

Critical behavior of ionic-fluid models

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It is argued that one should expect a fluid of symmetrically charged hard spheres (the restricted primitive model) to have an Ising-like critical point. It is further noted that the presence of a repulsive r^{-4} ion-ion interaction term (of the sort found in real ionic systems as a result of solvent-averaged ion-dipole-ion interaction) will prevent such a critical point from developing, although competing terms that suppress its effect may also be present in real electrolytes.

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Some time ago, on the basis of general arguments as well as a systematic investigation of several approximation schemes, we concluded [1] that the restricted primitive model (RPM) of an ionic fluid exhibits phase separation in the fluid state, with a fluid-state critical point at very low density. Further work by others [2], including very recent computer simulations [3], have borne out this conclusion, and have led to a considerably more precise and accurate estimate of the location of the critical point and fluid-fluid phase boundary.

We further concluded in a later study [4] that the RPM was in the same universality class as the Ising model with respect to the critical point. Our published remarks in this connection were brief, however, and we gave few technical details concerning the argument that led us to this conclusion. In light of the rapidly growing current interest, both experimental [5–7] and theoretical [8–10], in the critical behavior of three-dimensional ionic fluids and ionic-fluid models such as the RPM, it seems useful to give the argument here, especially since its conclusion appears to be somewhat controversial [11], as does the experimental picture [12].

In Ref. [4] we also asserted that if attractive ion-induced-dipole r^{-4} interactions are added to the RPM Hamiltonian, the thermodynamic critical behavior would become mean-field-like, referring to earlier work [13] of ours on the effect of power-law potentials on critical behavior as the basis of our assertion. Here we shall discuss the much more spectacular effect of a *repulsive* r^{-4} term. We find that when added to the RPM Hamiltonian such a term can be expected to suppress the critical point and phase separation, giving rise instead to a different kind of singular behavior that can be thought of as the fluid analog of an antiferromagnetic Néel point associated with a transition to a spatially ordered state. Models in which such a repulsive r^{-4} term is present have a well-established place in ionic-solution theory [14–16]. If the critical properties of real ionic solutions prove to be well described by such models that share the critical properties of the RPM with an added repulsive r^{-4} term, our assertion here would require a major reassessment of the thermodynamic singularities in such systems. In discuss-

ing the singular thermodynamic behavior of the models we consider, we note some of the issues that we feel must be better understood before one can be confident that one comprehends real ionic-fluid behavior in this connection.

We begin our technical discussion with the RPM, which we shall describe in three dimensions classically (nonquantally and nonrelativistically) in the thermodynamic limit. It is a system of charged hard spheres of equal diameter σ in which the potential energy associated with n particles is a sum of pair-potential terms of the form $\varphi_{ij}(r) = \infty$ for $r < \sigma$ and $\varphi_{ij}(r) = s_i s_j u(r)$ for $r \geq \sigma$ where

$$u(r) = q^2 / \epsilon r, \quad (1)$$

with species indices i and j either 1 or 2 and charge numbers $s_1 = -s_2$, with the electroneutrality condition $s_1 \rho_1 + s_2 \rho_2 = 0$, where ρ_i is the number density of species i . Thus $\rho_1 = \rho_2$ with total density $\rho = \rho_1 + \rho_2$. The ϵ in (1) is the dielectric constant (relative to that of the vacuum) of the uniform structureless continuum solvent in which the spheres are immersed and q is electronic charge. The r is distance between ion centers.

One has an Ornstein-Zernike (OZ) equation relating the total correlation functions $h_{ij}(r)$ to direct correlation functions $c_{ij}(r)$

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \sum_k \rho_k \int h_{ik}(r_{13}) c_{kj}(r_{32}) d\mathbf{r}_3 \quad (2)$$

and a second independent relation expressing $c_{ij}(r) - \Phi_{ij}(r)$ as a functional of ρ_i and h_{ij} (and no other functions) as well as a function of r_1 where $\Phi_{ij}(r) = -\beta \varphi_{ij}(r)$, $\beta = (k_B T)^{-1}$, T is the temperature and k_B is Boltzmann's constant:

$$c_{ij}(r) = \Phi_{ij}(r) + R_{ij}(r, h_{ij}, \rho_i). \quad (3)$$

We have the boundary condition $h_{ij}(r) = -1$ for $r \leq \sigma$ and so we only need (3) for $r > \sigma$.

