Journal of Statistical Physics, Vol. 78, Nos. 1/2, 1995

Criticality and Phase Transitions in Ionic Fluids

George Stell[1,2]

Received December 6, 1993; final June 3, 1994

Recent experimental investigations of criticality and phase separation in ionic fluids have revealed behavior of great theoretical interest. In seeking to understand the experiments, some of which appear to exhibit argonlike criticality and some of which exhibit "classical" (mean-field) criticality, a convenient starting point is the restricted primitive model (RPM) of symmetrically charged hard spheres, all of equal diameter σ, each sphere bearing a positive or negative charge of magnitude q. There is overall charge neutrality, so that the expected number densities of the anions and cations are equal, $\rho_+ = \rho_-$. Studies of RPM charge–charge and density–density correlation functions indicate that the fluctuation-suppressing mechanism that yields mean-field critical behavior in nonionic systems with long-range interparticle potentials is not operative in the RPM. On the basis of plausible assumptions, Ising-like behavior is instead expected. The above work is summarized. New work of Zhang and the author is outlined, showing that when one loses the RPM symmetry (through, e.g., different valence, diameter, or dipole moment of anions and cations) a strong coupling between charge-charge and density-density correlation ensues. The way in which this can be expected to give rise to mean-field or mean-field-like behavior is noted. Other new observations concern the mean-field analogy found by Høye and the author between the parameter $2/(d-2)$ (d is the dimensionality) in that model and the monomer number in high polymers, with respect to the coexistence-curve shape dependence on those parameters.

KEY WORDS: Ionic fluids; primitive model; criticality; phase transitions; second moment condition.

1. INTRODUCTION

Lars Onsager is well known for his major contributions to the theory of ionic fluids as well as his celebrated work on the Ising model, which has

---

[1] Gruppe for Teoretisk Fysikk, Universitetet i Trondheim, 7034 Trondheim - NTH, Norway.

[2] Permanent address: Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794.

so deepened our understanding of criticality and phase transitions. It therefore seems particularly appropriate to consider here the intersection of these two major interests of Onsager's—the subject of criticality and phase transitions in ionic systems. This is an active area of research today, in which a number of quite recent new results have been obtained, including both experimental results(1-8) and computer-simulation results.(9-12) As we shall see, these results present major challenges to our current theoretical understanding. But as we shall also see, that understanding appears to be rapidly deepening.

In seeking to comprehend the recent experiments on such systems —some of which exhibit argonlike criticality(3) and some of which exhibit "classical" (i.e., mean-field) criticality(2, 7)—I shall be drawn into a consideration of dipolar fluids, too, as well as charge-dipole interaction in ionic fluids, simply because the best and most common solvents in ionic solutions are dipolar. In fact in discussing ionic-fluid criticality and phase separation, it is useful to begin by contrasting two quite distinct cases, one of which does not hinge crucially on the critical properties of the solvent, which is typically dipolar, the other of which does. In the case it does not—I shall refer to it as Case I criticality—one considers a solvent that is well away from its own critical point and, as far as its effect on criticality goes, behaves passively. Into it one introduces ions that are sufficiently simple (in their interaction with each other and with the solvent) to be treated as charged hard spheres immersed in a medium that can be regarded as a structureless continuum that is characterized by the solvent dielectric constant ε. (The vacuum, of course, is one such solvent.) Neglecting the effects of everything but the hard cores of the ions and their charges, one can ask whether one should expect a critical point in this system in the first place and, if so, what it will be like. The answer to the first part of the question appears to by "Yes." I shall return shortly to consider the second part. Perhaps the simplest nonlattice Hamiltonian model that embodies Case I features is the restricted primitive model (RPM)—charged hard spheres in a continuum background of dielectric constant ε, with anions and cations of equal charge magnitude q and diameter σ.

In a case that is conceptually different in a fundamental way (I shall call it Case II), one supposes that one has a pure solvent at or near its liquid–gas critical point. Then one adds some salt. One now has an ionic fluid, which typically will have been perturbed somewhat by the addition of the salt but which remains near its critical point, or can be kept near it by smoothly adjusting its temperature T and density ρ as the salt is added. This also gives one an ionic fluid near criticality, but it seems prudent to be prepared for the systems considered in Case I and Case II to have quite different critical behavior, with Case II criticality not essentially different from the pure-solvent criticality found before the addition of the ions.

There are yet other cases of interest that one can imagine. For example, suppose one has a mixture of two fluids, A and B, that are immiscible over a range of conditions because the AB pair potential is repulsive relative to the AA and BB potentials. [A simple model with this property is the Widom–Rowlinson mixture(13) in which the pair potentials are given by

$$\begin{aligned} \varphi_{\mathrm{AA}}(r) &= \varphi_{\mathrm{BB}}(r) = 0 \\ \varphi_{\mathrm{AB}}(r) &= \varphi^{\mathrm{HS}}(r) \end{aligned} \tag{1.1}$$

where r is the distance between particle centers and $\varphi^{\mathrm{HS}}(r)$ is the potential between hard spheres of diameter σ

$$\varphi^{\mathrm{HS}}(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma \end{cases} \tag{1.2}$$

The model phase-separates with a critical point.(13)] A widely held expectation is that this sort of mixture will have argonlike critical behavior when described in the appropriate thermodynamic variables, because of the relatively short range of the potentials responsible for the phase separation and the fact that there appears to be no fundamental difference in symmetry between this system and those in the Ising model universality class.

Now, suppose that one lets the A species ionize, so that some appreciable fraction of A particles are replaced by A^+ cations and A^- anions, with B remaining an un-ionized solvent. We shall call this Case III. As in Case II, one expects the critical parameter to be perturbed by the introduction of charge, but as in Case II, one might expect the criticality to be essentially that of the system in the absence of the charges.

Criticality in Case III, because solvent–solute repulsion is a driving force behind the phase separation one finds there, is sometimes referred to as *solvophobic*, and criticality in Case I as *Coulombic* or *Coulomb-dominated*, because it would vanish along with the associated phase separation if one turned off the charges.(4, 5, 8, 14) Case II, although solvophobicity in the literal sense is not an active ingredient of its critical behavior, is currently often categorized along with Case III as "solvophobic," because it is expected to share with Case II the same critical exponents and other features that define the universality class of a critical point. Perhaps it would be better to broadly categorize both Cases II and III as *non-Coulombic* or *solvent-dominated* criticality and phase separation and reserve the term *solvophobic* for criticality and phase separation in systems, such as those described under Case III, in which solvophobicity is active in a literal sense.

