by

$$\tan k_b = -\frac{2}{k_b} \tag{12b}$$

10

from which one obtains $k_b \approx 2.46$ and the slope of the bifurcation line ≈ 1.61.

on the lattice

$$T_b^* = 2\pi \left(V_0 - \frac{1}{6} \right) \rho_0^* \tag{13a}$$

and the wave vector at the bifurcation is

$$\mathbf{k}_b = (\pm\pi, \pm\pi, \pm\pi). \tag{13b}$$

The line of a continuous transition to a charge-ordered phase becomes first order at a **tricritical point** (tcp). To find the position of the tcp we first minimize Ω with respect to η. From the condition $\delta\Omega/\delta\eta = 0$, we can express η in terms of ϕ,

$$\eta(\mathbf{r}) = \eta_0(\mathbf{r}) = -\frac{b_3}{3!A_2}\phi^2(\mathbf{r}) \tag{14}$$

and in the vicinity of the bifurcation we have

$$\beta\Omega = \frac{1}{2} \int \frac{d\mathbf{k}}{(2\pi)^d} \tilde{C}_{\phi\phi}^0(k)|\tilde{\phi}(\mathbf{k})|^2$$
$$+ \frac{A_4}{4!} \int \frac{d\mathbf{k}_1}{(2\pi)^d} \int \frac{d\mathbf{k}_2}{(2\pi)^d} \int \frac{d\mathbf{k}_3}{(2\pi)^d} \int \frac{d\mathbf{k}_4}{(2\pi)^d} (2\pi)^d \delta(\sum_{i=1}^{4} \mathbf{k}_i) \prod_{i=1}^{4} \tilde{\phi}(\mathbf{k}_i) + O(\epsilon^6) \tag{15}$$

where

$$\mathcal{A}_4 = a_4 - \frac{b_3^2}{3A_2} = 3\rho_0^{*-3} \left(\rho_0^* - \frac{1}{3} \right), \tag{16}$$

ϵ is the bifurcation parameter, $\epsilon \sim \sqrt{|T^* - T_b^*|/T_b^*}$, such that $\tilde{C}_{\phi\phi}^0(k) = O(\epsilon^2)$. At local minima of Ω ($\delta\Omega/\delta\phi = 0$ and $\delta\Omega/\delta\eta = 0$) $\phi = O(\epsilon)$ and $\eta = O(\epsilon^2)$. ¿From the above we find that the tcp occurs at $\rho_{0t}^* = 1/3$ for the model given by (9) -(10).

Just below the bifurcation various metastable structures can be described as linear combinations of planar waves

$$\phi(\mathbf{r}) = \Phi \cos(\mathbf{k}_b \cdot \mathbf{r}) \tag{17}$$

where $\hat{\mathbf{k}}_b$ is a direction of oscillations and the amplitude is $\Phi = O(\epsilon)$.

on the lattice

$\mathbf{r} = (r_1, r_2, r_3)$ are restricted to integer r_i. For the integer r_i (17) and (13b) give $\phi(\mathbf{r}) = \pm\Phi$. Thus two sublattices, one positively- and the other one negatively charged occur. A charge-ordered phase with such a structure has been also found directly in the lattice RPM in MF results and in Monte Carlo simulations [12,13].

in the continuum

To determine the structure stable just below the continuous transition, one has to find for what linear combinations of planar waves (17) Ω assumes the global minimum. For example, the structure of ionic crystal (like NaCl) corresponds to a superposition of four waves, with the four vectors $\hat{k}_b$ forming a tetrahedron [17]. In [17] we verify by explicit calculations of Ω approximated by (15) and (16) that for a single wave (17), i.e. for a lamellar structure, Ω assumes a lower value than for the other structures. Formation of charged layers, with the neighboring layers oppositely charged, is energetically favorable compared to the disordered phase when the average distance between alike ions within one layer is larger than the distance between oppositely charged layers. The ratio between the average distance between the ions within one layer and the distance between oppositely charged layers can be estimated on the basis of ρ_0^* and the period of modulations $\lambda = 2\pi/k_b \approx 2.55a$. Near the tcp this ratio is $\geq \sqrt{(2/\lambda)^3/\rho_0^*} \approx 1.2$.

We should stress here that for $a \to 0$ (or with $\theta(r-1)$ in (2e) omitted), i.e. for point charges, no such instability takes place, because then $\tilde{C}_{\phi\phi}^0(k) > 0$, and consistently, $\lambda \to 0$ for $a \to 0$. Note also that the tcp lies far away from the critical point (cp), for which the latest simulation estimate is [2-4] $(\rho_c^*, T_c^*) \approx (0.08, 0.05)$.

The charge-charge correlation function in the MF approximation, $\tilde{G}_{\phi\phi}^0 = \tilde{C}_{\phi\phi}^{0-1}$, never diverges for $k \to 0$, rather, $\tilde{G}_{\phi\phi}^0 \to 0$ for $k \to 0$ (see (11b) and (11c)), i.e. $\int dr G_{\phi\phi}^0(r) = 0$. By inspection of Eq.(11b) and (11c) for $k \to 0$ we can easily identify the inverse Debye screening length $\kappa a = \sqrt{4\pi\rho_0^*\beta^*}$, describing the decay of the charge-charge correlations.