For our purposes it is convenient to introduce the sum and difference combinations of h_{ij} that describe density and charge fluctuation, respectively. The critical point is most directly described in terms of the former, so

we focus on them. We have $h_S = (h_{11} + h_{12})/2$, $h_D = (h_{11} - h_{12})/2$. (Note that $h_{11} = h_S + h_D$ and $h_{12} = h_S - h_D$, with $h_{11} = h_{22}$ and $h_{12} = h_{21}$ by symmetry.) Similarly one has c_S and c_D , R_S and R_D , and Φ_S and Φ_D , with $\Phi_S \equiv 0$. The pair h_S and c_S satisfies an OZ equation induced by (2) as do h_D and c_D . For the former

$$h_S(r_{12}) = c_S(r_{12}) + \rho \int h_S(r_{13}) c_S(r_{31}) d\mathbf{r}_3, \quad (4)$$

where

$$c_S = R_S[h_{ij}, \rho_i]. \quad (5)$$

We drop the argument r in (5) and below for notational simplicity. Notice that Φ_{ij} does not appear in (5) since $\Phi_S \equiv 0$. This is important and is a major reason for the absence of significant density-fluctuation differences between a simple one-species fluid and the RPM. A related remark of importance is that the equation of state that yields the pressure (via integration with respect to ρ of the inverse compressibility) as a function of β and ρ is wholly determined by h_S and ρ . On the other hand, the configurational internal energy is wholly determined by h_D and ρ . See [4] for details.

Our strategy now is to call upon some techniques and results of [17] and [18], extended from the simple-fluid and lattice-gas case to the RPM and its discretized version. In the case of a simple one-component fluid one has a single OZ equation satisfied by an h and a c , and a single $c - \Phi = R$. In the analysis of [17] we note that in the critical region $h(r)$, $c(r)$, and $R(r)$ can each be regarded as the sum of a homogeneous function of r and κ , an inverse correlation length, and the rest—a part which is either short ranged or, if homogeneous, is of higher degree than the dominant homogeneous term. We use a superscript N to denote this second term. Thus $h(r) = h^H(r) + h^N(r)$ with $h^H = f_h(\kappa r)/r^{1+\eta}$, $c(r) = c^H(r) + c^N(r)$, $c^H(r) = f_c(\kappa r)/r^{1+\zeta}$, $R(r) = R^H(r) + R^N(r)$, and $R^H = c^H$. Summarizing, and extending somewhat, the analyses of [17] and [18] we find that it is the functional dependence of R^H upon h^H that determines the universality class one has, and hence the value of the critical exponents. (A key point in this connection, important in our argument to follow, is that $R^H[h^H]$ is insensitive to the form of h^N , which is model dependent even among models in the same universality class.) In particular we have, as $\kappa \rightarrow 0$,

$$c = c^N + R^H[h^H], \quad (6)$$

$$c^N = \Phi + R^N, \quad (7)$$

$$R^H[h^H] = A_2(h^H)^2 + A_3(h^H)^3 + \dots, \quad (8)$$

$$r \gg \sigma, \kappa r \gg 1,$$

$$R^H[h^H] = B(h^H)^\delta + \dots, \quad r \gg \sigma, \kappa r \ll 1. \quad (9)$$

(If we consider a lattice gas with hole-particle symmetry about the critical isochore, then $A_2 \equiv 0$ along that isochore.)

We note that these results, as well as the assumptions that have gone into them, are consistent with the assumptions and results of renormalization-group theory

developed subsequent to the work of [17]. Similarly consistent is the conclusion that it is the functional dependence of R^H upon h^H that determines the universality class one has, and hence the values of the critical exponents in particular. As it stands, the analysis of Ref. [17] is not powerful enough to find those exponents, and we do not attempt to extend it in a way that would permit their *ab initio* determination here. Instead we compare the c_S of the RPM with the c of the simple fluid to determine whether the two systems have the same exponents. To do this, we turn to the RPM equation (5). We assume $h_S = h_S^H + h_S^N$, where the density correlation function h_S also can be decomposed into a dominant homogeneous part $h_S^H = f_S(\kappa r)/r^{1+\eta}$ and the rest, h_S^N , with $\kappa \rightarrow 0$ at the critical point. The charge correlation function h_D , on the other hand, does not have a homogeneous part with respect to κ of degree $1+\eta$ that is co-dominant with h_S^H . Instead it (and therefore h_{11}^N and h_{12}^N introduced below) can be expected to have a dominant homogeneous part (of Yukawa form at low densities) with respect to an inverse shielding length Γ that is only very weakly sensitive to the singularity in density fluctuation associated with $\kappa \rightarrow 0$. [At low densities Γ will just be the inverse Debye length $(4\pi\beta s^2 q^2/\epsilon)^{1/2}$.] In particular $\Gamma \neq 0$ at the critical point we are considering. One also expects a short-ranged model-dependent term in h_D .