In my Onsager Symposium lecture I also considered some aspects of phase transitions in dipolar fluids that I shall not touch upon in this article—in particular, ferroelectric ordering. I intend to consider that omitted work in a companion article(15) to this one that includes some of the details of the Høye and Stell work cited here concerning the effect of charge–dipole terms as well as a summary of the relation between recent computer-simulation results on dipolar and spin fluids(16–20) and related theoretical advances.

2. COULOMB-DOMINATED CRITICALITY

2.1. The Restricted Primitive Model (RPM)

2.1.1. Existence and Location of the RPM Critical Point and Phase Boundary. Until the mid-1970s there appear to be no references in the ionic-field literature that seriously questioned whether one should assume that a Case I critical point exists in the first place, and only a few touched upon where one might expect such a point to be located. In the ionic-solution literature, this was most likely due to the fact that typical strong aqueous electrolytes do not tend to phase-separate at or near standard conditions (room temperature and pressure), so there was no compelling experimental reason to focus upon the question, which tends to be obscured by the freezing and boiling of most ionic solutions as soon as one departs substantially from room temperature as a result of the presence of the solvent. Molten-salt criticality can be expected to be Case I criticality, too, and has the simplifying feature that there is no molecular solvent in a pure molten salt. However, in the molten-salt literature, there was a similar lack of focus upon criticality, although for different reasons. The existence of molten-salt critical points has long been taken for granted, since at elevated temperatures one finds liquid–gas phase separation, which is typically associated with a critical point. But for most known molten salts the inferred point was at too high a temperature to be experimentally accessible, precluding any detailed comparison of theoretical prediction with experiment.

In a 1962 paper by McQuarrie(21) considering fused-salt thermodynamics using a cell-model version of the restricted primitive model, a critical point was located on the basis of a cell-model treatment, which is intrinsically a mean-field approach. Very shortly thereafter, Friedman(22) discussed some interesting ionic fluids that demix under easily accessible conditions, and proposed a mechanism driven by enhanced dielectric constant as a means of understanding the resulting fluid–fluid phase separation. In a subsequent paper by Stillinger and Lovett(23) on concentrated electrolytes modeled by the RPM, an RPM critical point was shown without further comment in a schematic phase diagram; the implicit assumption that an RPM critical point exists was in keeping with the earlier use of RPM-like models by Stillinger in the theory of fused salts.(24, 25) In a Monte Carlo computer-simulation study(26–28) of the RPM thermodynamics reported in 1970, behavior was found that suggested criticality and phase separation. However, the simulation consisted of relatively short runs done for 32 particles and it seems fair to say that it involved far too great a degree of uncertainty to be reliable. (In the light of subsequent work the critical density originally surmised from the study is almost an order of magnitude too high.)

In 1974 the author undertook a systematic theoretical investigation of RPM thermodynamics with K. C. Wu and Bjørn Larsen (now Bjørn Hafskjold)(29) using a variety of approximations for $-\beta f^{\mathrm{EX}}$, where f^{EX} is the Helmholtz free energy excess to the ideal-gas value per unit volume. I shall refer to the simplest approximation we considered as "hard-sphere plus Debye–Hückel limiting law" (HS + DHLL). Expressed in terms of f^{EX}, it consists of the sum of a hard-sphere contribution $-\beta f^{\mathrm{HS}}$ plus the famous Debye–Hückel limiting-law term $\Gamma_0^3/12\pi$, where Γ_0 is the Debye inverse screening length, $\Gamma_0^2 = 4\pi\rho\beta q^2/\varepsilon$, with ρ the total number density of the ions, $\rho = \rho_+ + \rho_-$. [For the RPM this approximation is the Coulombic analog of the three-dimensional version of the van der Waals equation, $-\beta f^{\mathrm{HS}} + \beta a\rho^2$, the mean-field result for a fluid of particles with attractive dispersion-force pair interaction $\varphi(r)$, $a = -\frac{1}{2}\int \varphi(r)\,d\mathbf{r}$.] Stell *et al.* also added to this expression all further terms in the systematic expansion of $-\beta f^{\mathrm{EX}}$ in Γ_0 through Γ_0^6 (i.e., through third order in the charge-strength parameter $\beta^* = \beta q^2/\sigma\varepsilon$)(30) and formed the Padé approximant(31, 32) that correctly "saturates" to linear behavior in β^*, thus interpolating between the correct small-β^* and large-β^* behavior (ref. 33, Section 3). We also considered the mean spherical approximation (MSA) result,(34) which outside the hard-core region, $r < \sigma$, is a linear theory in β^*, but correctly accounts for the impenetrability conditions $g_\rho(r) = g_q(r) = 0$ for $r < \sigma$ shared by the density distribution function $g_\rho(r)$ and the charge distribution function $g_q(r)$ resulting from the hard cores of the charged spheres (ref. 35; ref. 33, Section 4). The MSA is a considerable improvement over the standard linearized Debye-Hückel theory (LDH), which accounts for only the electrostatic boundary condition on $g_q(r)$ that results from the absence of charge within the core region, and does not include the $-\beta f^{\mathrm{HS}}$ term at all. Approximations that include the full Boltzmann-factor nonlinearity of the second ionic virial coefficient $B(\Gamma)$(36) were also assessed by Stell *et al.* Each of the approximations evaluated thus embodied a different combination of the physical effects that go into the full thermodynamic behavior of the RPM; *all* of them yielded the simple liquid–gas–type critical point characterized by a very much lower critical density than that of a simple argonlike fluid. Beyond the strong support the study gave to the conclusion that an RPM critical point indeed exists, the very low set of values of the critical density ρ_c obtained from the various approaches was one of the most striking results of the study. The critical temperature T^* $[=\sigma\varepsilon/\beta q^2]$, density ρ^* $[=\rho\sigma^3]$, and pressure P^* $[=P\varepsilon\sigma^4/q^2]$ for the hard-sphere term plus Debye–Hückel limiting law (HS + DHLL), Padé, and MSA, were found to be as follows:

$$\begin{array}{llll} \text{HS + DHLL} & T_c^* = 327 \times 10^{-3} & \rho_c^* = 0.123 & P^* = 790 \times 10^{-5} \\ \text{Padé} & T_c^* = 74 \times 10^{-3} & \rho_c^* = 0.010 & P^* = 6 \times 10^{-5} \\ \text{MSA} & T_c^* = 79 \times 10^{-3} & \rho_c^* = 0.014 & P^* = 9.7 \times 10^{-5} \end{array} \tag{2.1}$$