IV. Critical mass fluctuations

Although there is no 'ordinary' criticality within the MF, the charge fluctuations may lead to the critical behavior of the mass-mass correlation function for $k \to 0$, because the two OP-s are coupled beyond the Gaussian part of Ω. Fluid theories [5-12] and simulations [2-4] predict low ρ^* at critical; thus we concentrate on $\rho_0^* < \rho_{0t}^* = 1/3$.

In order to determine whether the criticality of the liquid-gas type occurs in this model, we calculate the correlation function for the mass fluctuations $G_{\eta\eta}$, defined as

$$G_{\eta\eta}(\mathbf{r}_1, \mathbf{r}_2) = \langle \eta(\mathbf{r}_1)\eta(\mathbf{r}_2) \rangle - \langle \eta(\mathbf{r}_1) \rangle \langle \eta(\mathbf{r}_2) \rangle, \tag{18}$$

in standard perturbation expansion about the Gaussian solution. Next we examine the behavior of the Fourier transform of $G_{\eta\eta}$ for $k \to 0$, searching for singular behavior.

The most probable mass fluctuation $\eta_0(\mathbf{r})$, accompanying a given charge fluctuation $\phi(\mathbf{r})$, is given by (14) (if the h.o.t. in (9) are included, $\eta_0(\mathbf{r})$ contains additional contributions of a form $\sim \phi^{2n}$[17]). Arbitrary mass fluctuation can be written as $\eta = \eta_0 + \Delta\eta = -\frac{b_3}{3!A_2}\phi^2 + \Delta\eta$. The functional $\Omega[\phi, \eta]$ given by (9) can be expanded about the minimum at η_0. Then the functional of $\phi, \Delta\eta$ is obtained

$$\beta\Omega[\phi, \Delta\eta] = \beta\Omega_{aux}[\phi] + \frac{1}{2}A_2 \int dr(\Delta\eta(r))^2 + O(\Delta\eta^4). \tag{19}$$

$\Omega_{aux}[\phi]$ is given by (15), or in the real space representation by

$$\beta\Omega_{aux} = \int dr \left(\frac{1}{2} \int dr' C_{\phi\phi}^0(|\mathbf{r} - \mathbf{r}'|)\phi(\mathbf{r})\phi(\mathbf{r}') + \frac{1}{4!}\mathcal{A}_4\phi^4(\mathbf{r}) + O(\phi^6) \right) \tag{20}$$

It is convenient to introduce the functional (19), because A_2 is just a constant in this model and $\Delta\eta(\mathbf{r})$ contribute only to local parts of the mass-mass correlation functions. The nonlocal correlations, relevant in the critical region, are determined by the auxiliary functional Ω_{aux} (20), depending only on the single OP ϕ.

In this description the one- and n-point correlation - functions for mass fluctuations can be expressed in terms of average values of the field $\phi^2(\mathbf{r})$ and of a product of ϕ^2

13

at n points, respectively. The explicit relations for the nonlocal parts of the correlation functions read

$$\langle \eta(\mathbf{r}) \rangle = -\frac{b_3}{3!A_2} \langle \phi^2(\mathbf{r}) \rangle_{aux} \tag{21a}$$

$$G_{\eta\eta}^{nl}(\mathbf{r}_1, \mathbf{r}_2) = \left(\frac{b_3}{3!A_2} \right)^2 G_{\phi^2\phi^2}(\mathbf{r}_1, \mathbf{r}_2) \tag{21b}$$

where

$$G_{\phi^2\phi^2}(\mathbf{r}_1, \mathbf{r}_2) = \langle (\phi^2(\mathbf{r}_1) - \langle \phi^2(\mathbf{r}_1) \rangle_{aux})(\phi^2(\mathbf{r}_2) - \langle \phi^2(\mathbf{r}_2) \rangle_{aux}) \rangle_{aux} \tag{21c}$$

and

$$G_{\eta\eta}^{nl}(\mathbf{r}_1, ..., \mathbf{r}_n) = \left(\frac{b_3}{3!A_2} \right)^n G_{n\phi^2}(\mathbf{r}_1, ..., \mathbf{r}_n) \tag{22}$$

In the above $G_{n\phi^2}$ is defined in a way similar to the definition of $G_{\phi^2\phi^2}$ in Eq.21c. $\langle ... \rangle_{aux}$ means averaging with the Boltzmann factor $\sim \exp(-\beta\Omega_{aux})$.

In order to find the critical point we consider $G_{\phi^2\phi^2}$, which is just proportional to $G_{\eta\eta}^{nl}$, in the perturbation expansion and verify whether there occur singular contributions for $k \to 0$. $G_{\phi^2\phi^2}(\mathbf{r}_1, \mathbf{r}_2)$ can be expressed, in the standard way [18], in terms of Feynmann diagrams of the connected four-point function, with the vertex $\mathcal{A}_4$ and the free - propagator $G_{\phi\phi}^0$, in which two pairs of external points are identified with each other. Next the Fourier transform for every diagram is calculated. Because $\tilde{G}_{\phi\phi}^0(k)$ is regular for $k \to 0$, and even tends to zero (see Eqs.(11b) and (11c)), every individual diagram is regular for $k \to 0$; hence, any finite sum of diagrams is regular as well.