Thus we have $h_S = h_S^H + h_S^N$, $h_D = h_D^N$, $h_{11} = h_S^H + h_{11}^N$, and $h_{12} = h_S^H + h_{12}^N$. This induces a decomposition of R_S , and hence c_S , into a dominant homogeneous term with respect to κ plus the part R^N that includes the nonhomogeneous shorter-range terms:

$$c_S = R_S[h_{ij}, \rho] \approx R_S^N + R_S^H[h_S^H]. \quad (10)$$

It is through R_S^N that the crucial coupling between density and charge fluctuations appears. In order for there to be a critical point of the form we seek in the first place, R_S^N must be predominantly positive (at the very least have a positive volume integral) and this is consistent with the results of our analysis, from which we can easily extract the exact low-density behavior of R_S through $O(\rho)$. In fact, at low density, for $r \gg \sigma$, we find R_S^N dominated by a term of the form $\frac{1}{2}h_D^2$, with $h_D = -\beta s^2 q^2 e^{-\Gamma r}/\epsilon r$. (Such low-density information is useful, since the RPM critical point appears to occur at very low density [1–3].) The $R_S^H[h_S^H]$ appears to have the same form as a functional of h_S^H that $R^H[h^H]$ has as a functional of h^H . Thus the RPM appears to have a critical point in the same universality class as the Ising model. The result hinges on the following key observation, which is simple but striking.

Compare the “ h^N -free” part of the h -bond, ρ -vertex representation of $R[h, \rho]$, obtained by replacing h by h^H , with the “ h^N -free” part of the h_{ij} -bond, ρ_i -vertex representation of $R_S[h_{ij}, \rho_i]$, obtained by replacing each h_{ij} with h_S^H . One finds that one has identical functionals of h^H and h_S^H , respectively.

The meaning of the result clearly transcends the particular cluster-sum representation we have used to obtain it. If one has a binary mixture of two species of particles and the two species become identical to give a single-species fluid, then the thermodynamics of the mixture becomes identical to the thermodynamics of the resulting single-species fluid. This will naturally be reflected in all cluster sums, functional Taylor series, etc., that describe the mixture. If the two species instead become asymptotically identical in some way, then the mixture thermodynamics can only be identified with pure-fluid thermodynamics in an appropriate asymptotic sense. That is what is happening here in the critical region, and it will be reflected in cluster sums, functional Taylor series, etc., in that region. The asymptotically important parts of both h_{11} and h_{12} (the h_{11}^H and h_{12}^H , respectively, in our notation) become identical to h^H , the asymptotically important part of the single-species h^H . However, because $\Phi_S \equiv 0$ in our problem, the nonasymptotic parts of h_{11} and h_{12} have to include correlation to set up a critical point in the first place. The correlation is R_S^N , which plays the role of an effective one-species potential and drives the system to singular behavior (a “fixed point” in renormalization-group language). Since the effective potential R_S^N is attractive and relatively short ranged, the fixed point will look like a critical point driven by such a potential, assuming the form of R_S^H is compatible with such behavior. Equation (11) shows that it is.

Several comments on these RPM results are worth making.

(i) The OZ formalism lends itself to making contact with important limits, models, and approximations and it is worthwhile to note a few of these here. One obtains the mean spherical approximation (MSA) by setting $R_{ij} \equiv 0$, and hence $R_S \equiv 0$, for $r > \sigma$. Thus $c_S \equiv 0$ for $r > \sigma$ and h_S is the pure hard-core result, with no trace of any critical behavior in h_S , c_S , or the density fluctuations associated with $\int h_S(r) d\mathbf{r}$, since one has lost the charge-density coupling that sits in R_{ij} . However, the MSA is thermodynamically inconsistent, and by first assessing the internal energy via $\sum_{i < j} \rho_i \rho_j \int g_{ij}(r) \varphi_{ij}(r) d\mathbf{r}$, $g_{ij} = h_{ij} + 1$, and then integrating up with respect to β to get βf , f is the free energy per particle, one will pick up mean-field critical behavior (correct through order $\beta^{3/2}$, it turns out). One gets the Gaussian approximation also by setting $R_{ij} \equiv 0$ for $r > 0$ but replacing the exact boundary condition $g_{ij} = 0, r < \sigma$, with the condition that $c_{ij} = c_{ij}^{HS}$ for $r < \sigma$, where c_{ij}^{HS} is the unperturbed hard-sphere result. In the mean spherical and spherical lattice models, which should be kept conceptually distinct from the MSA, one also has $R_{ij} \equiv 0$ pointwise for all $r > \sigma$, but one picks up long-range correlation in the h_{ij} from the spherical constraint, or an equivalent extra term in the fluctuation equations associated with the mean spherical constraint, which is just the lattice core condition [19] $g_{ij} = 0$ for $r = 0$. The removal of the constraint yields the Gaussian model.

(ii) The above analysis hinges on the separate behavior of Γ and κ , with Γ remaining nonzero as $\kappa \rightarrow 0$, so that there is a critical region in which $\kappa \ll \Gamma$. The estimates

of the critical parameters given in Ref. [3] yield $\Gamma_D \sigma \approx 10$ at the critical point where Γ_D is the inverse Debye length. One expects the true Γ to be somewhat smaller than Γ_D at critical, but unless it is several orders of magnitude smaller, crossover effects occurring at $\kappa \approx \Gamma$ will be well removed from the critical point.