(In order to facilitate comparisions, I note that Fisher,$^{(37)}$ on the basis of the recent Monte Carlo simulation results of Valleau$^{(9)}$ and Panagiotopoulos,$^{(10)}$ has concluded that reasonable estimates for T_c^* and ρ_c^* are

$$T_c^* = 57 \times 10^{-3}, \qquad \rho_c^* = 0.030 \tag{2.2}$$

with not enough known from simulation to give a reliable P_c^*.) One sees that the HS + DHLL result differs enormously from the other two given in (2.1), which are not too different from each other. The HS + DHLL T_c^* appears to be about 6 times too big and the ρ_c^* about 4 times too big; the Padé and MSA values for T_c^* are about 4/3 of the most likely value and the ρ_c^* about 1/3 or so of the most likely value. (One thing this reveals is the great importance of the core condition imposed by the MSA, since it is only the core condition that distinguishes the MSA from the HS + DHLL result.) The major source of error in the MSA and Padé results can be best understood in terms of ionic association, to which I now turn.

Although a wide variety of theories were compared in the study by Stell *et al.*, no attempt was made to incorporate the results of approaches, which go back to Bjerrum,$^{(38)}$ that explicitly take into account the association of ions into neutral pairs or larger clusters. Subsequently in 1979 Friedman and Larsen$^{(39)}$ used the approach to association developed earlier by Ebeling$^{(40)}$ to locate the coexistence curve and critical point of the RPM. This approach employed Bjerrum's original treatment of ion pairing to augment linearized Debye–Hückel (LDH) theory through the addition of a neutral associated species of ion pairs treated by means of the law of mass action. Shortly thereafter, Ebeling and Grigo$^{(41)}$ elegantly incorporated ionic pairing via a law of mass action into the MSA augmented by the second ionic virial coefficient $B(\Gamma)$, and located the resulting critical point. Subsequently, Gillan(42) systematically estimated the thermodynamic effects of association in the RPM due to ionic clusters through hexamers, neglecting interactions among clusters, while Tani and Henderson(43) made similar estimates that included cluster–cluster interaction in the MSA but neglected clusters beyond trimers. Pitzer and Schreiber(44) then extended the Tani and Henderson treatment to hexamers and considered the effect of clustering on the critical parameters, which Tani and Henderson had not done. More recently Given and Stell(45) have generalized this approach still further in a way that frees it from the necessity of using Monte Carlo estimates of the cluster contributions, while Fisher and Levin,(46) building upon the Friedman–Larsen computation, have included the ion–dipole interaction between free ions and ionic pairs. When added to the LDH result, this proves to be of great importance in yielding a coexistence curve of reasonable shape, an issue studied in detail in ref. 46.

In the RPM, ionic clustering is a result of the extremely strong Coulombic attraction between ions of unequal sign when they are close to one another—this effect is a highly nonlinear one in charge strength and is not captured by linearized approaches such as the LDH or MSA theories. Less obviously, it is not well described quantitatively even by those theories that have captured important features of the nonlinear behavior such as the Padé or Padé $\bigcup B_2(\Gamma)$ (the union of the Padé approximant and the second ionic virial coefficient) which Stell *et al.* also considered. Such approaches are not well suited to describing association, because of the very stringent dictates of the law of mass action; using such approaches to describe accurately the increasing association at fixed ρ as the temperature is lowered would require one to describe faithfully the nonlinearities through higher and higher order in the ionic virial expansion.

Unfortunately there is a vexing degree of arbitrariness in the usual approaches to ionic association with regard to what one should mean by an "associated pair of unlike ions" and its density ρ_{+-}; the definition of association thus becomes a central problem in itself. Bjerrum regarded as associated two ions that have their centers a distance r apart with $\sigma \leqslant r \leqslant D$ and chose $D = 2q^2\beta/\varepsilon$, while Gillan as well as Pitzer and Schreiber used the simpler $D = 2\sigma$. Tani and Henderson considered a range of D values. Ebeling and Grigo use a natural but somewhat subtle definition of association and association constant $K = \rho_{+-}/\rho_+^F \rho_-^F$, where ρ_+^F and ρ_-^F are the densities of free cations and anions, respectively, so $\rho = \rho_+^F + \rho_-^F + 2\rho_{+-}$. The Ebeling–Grigo definition is based on the Ebeling formulation of a minimization condition on the free energy with respect to the ρ_i^F's with ρ fixed. Fisher and Levin retain the Bjerrum definition after concluding that in the region of phase separation its use would yield numerical consequences that differ only negligibly from those based on Ebeling's approach. In their interesting study of the two-dimensional Coulomb gas, Høye and Olaussen(47) introduce a definition of K that can be regarded as a generalization of the Ebeling and Grigo definition, in which the Ebeling–Grigo use of Γ_0 as a screening parameter via $B(\Gamma_0)$ is replaced by the use of the renormalized parameter that screens their charge correlation function $h_q(r)$. Høye and Stell, in as yet unpublished work, have subsequently extended this approach to three dimensions and have shown how it can be recovered from an appropriate minimization of the free energy, as well as how it can be used to estimate the way association will change the MSA value of ρ_c^*.

The most obvious effect of incorporating association into linearized theories such as the LDH theory and the MSA in the neighborhood of their critical points is to lower the inverse charge correlation length Γ as a result of substituting the concentration of free ions $\rho_+^{\mathrm{F}} + \rho_-^{\mathrm{F}}$ for the total concentration of ions ρ in the expression for Γ in each theory. This shifts the critical density upward by a substantial amount, but one that depends quite sensitively on the details of the theory being considered, as the results given below will indicate.