From Eq. (16) we see that the effective coupling constant $\mathcal{A}_4$ is **negative** for $\rho_0^* < 1/3$, i.e. for densities lower than the tcp density. The negative $\mathcal{A}_4$ is of crucial importance for the behavior of $\tilde{G}_{\phi^2\phi^2}$. For illustration consider a Fourier transform of a series of chains of loops, with the n-th order term (n vertices $\mathcal{A}_4$ and n+1 loops) given by

$$\alpha_n(k) = (-\mathcal{A}_4)^n \tilde{g}_0^{n+1}(k) \tag{23a}$$

with

$$\tilde{g}_0(k) = \frac{1}{2} \int d\mathbf{r} G_{\phi\phi}^0(r)^2 e^{i\mathbf{k}\mathbf{r}} = \frac{1}{2} \int d\mathbf{k}' \tilde{G}_{\phi\phi}^0(\mathbf{k}') \tilde{G}_{\phi\phi}^0(\mathbf{k} - \mathbf{k}'). \tag{23b}$$

14

A contribution to $\tilde{G}_{\phi^2\phi^2}$ given by the sum of such diagrams has a form

$$\sum_0^\infty \alpha_n(k) = \tilde{g}_0(k) \left[1 + \mathcal{A}_4\tilde{g}_0(k)\right]^{-1}. \tag{24}$$

In the part of (ρ_0^*, T^*) to which we restrict our attention here, $\tilde{g}_0(k)$ is a smooth function (see (23b) and (11b),(11c)). For $\mathcal{A}_4 < 0$, however, (24) represents a singular contribution to $G_{\eta\eta}^{nl}$ for $k \to 0$ if

$$1 + \mathcal{A}_4\tilde{g}_0(0) = 0. \tag{25}$$

The above equation is the lowest order approximation for the critical singularity. A more accurate equation has a form

$$1 + \mathcal{A}_4\tilde{g}(0) = 0, \tag{26}$$

where $\tilde{g}(k)$ is a Fourier transform of the function representing a sum of all connected diagrams of four-point functions with two pairs of external points identified, which cannot be split into two distinct diagrams by splitting a single hyper-vertex $\mathcal{A}_4$ into two two-point vertices. In other words, $g(r)$ has no contributions which are of a form of chains; g_0 is the lowest order approximation for g. For $\rho_0^* \to 0$ and with $g(\mathbf{r})$ approximated by $G_{\phi\phi}^2(\mathbf{r})/2$, where $G_{\phi\phi}$ is the charge-charge correlation function, (26) reduces to an equation obtained previously by one of us within fluid theory [7].

By summing up a related geometric series (as in Eqs.(23a) and (24), with g_0 replaced by g) we obtain a more accurate form of the singular part of $G_{\eta\eta}^{nl}$, which we will denote by $\tilde{G}_{\eta\eta}^0$,

$$\tilde{G}_{\eta\eta}^0(k) = \tilde{g}(k) \left[1 + \mathcal{A}_4\tilde{g}(k)\right]^{-1}. \tag{27}$$

In the critical region we can expand $\tilde{C}_{\eta\eta}^0(k) = \tilde{G}_{\eta\eta}^0(k)^{-1}$ about $k = 0$ and we obtain

$$\tilde{C}_{\eta\eta}^0(k) = \alpha_0 + \alpha_2 k^2 \tag{28}$$

with α_0 and α_2 expressed in terms of $\tilde{g}(0)$ and $\tilde{g}(0)''$ in a standard way.

15

Consider the higher-order mass - correlation functions $G_{n\eta}^{nl}$ and related vertex functions $\Gamma_{n\eta}$ for $n \geq 3$ and with the two-point function approximated by (27)

$$G_{n\eta}^{nl}(\mathbf{r}_1,...,\mathbf{r}_n) = -\int d\mathbf{r}'... \int d\mathbf{r}^n \Gamma_{n\eta}(\mathbf{r}',...,\mathbf{r}^n) \times$$
$$G_{\eta\eta}^0(\mathbf{r}_1,\mathbf{r}')...G_{\eta\eta}^0(\mathbf{r}_n,\mathbf{r}^n) \tag{29}$$

Unless the terms $\sim \phi^6, \sim \phi^8$ are explicitly included in (9), there are no contributions to $\Gamma_{n\eta}$ at the zero-loop level. At the one-loop approximation, for $\Gamma_{3\eta}$, for example, we have

$$\Gamma_{3\eta}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = G_{\phi\phi}^0(\mathbf{r}_1,\mathbf{r}_2)G_{\phi\phi}^0(\mathbf{r}_2,\mathbf{r}_3)G_{\phi\phi}^0(\mathbf{r}_3,\mathbf{r}_1) \cdot \text{num.fac.} + O(2-\text{loop}) \tag{30}$$

and similarly for $n > 3$. After integration (30) yields

$$\Gamma_n = \int d\mathbf{r}_1...d\mathbf{r}_n \Gamma_{n\eta}(\mathbf{r}_1,...,\mathbf{r}_n) \sim \tilde{G}_{\phi\phi}^0(0)^n = 0 \tag{31}$$

Higher-order contributions to Γ_n also contain a factor $\tilde{G}_{\phi\phi}(0) = 0$. Hence, for $n \geq 3$ Γ_n give negligible contribution to the effective potential [18].