(iii) In real ionic systems, there are terms in the Hamiltonian not included in the RPM. These include polarization terms in the ion-ion pair potentials and solvent-averaged potentials that have a large- r spatial dependence of the form r^{-4} . Such terms—for example, those arising from the polarizability of the ions themselves—can be attractive, resulting in a contribution to $\Phi_S(r)$ of the form $\beta a r^{-4}$, $a > 0$. In [4] we noted that these terms will give rise to mean-field or “classical” thermodynamic behavior in a neighborhood of the critical point, the size of which depends upon the magnitude of a . This result emerges from our OZ-equation analysis, as discussed in some detail in [13]. Here we note that one can also expect repulsive solvent-mediated r^{-4} terms in ionic solutions [14–16, 20, 21]. Such terms are often called cavity terms because they are present in a well-known “cavity model” [14, 16] consisting of charged hard spheres immersed in a structureless continuum solvent of dielectric constant ϵ that does not permeate the spheres, each of which is thought of as bearing a dielectric constant $\epsilon > \epsilon_0$. (We shall consider spheres of equal diameter and charge magnitude.) One then recovers the RPM when $\epsilon_0 = \epsilon$, which can be thought of as the case in which the solvent can freely and uniformly penetrate the spheres. In the cavity model the ion-ion pair potential consists of the RPM term plus a sum of contributions of the form

$$\varphi_{ij}^{cc}(r) = a_4 r^{-4} + a_6 r^{-6} + a_7 r^{-7} + \dots \quad (12)$$

For the dominant first term of this sum, often called the cavity term, one has

$$a_4 = (s_i^2 \sigma^3 + s_j^2 \sigma^3)(\epsilon - \epsilon_0) q^2 / 16(2\epsilon + \epsilon_0). \quad (13)$$

Under the usual assumption that $\epsilon_0 < \epsilon$, we have $a_4 > 0$, but if the ions were characterized by a dielectric constant somewhat greater than the solvent, one would have $a_4 < 0$. For a solvent of nonpolarizable dipolar spheres, rather than a continuum, Jepsen and Friedman [20] found a cluster-integral contribution to the solvent-averaged ion-ion potential that is of the form $a_4 r^{-4}$, $a_4 > 0$ with a_4 a function of the ion-solvent potential parameters that exactly coincides with (13) for solvent ϵ approaching ϵ_0 .

Adding a cavity term to the RPM pair potential will have a striking effect on the critical behavior of the model, which can be best understood by considering the inverse structure factor $S(k)^{-1}$, which is $1 - \rho c_S(k)$. At critical one must have for small $|k|$, k real,

$$S(k)^{-1} = c_{2-\eta} |k|^{2-\eta} + \dots, c_{2-\eta} > 0. \quad (14)$$

In the RPM, we expect a very small Ising-like $\eta \approx \frac{1}{20}$, so that $S(k)^{-1}$ as a function of k will look very smooth and very nearly parabolic at the origin. Adding the cavity term to $\varphi_S(r)$ will add to $S(k)^{-1}$ a dominant small- k contribution given by the Fourier transform of $-\rho \Phi_S(k)$,

which has the form $-\beta\rho\pi^2a_4|k|$ at small k . Hence the smooth nearly parabolic profile of $S(k)^{-1}$ in the neighborhood of $k=0$ will develop a sharp dimple centered at $k=0$ that moves the minimum of $S(k)^{-1}$ from $k=0$ to some nonzero k_0 , the magnitude of which depends upon a_4 and goes to zero as a_4 does. Thus the singularity defined by $S(k)^{-1}=0$ can no longer be a critical point associated with zero $S(0)^{-1}$, which is $\partial\beta\rho/\partial\rho$. Instead it is a singularity associated with $S(k_0)^{-1}=0$ and hence an oscillatory term in $h_S(r)$.

The presence of the higher inverse-power terms in (12) cannot be expected to alter the effect of the r^{-4} term significantly. The intrinsic n -body potential terms for $n \geq 3$ in the cavity model cannot be expected to dominate the r^{-4} term either, although one cannot rule out their codominance, so their signs and relative magnitudes deserve to be studied carefully.

The cavity term can be exactly recovered from a model with a dipolar molecular solvent that is taken to the continuum-solvent limit [21,22]. Taken together with the fact that the cluster-integral contribution found by Jepsen and Friedman also yields the cavity term for small solvent dipole moment *without* taking that limit, it seems hard to escape the conclusion that such a term is present in real ionic solutions. However, the competition between the repulsive cavity term and all possible attractive r^{-4} terms arising from polarization effects in real solutions remains to be quantitatively assessed.

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