I pause here in the discussion of association to summarize the most reliable current assessments of the RPM critical-point location, which are those based on recent Monte Carlo simulation results. Such simulations have been made by Valleau,(9) who estimated $T_c^* = 0.070$ and $\rho_c^* = 0.07$ from his results, Panogiotopoulos, who estimated $T_c^* = 0.056$ and $\rho_c^* = 0.040$ in an initial study(10) and $T_c^* = 0.053$ and $\rho_c^* = 0.025$ in further work with Orkoulas,(11) and Caillol,(12) who estimated $T_c^* \geqslant 0.057$, and regarded $\rho_c^* = 0.040$ as reasonable. Caillol further noted that although his $\beta_c^* P_c^*$ $[= \beta_c P_c \sigma^3]$ cannot be reliably estimated, it appears to be of magnitude $\approx 10^{-3}$, which would put the magnitude of P_c^* at $\approx 6 \times 10^{-5}$, since $\beta^* = 1/T^*$. Analytic estimates of P_c^* were made by Pitzer and Schreiber, who concluded that $P_c^* \approx 50 \times 10^{-5}$ is reasonable, and who reanalyzed the earlier discussion of Gillan in this connection to find that the results suggested $P_c^* \approx 26 \times 10^{-5}$. For the moment, all one can say is that P_c^* probably lies within the spread of values

$$P_c^* \approx 6 \times 10^{-5} \quad \text{to} \quad 50 \times 10^{-5} \tag{2.3}$$

I have already quoted in Eq. (2.2) the values of T_c^* and ρ_c^* favored by Fisher(37) and Fisher and Levin,(46) who base them on a critical appraisal of the results of Valleau(9) and Panagiotopoulos(10) that includes an analysis of finite-size scaling effects not made by those workers themselves.

When one turns to the quantitative effects of ionic association, one finds that the different approaches to association that are available lead to an array of different numerical estimates of critical parameters—the ambiguity in the value of the cut off parameter D introduced by Bjerrum is itself enough to yield a whole spectrum of possibilities. It is clear therefore that one can arrive at almost any target set of critical parameters by judiciously selecting from among the linearized theories with which one can start and from the range of association approaches one can use to supplement them, and finally from a variety of embellishments with which one can decorate the final result. Nevertheless, out of this welter of choices one can identify a few important trends that deserve to be pointed out. Here the focus will be on a comparison of the linear theories and the effect of incorporating association into them through a law of mass action.

First of all, it is worth noting that the MSA is much more quantitatively accurate than the LDH theory with regard to RPM criticality. The critical parameters of LDH theory are(46, 48, 49)

$$T_c^* = 62.5 \times 10^{-3}, \qquad \rho_c^* = 0.0049, \qquad P_c^* = 2.81 \times 10^{-5} \tag{2.4}$$

One sees that ρ_c^* is an order of magnitude too low and P_c^* quite likely an order of magnitude too low also. Only T_c^* is of the right order of magnitude. The MSA values are given in Eq. (2.1)—the MSA T_c^* is a little high and ρ_c^* perhaps one-half the correct value; P_c^* is probably low, but is three times higher than the LDH value.

The HS + DHLL critical values have already been discussed [see Eq. (2.1)]; T_c^* and ρ_c^* are too high by something less than half an order of magnitude (P_c^* is probably over an order of magnitude too high also). It is interesting that the much less accurate "free-volume" correction considered by Fisher in place of an accurate HS term in his discussion of the DHLL yields T_c^* and ρ_c^* that are very different from these values and considerably worse ($T_c^* = 560 \times 10^{-3}$, $\rho_c^* = 0.283$, $P_c^* = 2946 \times 10^{-5}$). The treatment of the hard-sphere term makes a big difference even at the very low critical densities involved.

I shall select just a few of the various ways of adding association to both LDH theory and the MSA. The approach based on the LDH theory used by Friedman and Larsen(39) and by Fisher and Levin(46)—DHBj in the latter's terminology—yields the good values

$$\text{LDH} + \text{Bj:} \qquad T_c^* = 62.5 \times 10^{-3}, \qquad \rho_c^* = 0.0453 \tag{2.5}$$

with P_c^* not reported. The coexistence curve, however, has an unreasonable shape, as both groups have noted. Ebeling, who added the second hard-sphere virial-coefficient contribution and used a slightly more sophisticated means of defining the association constant, appears to have obtained the values

$$\mathrm{B}^{\mathrm{HS}} + \mathrm{LDH} + \mathrm{Eb}: \qquad T_c^* = 0.0617, \qquad \rho_c^* = 0.042 \tag{2.6}$$

but owing to ambiguities and a probable misprint in his reported values, these *very* good results are not certain.

McGahay and Tomozawa(48, 49) have recently supplemented the LDH theory with a treatment of association introduced by Fuoss. Their critical values for the RPM are

$$\mathrm{LDH} + \mathrm{Fuoss}: \qquad T_c^* = 0.0625, \qquad \rho_c^* = 0.159, \qquad P_c^* = 90 \times 10^{-5} \tag{2.7}$$

The ρ_c^* is far higher than the best estimates of this quantity. Moreover, as has been pointed out,(50) this treatment of association does not appear to be appropriate to hard-core models such as the RPM.

As already noted, Fisher and Levin have augmented the LDH + Bj approach by inclusion of the dipole–ion interaction between associated ion pairs and free ions with good results. Their critical values are

$$\mathrm{LDH} + \mathrm{Bj} + \mathrm{DI}: \qquad T_c^* = 0.0574, \qquad \rho_c^* = 0.028 \tag{2.8}$$

I turn next to the use of the MSA as a starting point upon which to superimpose association. When corrected for association into neutral pairs by Ebeling and Grigo,(41) the MSA critical value of ρ^* is considerably improved (as P_c^* may also be), although T_c^* is not: One has

$$\mathrm{MSA} + \mathrm{EG}: \qquad T_c^* = 0.08368, \qquad \rho_c^* = 0.018, \qquad P^* = 35.4 \times 10^{-5} \tag{2.9}$$

Moreover, the coexistence curve has a reasonable shape. It will be of great interest to see how these values change when further corrected for the presence of interaction between the free ions and the dipolar pairs of associated ions. This computation is in progress. The systematic addition of the effect of association into trimers and larger clusters is also possible, although it would be formidable if done in a way strictly analogous to the Ebeling–Grigo treatment of pair association.