In the perturbation expansion for the charge-charge correlations $\tilde{G}_{\phi\phi}(k)$, every Feynmann diagram in the Fourier representation contains a factor $\tilde{G}_{\phi\phi}^{0n}(k)$ with $n \geq 1$, which for $k = 0$ vanishes. In an infinite series of diagrams, similar to those which lead to divergent mass correlations, a segment of a corresponding chain for $\tilde{G}_{\phi\phi}$ is proportional to $\tilde{G}_{\phi\phi}^0(k)$. The infinite series of Feynmann diagrams gives a contribution to charge-charge correlations which vanishes for $k \to 0$ (compare (24) with $\tilde{g}_0(k)$ replaced by a term proportional to $\tilde{G}_{\phi\phi}^0(k)$). Hence the charge-correlation length remains finite at the critical point, at which the mass-correlation length diverges. For details, see [17].

V. Construction of the effective functional for $\rho_0^* < 1/3$

In order to construct an appropriate effective functional depending only on η in the critical region, we recall that Ω given by (9) without the $h.o.t.$ is unstable for $\phi, \eta \to \infty$ with $\eta \sim \phi^2$ if $\rho_0^* < 1/3$. We thus include the terms stabilizing Ω and we consider the functional

$$\mathcal{F}[\phi,\eta] = \Omega[\phi,\eta] + \Omega_\eta[\eta] \tag{32a}$$

16

with

$$\Omega_\eta[\eta] = \int d\mathbf{r} \left(\frac{A_3}{3!} \eta(\mathbf{r})^3 + \frac{A_4}{4!} \eta(\mathbf{r})^4 \right) \tag{32b}$$

where, by construction of the functional [17]

$$A_3 = \frac{1}{(1 - \rho_0^*)^2} - \frac{1}{\rho_0^{*2}} \tag{32c}$$

$$A_4 = 2 \left[\frac{1}{(1 - \rho_0^*)^3} + \frac{1}{\rho_0^{*3}} \right] \tag{32d}$$

if F^h is approximated by (2).

The effective functional of η is formally defined by

$$e^{-\beta\Omega_{eff}[\eta]} = \int D\phi e^{-\beta\mathcal{F}[\phi,\eta]} = e^{-\beta\Omega_\eta[\eta]} \int D\phi e^{-\beta\Omega[\phi,\eta]}. \tag{33}$$

Thus,

$$\Omega_{eff}[\eta] = \Omega_\eta[\eta] + \mathcal{F}_0[\eta] \tag{34a}$$

with

$$e^{-\beta\mathcal{F}_0[\eta]} = \int D\phi e^{-\beta\Omega[\phi,\eta]} \tag{34b}$$

It is not possible to perform the functional integration in (34b) exactly, but it is also not necessary for the purpose of characterizing the mass-correlation singularity. We only need an approximate functional, which leads to the same behavior of the correlation functions at large distances in the critical region that the full $\mathcal{F}$ does. The above-described analysis of the critical behavior of the correlation functions leads to

$$-\beta\mathcal{F}_0[\eta] = \int d\mathbf{k} \left[\frac{\tilde{C}_{\eta\eta}^0(k)}{2} \eta(\mathbf{k})\eta(-\mathbf{k}) - A_1\eta(\mathbf{k}) \right] + \text{corr.} \tag{35}$$

where $\tilde{C}_{\eta\eta}^0(k)$ is given by (28) and

$$A_1 = -\frac{b_3}{3!A_2} \langle\phi^2\rangle_{aux} \tilde{C}_{\eta\eta}^0(0) \tag{36}$$

17

With the above form of $\mathcal{F}_0$ both the two-point mass correlations (27) and $\langle \eta \rangle$ given by (21a) are recovered. Terms $\sim \eta^n$ with $n \geq 3$ are neglected in (35). As usual, for small amplitude fluctuations such terms are negligible compared to terms $\sim \eta^2$, except for the critical fluctuations for which the second-order term vanishes at the critical point. For such fluctuations, i.e. $\eta(\mathbf{r}) = const$, however, the higher-order contributions to $\mathcal{F}_0$ vanish (unless the terms $O(\phi^6), O(\phi^8)$ are explicitly included in $\Omega[\phi, \eta]$, see (31)).