Høye and Stell have also made an estimate of the effect of association on the MSA that is based upon the use of the Høye–Stell extension to three dimensions of the Høye–Olaussen(47) approach to the two-dimensional Coulomb gas. In a computation that leaves T_c^* fixed they find $\rho_c^* = 0.045$ with P_c^* unassessed. It seems clear that the MSA, like the LDH theory, will prove quite sensitive to the details of the association theory into which it is incorporated.

In Section 4 of the article based upon his own Onsager Symposium contribution on ionic criticality, Fisher(37) notes that the very low density of the RPM critical point is associated with an asymmetric, sharply peaked coexistence-curve shape in a ρ vs. T plot that is highly reminiscent of the similarly skewed coexistence curve of polymer solutions in poor solvents and in polymer blends. There the polymer length measured in monomer number M is an important parameter, such that in the $M \to \infty$ limit one expects the critical point to become a zero-density tricritical point in Flory's mean-field theory,(51) which appears to be particularly useful in describing polymer blends.(52) As $M \to \infty$, deviations from mean-field behavior become harden and harder to detect, and Fisher points out that it would be valuable to be able to identify some quantity analogous to M in the ionic problem, in which the apparent mean-field nature of some ionic fluids might be due to a similar effect, at least in part.

On the basis of work with Høye, I propose that one such analog is $2/(d-2)$, where d is the dimensionality. As noted in the beginning of this section, in a three-dimensional system, the version of mean-field theory appropriate to an ionic fluid yields the Debye–Hückel analog of the van der Waals attractive term, which is of the form $\text{const}(\beta\rho)^{3/2}$ in $-\beta f$ and βP. In d dimensions this becomes $\text{const}(\beta\rho)^{d/2}$ and the limit $d \to 2$ is analogous to the polymer limit $M \to \infty$. One can see this easily by writing down the van der Waals-like equation of state for the RPM,

$$\beta P = \frac{\rho}{1-b\rho} - \text{const}(\beta\rho)^{d/2}, \qquad 2 \leqslant d \leqslant 4 \tag{2.10}$$

and considering the shape of the coexistence curve. As $d \to 2$ the coexistence curve approaches a pair of straight lines in the ρ, T plane—a vertical line from $\rho, T = 0, 0$ up to ρ_c, T_c (with $\rho_c = 0$) and a line with negative slope for $\rho > \rho_c$ starting at ρ_c, T_c. One has $b\rho_c = (d-2)/(d+2)$.

2.1.2. Correlation Functions and the Nature of Criticality in the RPM. The discussion of the last section concerns the existence and location of the coexistence curve and critical point in a fluid of charged hard spheres, but not the structure of the correlation functions or the universality class of the critical behavior; none of the analysis considered there is suitable for probing these issues, which I begin to take up here. The discussion will follow closely an earlier treatment(53) of this material by the author. At a certain point I also make contact with an still earlier formalism of Stillinger and coworkers,(24, 25) as described at the end of this section.

The first point will be that although in nature one finds no longer-ranged interaction than the Coulomb interaction, the usual arguments that lead one to conclude that certain types of long-range potentials will give rise to mean-field critical behavior do *not* apply to the Coulombic case. Such arguments apply most readily to a potential consisting of a repulsive core and an attractive Baker–Kac tail

$$\varphi(\gamma_r)=\gamma^d f(\gamma r) \tag{2.11a}$$

in the limit $\gamma \to 0$, if $-f(r)$ is a nonnegative, decreasing function of r with finite volume integral. Here d is the dimension.

The somewhat different case of an attractive potential tail of the form

$$\varphi(r)=A(\sigma/r)^{d+p} \tag{2.11b}$$

with $0<p<d/2$ will also give rise to mean-field thermodynamic behavior, as first shown by the results of Stell.(54), [3]

In both cases, the mean-field nature of the thermodynamics can be understood theoretically on the basis of the very long range of $\varphi(r)$. Each particle feels the pair potential of an arbitrarily large number of its fellow particles, and it is not hard to demonstrate that fluctuations around the resulting average field that each particle feels can be neglected. (One such demonstration will be outlined below.) It will be argued that when one *does* observe mean-field behavior in Coulombic criticality it is because of a far less direct and less obvious effect of field on correlation than in the case of (2.11).

It is convenient in examining this issue to use Ornstein–Zernike formalism. In the case of a spatially uniform system of one species of particle, in which the one-particle density function $\rho(\mathbf{r})$ is a constant number density ρ, one has a radial distribution function $g(r)$, a total correlation function $h(r)=g(r)-1$, and a direct correlation function $c(r)$, related to $h(r)$ through the convolution equation

$$h(r_{12})=c(r_{12})+\rho\int h(r_{13})\,c(r_{23})\,d\mathbf{r}_3 \tag{2.12}$$

in real space, or the equivalent algebraic relation,

$$h(k)=c(k)/[1-\rho c(k)] \tag{2.13}$$

in Fourier space, where

$$a(k)=\frac{1}{(2\pi)^d}\int a(r)\,e^{i\mathbf{r}\cdot\mathbf{k}}\,d\mathbf{r} \tag{2.14}$$

---

[3] See ref. 55 for the initiation of the formalism used in ref. 54.

There is a second relation that introduces the "tail" of the direct correlation function $T(r)$,

$$c(r) = \Phi(r) + T(r) \tag{2.15}$$

Equation (2.15) explicitly involves the pair potential through the function

$$\Phi(r) = -\beta\varphi(r) \tag{2.16}$$

with $\beta = 1/k_B T$ (k_B is Boltzmann's constant and T is the absolute temperature). Moreover, (2.15) need only be considered for $\sigma > 0$ in a system with a hard-core potential of diameter σ, since with the boundary condition

$$g(r) = 0, \qquad r < \sigma \tag{2.17}$$

$c(r)$ need only be prescribed by (2.15) for $r > \sigma$ in order to yield a closed set of equations when taken together with (2.12). The $T(r)$ is a functional of h as well as a function of r and ρ and, in principle, is completely determined by r, ρ, and $h(r)$. In practice the precise dependence of $T(r)$ on r, ρ, h is intractably difficult to determine and one must be content with seeking limiting and asymptotic relationships of various degrees of generality on the basis of available cluster-integral,(56) functional Taylor-series,(54) hypervertex (ref. 33, Appendix), and renormalization-group(57) representations of T.

The formalism generalizes easily to a mixture of several species of particles. With i, j, and k species indices, (2.12) becomes

$$h_{ij}(r_{12}) = c_{ij}(r) + \sum_k \rho_k \int h_{ik}(r_{12})\, c_{kj}(r_{32})\, d\mathbf{r}_3 \tag{2.18}$$

and (2.15) becomes

$$c_{ij}(r) = \Phi_{ij}(r) + T_{ij}(r) \tag{2.19}$$

In the primitive model, there are two species, $i = a, b$ and $j = a, b$, and

$$\varphi_{ij}(r) = \varphi_{ij}^{\mathrm{HS}}(r) + \varphi_{ij}^{\mathrm{COUL}}(r) \tag{2.20}$$

where $\varphi^{\mathrm{HS}}(r)$ is the hard-sphere potential

$$\varphi_{ij}^{\mathrm{HS}}(r) = \begin{cases} \infty & \text{for} \quad r < \sigma_{ij} \\ 0 & \text{for} \quad r > \sigma_{ij} \end{cases} \tag{2.21}$$

The $\varphi_{ij}^{\mathrm{COUL}}(r)$ is expressed in terms of valences s_i and charge numbers $|s_i|$, with the electroneutrality condition

$$\sum_i \rho_i s_i = 0 \tag{2.22a}$$

In the RPM this is the first of a set of electrostatic odd-moment conditions that are satisfied by symmetry

$$\sum \rho_i s_i^{2I-1}, \qquad I = 1, 2, \ldots \tag{2.22b}$$

In (2.20), $\varphi_{ij}^{\mathrm{COUL}}(r)$ is given by $-s_i J(r)\, s_j$, where

$$J(r) = -q^2/\varepsilon r \tag{2.23}$$

In the highly symmetric RPM, $\sigma_{ij} = \sigma$ and

$$\rho_a = \rho_b = \rho/2\ , \qquad |s_a| = |s_b| \tag{2.24}$$

As a result of the symmetry the density–density and charge–charge correlations can be written in terms of simple sum and difference combinations of the h_{ij} and c_{ij}. One has

$$h_{\mathrm{S}} = (h_{aa} + h_{ab})/2, \qquad h_{\mathrm{D}} = (h_{aa} - h_{ab})/2 \tag{2.25}$$

and the inverse relations

$$h_{aa} = h_{\mathrm{S}} + h_{\mathrm{D}}, \qquad h_{ab} = h_{\mathrm{S}} - h_{\mathrm{D}} \tag{2.26}$$

with corresponding relations for the c's, Φ's, and T's. Both the pair h_{S} and c_{S} and the h_{D} and c_{D} satisfy their own OZ equations that are totally decoupled with respect to one another:

$$h_{\mathrm{S}}(r_{12}) = c_{\mathrm{S}}(r_{12}) + \rho \int h_{\mathrm{S}}(r_{13})\, c_{\mathrm{S}}(r_{23})\, d\mathbf{r}_3 \tag{2.27}$$

$$h_{\mathrm{D}}(r_{12}) = c_{\mathrm{D}}(r_{12}) + \rho \int h_{\mathrm{D}}(r_{13})\, c_{\mathrm{D}}(r_{23})\, d\mathbf{r}_3 \tag{2.28}$$

The coupling appears through the equations

$$c_{\mathrm{S}}(r) = \Phi_{\mathrm{S}}(r) + T_{\mathrm{S}}(r; \rho_i, h_{ij}] \tag{2.29}$$

$$c_{\mathrm{D}}(r) = \Phi_{\mathrm{D}}(r) + T_{\mathrm{D}}(r; \rho_i, h_{ij}] \tag{2.30}$$

The (;] notation is used here to emphasize that T is a functional of ρ_i and h_{ij} as well as a function of r. Notice that $\Phi_{\mathrm{S}}(r) = -\beta\varphi^{\mathrm{HS}}(r)$; *the Coulomb term has disappeared from (2.20).* Notice also that T_{S}, through (2.25) and (2.26), can be reexpressed as a functional of ρ, h_{S}, and h_{D}, which will continue to be designated as T_{S}:

$$c_{\mathrm{S}}(r) = -\beta\varphi^{\mathrm{HS}}(r) + T_{\mathrm{S}}(r; \rho, h_{\mathrm{S}}, h_{\mathrm{D}}] \tag{2.31a}$$

Moreover, (2.31a) need only be used for $r>\sigma$, where one has simply

$$c_{\mathrm{S}}(r)=T_{\mathrm{S}}(r;\rho,h_{\mathrm{S}},h_{\mathrm{D}}] \tag{2.31b}$$

which, along with Eq. (2.27) and the boundary condition

$$h_{\mathrm{S}}(r)=-1 \qquad \text{for} \quad r<\sigma \tag{2.32}$$

forms a closed set of equations if T_{S} is prescribed for $r>\sigma$.

For some purposes it is more convenient to work not with the tail functions T_{ij}, T_{D}, and T_{S}, but the parts of c_{ij}, c_{D}, and c_{S} that are excess to only the Coulomb parts of Φ_{ij}, Φ_{D}, and Φ_{S}, respectively, rather than the full Φ's. These shall be designated as the "remainder" terms R_{ij}, R_{D}, and R_{S}. One sees that $R_{ij}=-\beta\varphi^{\mathrm{HS}}+T_{ij}$, so $R_{\mathrm{D}}=T_{\mathrm{D}}$. Because Φ_{S} has no Coulomb part,

$$c_{\mathrm{S}}(r)=R_{\mathrm{S}}(r;\rho,h_{\mathrm{S}},h_{\mathrm{D}}] \tag{2.33}$$

for *all* r. For c_{D} one has, also for all r,

$$c_{\mathrm{D}}(r)=\Phi_{\mathrm{D}}(r)+R_{\mathrm{D}}(r;\rho_{ij},h_{ij}] \tag{2.34}$$