By shifting and rescaling the field,

$$\psi(\mathbf{r}) = \left(\eta(\mathbf{r}) + \frac{A_3}{A_4} \right) \sqrt{\alpha_2} \tag{37}$$

we obtain from (34a), (32b) and (35) a familiar form of the Ising universality-class functional, namely

$$\Omega_{eff}[\psi] = \int d\mathbf{r} \left[-h\psi(\mathbf{r}) + \frac{u_2}{2}\psi(\mathbf{r})^2 + \frac{1}{2}(\nabla\psi(\mathbf{r}))^2 + \frac{u_4}{4!}\psi(\mathbf{r})^4 \right] + h.o.t. \tag{38a}$$

with explicit expressions for the couplings corresponding to the functional (32) and (9) given by

$$h = \left(A_1 + \frac{A_3}{A_4}\alpha_0 - \frac{A_3^3}{3A_4^2} \right) \alpha_2^{-1/2} \tag{38b}$$

$$u_2 = \left(\alpha_0 - \frac{A_3^2}{2A_4} \right) \alpha_2^{-1} \tag{38c}$$

and

$$u_4 = A_4 \alpha_2^{-2} \tag{38d}$$

Higher-order contributions to (32) would modify the couplings, but otherwise would have no qualitative effect especially on the universality class. For the present model the critical point in the MF approximation is given by $h(\rho_0^*, \beta^*) = u_2(\rho_0^*, \beta^*) = 0$. Both h and u_2 are mixed fields [19] and near the cp can be expressed as linear combinations of $\delta T^* = T^* - T_c^*$ and $\delta\rho_0^* = \rho_0^* - \rho_{0,c}^*$. The density of ions is $\rho^* = \rho_0^* + <\eta>$. Its deviation from the critical value, $\delta\rho^*$, can also be represented as a similar linear combination. If ρ^* is fixed at the

18

critical value (critical isochore), $\delta\rho^* = 0$, then $\delta\rho_0^*$ is proportional to δT^* in the vicinity of the cp and $u_2 \sim \delta T^*$. In this case, i.e. along the critical isochore, the linear field h vanishes [17]. We have thus mapped our model near the cp onto the usual "ϕ^4" functional, representing the Ising universality class.

Both h and u_2 depend on β^* through α_0 and α_2, which in turn are functions of $\tilde{g}(0)$ and $\tilde{g}(0)''$ (see Eq.(28) and below). The function $\tilde{g}(k)$ is determined by the charge fluctuations, and for $k \to 0$ depends on the whole spectrum of the fluctuations, as one can see from the lowest-order approximation for $\tilde{g}$, $\tilde{g}_0$, given by Eq.(23b). Because of that dependence of $h(\rho_0^*, T^*)$ and $u_2(\rho_0^*, T^*)$ on the shape of $\tilde{G}_{\phi\phi}^0(k)$, the position of the cp, $h = u_2 = 0$, also depends on the form of $\tilde{G}_{\phi\phi}^0(k)$. In particular, for different systems, characterized in our theory by different forms of $\tilde{G}_{\phi\phi}^0$ (as, for example, the continuous (11b) and the lattice (11c) models) the relative locations of a possible cp signaling an Ising-like transition and a possible locus of transitions to a charge-ordered phase can be quite different. As a result, one or the other of these transitions can be preempted by the occurrence of the other. Thus the continuum-space RPM fluid appears to support only the cp while the cubic lattice-gas RPM appears to support only the charge-ordering transition with an attendant tcp. It will require analysis beyond that given here to locate the cp in our field-theoretic approach.

VI. Beyond the RPM (short-range interactions included)

Here we limit ourselves to the continuous case. The lattice case and the systematic analysis will be described in Ref.[17]. On our level of description the short-range interactions, including those between the ions and the solvent, can be represented by terms $a_2\xi_\phi^2(\nabla\phi)^2/2$ and $A_2\xi_\eta^2(\nabla\eta)^2/2$ as in standard Landau theories for short-range interactions. In general, a_2 and A_2 differ from those of Eq.(10), which refers to the absence of the short-range interactions. ξ_ϕ and ξ_η are the (MF) spin and mass correlation lengths, respectively, in a system with the Coulomb interactions turned off. They should be thus comparable to the typical distance between the ions and the particles of the solvent. For

our length unit both should be thus of order of unity. Here we restrict ourselves to the case of a_2 and A_2 given by (10a) and (10b) and to a single length $\xi = \xi_\phi = \xi_\eta$, to illustrate on the simplest level the crucial role of the interactions beyond the RPM on the position of the λ-line and the tricritical point.

The bifurcation analysis of the extended functional (9), which in addition contains the terms $a_2\xi^2(\nabla\phi)^2/2$ and $A_2\xi^2(\nabla\eta)^2/2$, gives the generalization of Eq.(12) for the bifurcation line

$$\tan k_b = -2\frac{1 + 2\xi^2 k_b^2}{k_b(1 + \xi^2 k_b^2)} \tag{39a}$$

and

$$T_b^*(\rho_0^*) = 2\frac{\pi \sin k_b}{k_b(1 + 2\xi^2 k_b^2)}\rho_0^*. \tag{39b}$$

The tcp is very sensitive to the changes of ξ and is given by the analysis of [17] as

$$\rho_{tcp}^* = \frac{1}{3 + 8\xi^2 k_b^2}. \tag{40}$$

For $\xi = 1$, for example, $\rho_{tcp}^*(\xi = 1) = 0.026$ and $T_{tcp}^*(\xi = 1) = 0.007$, which is well below the cp (compare the position of the tcp in the absence of the ion-solvent interactions, $\rho_{tcp}^*(\xi = 0) = 1/3$ and $T_{tcp}^*(\xi = 0) = 0.54$).