Here R_{D}, like R_{S}, can be reexpressed as a functional of ρ, h_{S}, and h_{D} rather than the ρ_i and h_{ij}:

$$c_{\mathrm{D}}(r)=\Phi_{\mathrm{D}}(r)+R_{\mathrm{D}}(r;\rho,h_{\mathrm{S}},h_{\mathrm{D}}] \tag{2.35}$$

As already noted, the Coulomb term Φ_{D} has disappeared from the equations relating h_{D} and c_{D}; its effect is felt only through the h_{D} dependence of R_{D}. It is therefore important that one tries to understand the behavior forced upon h_{D} by the Φ_{D}, which in Fourier space is given by

$$\Phi_{\mathrm{D}}(k)=-\Gamma_0^2/\rho k^2 \tag{2.36}$$

where Γ_0 is the Debye-Hückel inverse screening length

$$\Gamma_0^2=4\pi\beta q^2\sum_i \rho_i s_i^2/\varepsilon \tag{2.37}$$

which in the RPM is just $4\pi\beta q^2\rho s^2/\varepsilon$, with $s^2=|s_a s_b|$, which is usually taken to be unity. A crucial aspect of the h_{D} behavior is dictated by electroneutrality, which implies a zeroth moment condition on $1+\rho h_{\mathrm{D}}(k)$. In the RPM this is simply

$$1+\rho h_{\mathrm{D}}(k=0)=0 \tag{2.38}$$

This has long been known. There is also a much less obvious second-moment condition, first deduced and demonstrated by Stillinger and Lovett,(23) which in the RPM can be written, along with (2.38), as

$$\lim_{k\to 0}\,[1+\rho h_{\mathrm{D}}(k)] = k^2/\Gamma_0^2 = \Phi_{\mathrm{D}}^{-1}(k)/\rho \tag{2.39a}$$

Alternatively, the second-moment condition can be written as

$$\rho \int r^2 h_{\mathrm{D}}(r)\, d\mathbf{r} = -6/\Gamma_0^2 \tag{2.39b}$$

Notice the remarkable appearance of the *inverse* of Φ_{D} in (2.39a). Stillinger and Lovett also called attention to the fact that the dielectric response function $\varepsilon(k)$ of the RPM can be written in terms of $h_{\mathrm{D}}(k)$ through the simple relation

$$\frac{\varepsilon_0}{\varepsilon(k)} = 1 - \frac{\Gamma_0^2}{k^2}\,[1+\rho h_{\mathrm{D}}(k)] \tag{2.39c}$$

where ε_0 is the dielectric constant of the continuum solvent that one has in the RPM; we denote this simply as ε elsewhere throughout this article. Equation (2.39c) immediately implies that as $k \to 0$, $\lim \varepsilon_0/\varepsilon(k) = 0$, so $\lim \varepsilon(k) = \infty$, which is what one expects in a conducting electrolyte such as the RPM.

One expects the true charge–charge inverse screening length Γ to become Γ_0 for fixed $\beta \neq 0$ in the $\rho \to 0$ limit. In the same limit, one expects the Debye–Hückel result (for *both* $k \to 0$, $\Gamma_0 \neq 0$ and $\Gamma_0 \to 0$, $k \neq 0$)

$$1+\rho h_{\mathrm{D}}(k) \approx \frac{k^2}{\Gamma_0^2 + k^2} \tag{2.40a}$$

or

$$\rho h_{\mathrm{D}}(k) \approx \frac{-\Gamma_0^2}{\Gamma_0^2 + k^2} \tag{2.40b}$$

and (for large r)

$$\rho h_{\mathrm{D}}(r) \approx \frac{-\Gamma_0^2 e^{-\Gamma_0 r}}{4\pi r} \tag{2.40c}$$

As one goes to higher values of Γ_0, one expects the charge–charge inverse screening length to depart from Γ_0,(30) and (2.39a) puts powerful constraints on the expected form of the resulting h_D as this departure takes place. Considering only terms through k^2, one is led to

$$1+\rho h_D(k)=\frac{k^2+\cdots}{\Gamma_0^2+a^2k^2+\cdots}=\frac{1}{a^2}-\frac{(\Gamma_0/a)^2}{a^2[(\Gamma_0/a)^2+k^2]}+\cdots \quad (2.41a)$$

(where $a^2>0$), or

$$\rho h_D(k)\approx\left(\frac{1}{a^2}-1\right)-\frac{\Gamma^4/\Gamma_0^2}{\Gamma^2+k^2}+\cdots \quad (2.41b)$$

where

$$\Gamma^2=\Gamma_0^2/a^2 \quad (2.41c)$$

so for large r, one expects

$$\rho h_D(r)\approx-\frac{\Gamma^4/\Gamma_0^2\exp-\Gamma r}{4\pi r} \quad (2.42a)$$

instead of (2.40c).

For sufficiently large Γ_0, $\rho h_D(r)$ cannot remain negative for all r, however. Like (2.39a), this was first demonstrated by Stillinger and Lovett$^{(23)}$ and had been earlier found on the basis of plausible assumptions.$^{(24,25)}$ It suggests that the denominator of (2.41a) becomes singular in complex k space not at $k=\pm i\Gamma_0$ as in the case of the "Debye pole" characterizing (2.40) or at $k=\pm i\Gamma$ as in the case of (2.41) with Γ real, but at $k^2=\Gamma_C^2$ or $k=\pm\Gamma_R\pm i\Gamma$, where Γ_C is complex with $\Gamma_C=\Gamma_R+i\Gamma$. (By dominant singularity, the one with the smallest imaginary part is meant.) Hence in real space one expects a change from the monotonic decrease in $h_D(r)$ as $r\to\infty$ characterized by (2.42a), or more generally by

$$\rho h_D(r)\approx A(\exp-\Gamma r)/r,\qquad \Gamma r\gg 1 \quad (2.42b)$$

to oscillatory behavior characterized by

$$\rho h_D(r)\approx B(\exp-\Gamma r)\cos(\Gamma_R r+\theta)/r,\qquad \Gamma r\gg 1 \quad (2.42c)$$

where A, B, and θ depend upon the residue of the dominant pole at $k=\Gamma_R+i\Gamma$.