In the case of ions large compared to the particles of the solvent, as for example in the system $N_{2226}B_{2226}$ studied by several groups [20] a reasonable estimate for the typical distance between the ions and the particles of the solvent should be around 0.5. From (40) and (39) we find the tcp for two slightly different values of ξ, $\xi = 0.5$ and $\xi = 0.55$ at $(\rho^*, T^*) = (0.08, 0.055)$ and $(0.07, 0.043)$ respectively. Note that in the first case the tcp lies slightly above the RPM cp=(0.08, 0.05), actually found in the simulations [2-4], whereas in the second case the tcp lies below the observed cp.

It is important to note the approximations and assumptions we are making in using (39) and (40) as we do. There are precise values of ξ_ϕ and ξ_η associated with each thermodynamic state in our system and, in particular, with the states along the bifurcation

line associated with (39) and the tcp associated with (40). We do not know these precise values, however, so we make simple estimates of their magnitudes and then see how sensitive the tcp T^* and ρ^* that come out of (39) and (40) are to slight changes in ξ. We find great sensitivity, which suggests that the tcp location is very sensitive to the interaction parameters upon which the ξ_ϕ and ξ_η depend.

Whether a similar sensitivity of the cp location upon these parameter values exists is an important question that we cannot probe on the basis of our results here but which is deserving of further work. Such a sensitivity might help explain the remarkable disparities that different groups [20] have found in the cp location in $N_{2226}B_{2226}$ samples. An even more dramatic possibility is raised by the observation that comes out of our work that depending on the details of the short-range interactions in an ionic system one might have both a cp and a tcp [as in Fig. 3] or only one of these occuring in stable equilibrium, with the other describing metastable criticality that lies within the coexistence region defined by the stable singular point [as in Fig. 4]. We report further details in [17].
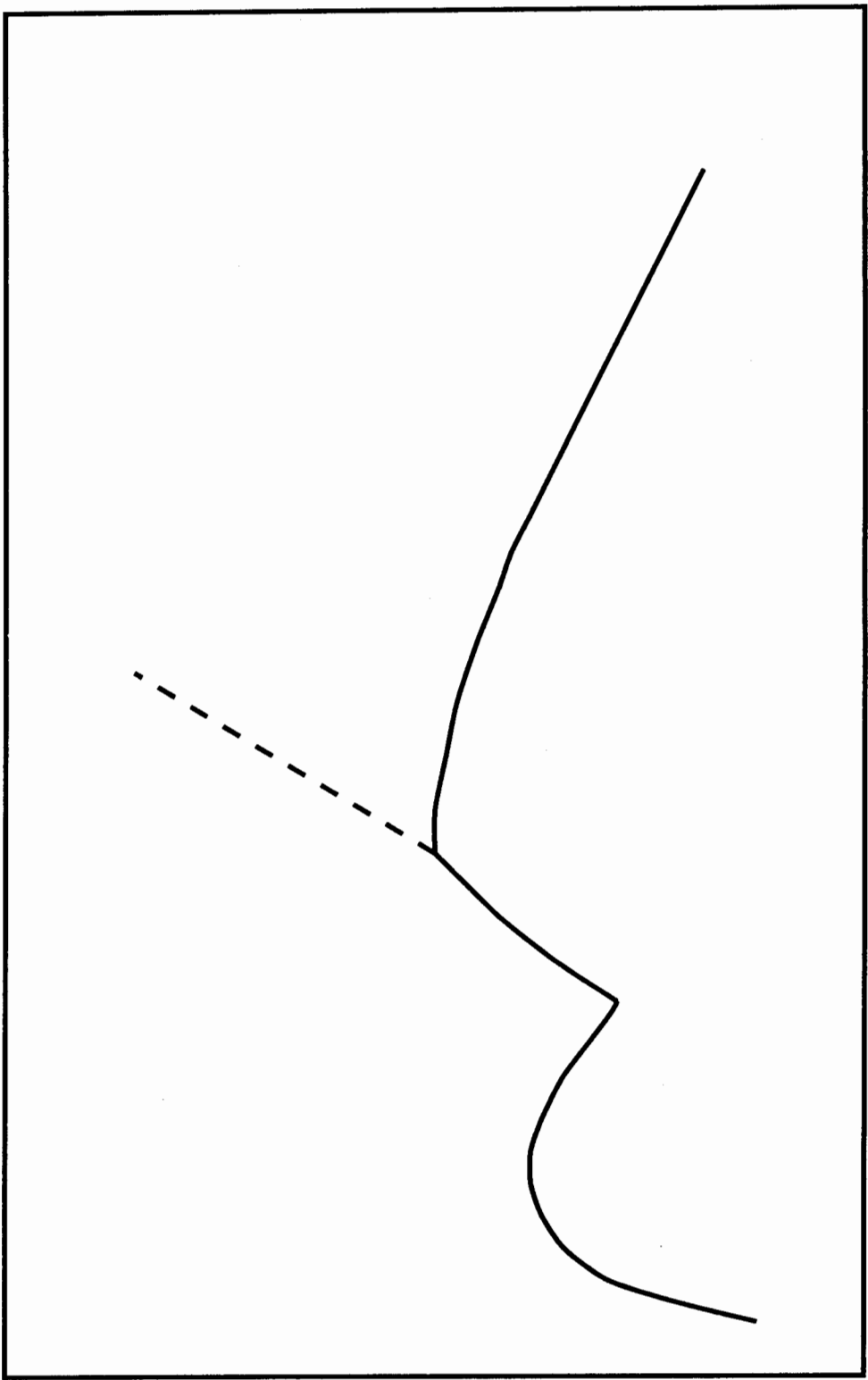
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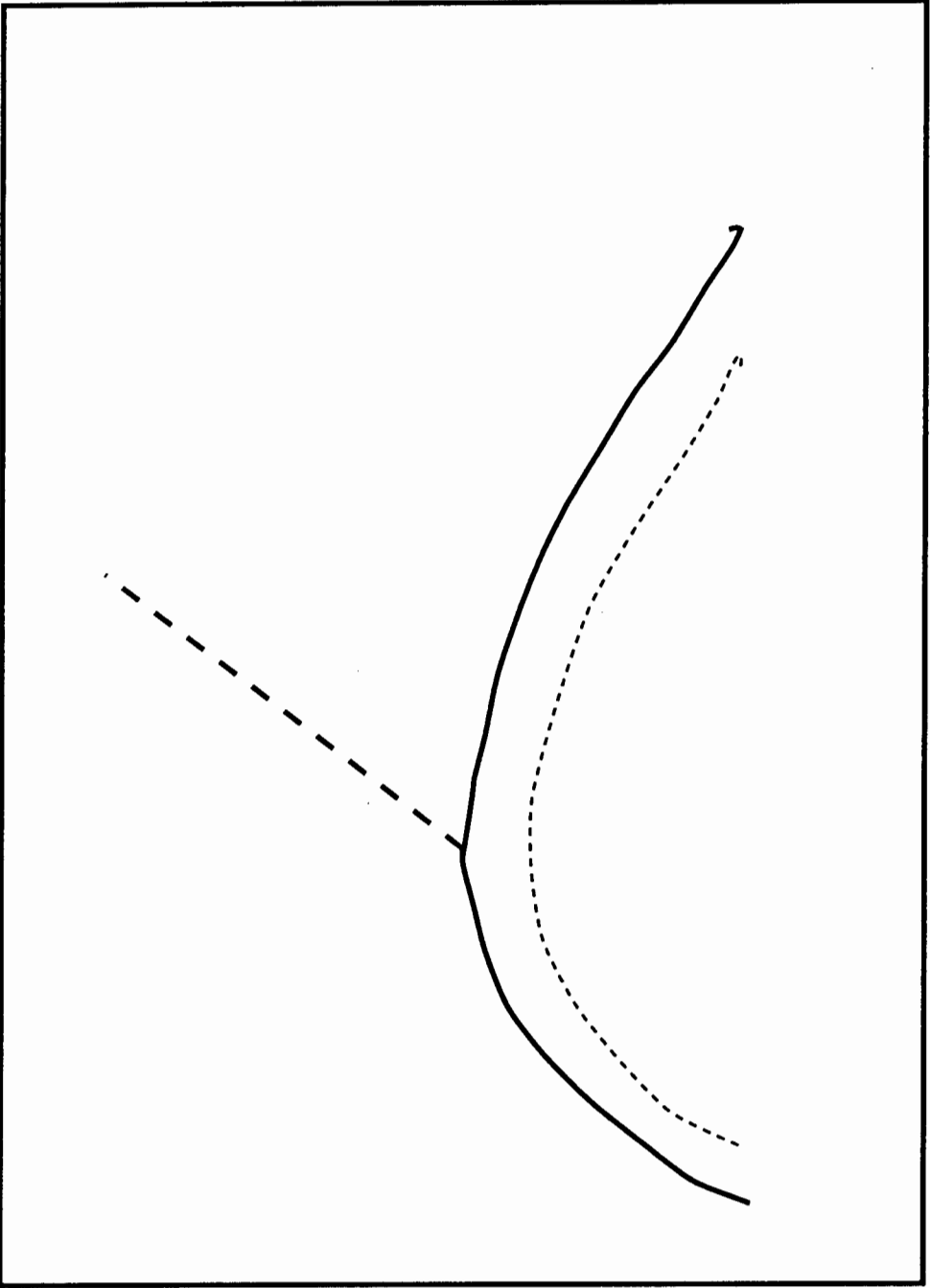**Figure captions**

Fig.1   Liquid-gas coexistence curve of the continuous RPM model according to recent simulation studies [2-4]. Here ρ_0^* is the dimensionless concentration of ions and T^* the reduced temperature, defined at Eq.(10).

Fig.2   (a) λ-line and coexistence curve from cell histograms taken from Monte Carlo simulation results for the lattice RPM desribed in Ref.[12]. (b) λ-line and coexistence curve from the simple mean-field theory described in the Appendix of Ref.[12] for the same lattice RPM. (Note the difference in the temperature scales.)

Fig.3   Generic phase-diagram associated with our field-theoretic description of the RPM, shown schematically. Here ρ and T denote the ion-concentration and temperature respectively in arbitrary units. We show the case in which both a critical point and a tricritical point are realized, along with a λ-line (dashed) representing a locus of transitions to a charge-ordered state lying below the λ-line in temperature.

Fig.4   Possible phase-diagrams associated with our field-theoretic description of the RPM with additional short-range interactions $a_2\xi^2(\nabla\phi)^2/2$ and $A_2\xi^2(\nabla\eta)^2/2$ included, shown schematically. Here ρ and T denote the ion-concentration and temperature respectively in arbitrary units. We show the two special cases described in the text: (a) the critical point is realized only as a metastable point. (b) the tricritical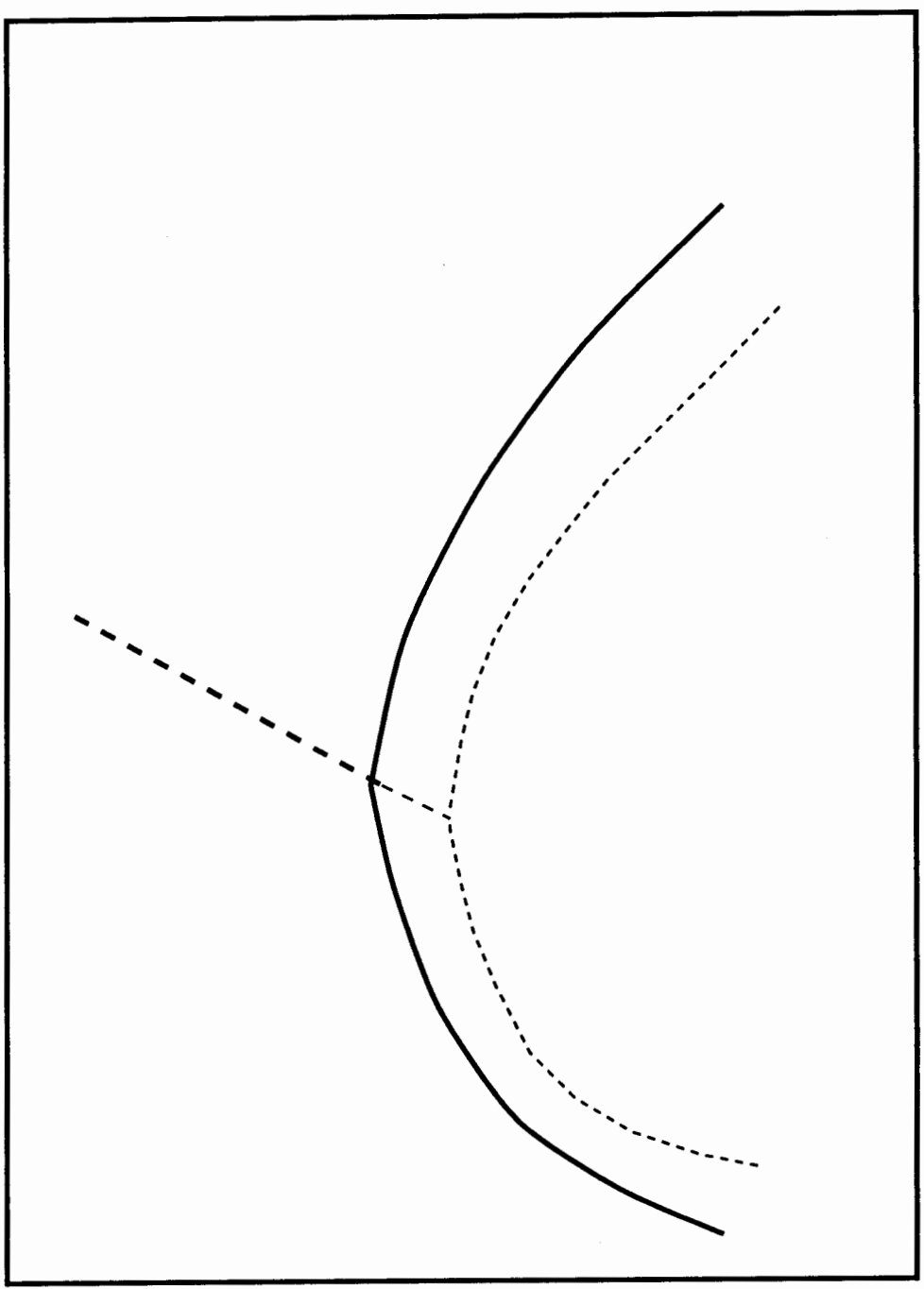 point is realized only as a metastable point.