In the MSA,$^{(58)}$ as well as a variety of other approximations that have been studied$^{(59)}$ (including the one considered in detail by Lovett and Stillinger$^{(60)}$) one finds the pole of the dominant singularity leaving the imaginary axis in complex k space—with the attendant change from

(2.42b) to (2.42c) in real space— when Γ_0 increases to a threshhold value, $\Gamma_0 = (\Gamma_0)_{\mathrm{DL}}$, where the $(\Gamma_0)_{\mathrm{DL}}$ defines a "disorder locus" that differs somewhat in the different approximations. Hence, in these approximations, the locus in the ρ, T plane that marks the onset of the oscillatory behavior is simply $\rho = \mathrm{const} \cdot T$. One expects the exact behavior of the RPM to similarly include a "disorder line" in the ρ, T plane marking the onset of oscillatory behavior, but there is no reason to assume it is a straight line.

As Γ_0 further increases, Γ_{R} increases and Γ begins to decrease in the MSA and similar approximations. This, too, seems likely to mirror the exact RPM behavior. In the MSA, Γ becomes zero only for $\beta = \infty$, but in other approximations $\Gamma = 0$ is attained for a finite $\Gamma_0 = (\Gamma_0)_{\mathrm{N}}$ associated with a nonzero Γ_{R}. As we pointed out in ref. 61,[4] such a $(\Gamma_0)_{\mathrm{N}}$ defines a "λ-line" of Néel points, and it is not all clear whether one should expect such a λ-line in the exact behavior of the RPM. As noted there, one might expect with considerably more confidence such a λ-line when one replaces the Coulomb interaction $J(r) = -q^2/r\varepsilon$ in Eq. (2.23) by a Yukawa interaction $J(r) = -q^2(\exp - \alpha r)/\varepsilon r$ with a large α; the resulting Yukawa RPM (YRPM) is a continuum analog of the nearest-neighbor spin-1 Ising antiferromagnet where the evidence for such a locus is very strong. However, when one goes to the continuum analog, one loses the periodicity of the lattice, which helps ensure the Néel-point singularity, so that one cannot be certain that the YRPM will have the λ-line even for large α. Assuming that it does, the behavior of the λ-line as $\alpha \to 0$ remains a largely unexplored issue.

As long as $\Gamma \neq 0$, one would expect the dominant singularity of $h_{\mathrm{D}}(k)$ to be a pole, but if $\Gamma \to 0$ (with either $\Gamma_{\mathrm{R}} \to 0$ or $\Gamma_{\mathrm{R}} \neq 0$) the generic behavior of such correlation-function singularities would lead one to expect branch-point behavior when $\Gamma = 0$ associated with a confluence of poles in the denominator of (2.41a) in the limit $\Gamma \to 0$). In r space this confluence would dictate the behavior of h_{D} for $\Gamma r \ll 1$, $r \gg \sigma$, rather than for the regime $\Gamma r \gg 1$ in which one expects (2.42b) or (2.42c). As one approaches a λ-line of Néel points, if one exists, one might expect $\rho h_{\mathrm{D}}(r)$ to have the form, for all $r \gg \sigma$,

$$\rho h_{\mathrm{D}}(r) \approx F(\Gamma r) \cos(\Gamma_{\mathrm{R}} r + \theta)/r^{1+\eta(D)} \tag{2.43}$$

in keeping with known results for the Ising antiferromagnet, for which in three dimensions, $\eta(D)$ is a very small positive number.

---

[4] This work appeared in shortened form as ref. 53.

In the Ising case, one expects

$$F(x)=\begin{cases}\text{const}\cdot x^{\eta(D)}e^{-x} & \text{for}\quad x\gg 1\\ \text{const} & \text{for}\quad x\ll 1\end{cases}$$

We return for a moment to the disorder line, which will only be realized in the one-phase region of the ρ, T plane. For the RPM, one would expect it to meet the coexistence curve in that plane. In Stell *et al.*(29) the MSA disorder line was plotted with the various coexistence curves studied there, and it meets most of them quite close to their critical points. In particular, it meets the MSA coexistence curve on the low-density side of the MSA critical point, so that at criticality, the MSA $h_D(r)$ already has the oscillating form given by (2.42c) rather than the monotonic form of (2.42b). This could well be the case for the exact RPM $h_D(r)$, too.

If there were a λ-line of Néel points associated with the exact RPM h_D, it, too, would be expected to emerge from the coexistence curve at a higher density than the disorder line. Generically, one expects special critical behavior, such as tricritical behavior, at the point at which such a λ-line meets a coexistence curve, and Kholodenko and Beyerlein(62) have suggested that the RPM critical point is a tricritical point induced by a λ-line emerging from the top of the coexistence curve. It seems to me likely that if there is such a λ-line at all in the RPM, it meets the RPM coexistence curve at a considerably higher density than that of the critical point appearing at the maximum coexistence temperature, so that it would not induce tricriticality at that critical point.

Since criticality is defined most directly in terms of the vanishing of the inverse correlation length κ associated with the density–density correlation function $h_S(r)$ [rather than in terms of $h_D(r)$ and Γ] further discussion of criticality shall be deferred until after a consideration of the expected behavior of $h_S(r)$.

Equation (2.39) is a small-k result. Because $h_D(r)$ is finite for $r=0$ [in fact $h_D(r)=0$ for $r<\sigma$] one also has the large-k result

$$\lim_{k\to\infty} h_D(k)=0 \tag{2.44}$$

Small-k forms such as those shown in (2.41) violate this condition unless additional terms of order higher than k^2 are appropriately taken into account.

In a simple one-species fluid described by Eqs. (2.12)–(2.17) liquid–gas phase separation and criticality imply the vanishing of the inverse isothermal compressibility, or

$$\beta\,\partial P/\partial\rho=0,\qquad \beta\text{ fixed} \tag{2.45}$$

where P is pressure. This is directly given by

$$1 - \rho c(k=0) = [1 + \rho h(k=0)]^{-1} = 0 \tag{2.46}$$

since

$$\beta\, \partial P/\partial \rho \,|_{\beta} = 1 - \rho c(k=0) \tag{2.47}$$

In the RPM, criticality continues to imply (2.45), and (2.46) and (2.47) are replaced by

$$1 - \rho c_{\mathrm{S}}(k=0) = [1 + \rho h_{\mathrm{S}}(k=0)]^{-1} = 0 \tag{2.48}$$

and

$$\beta\, \partial P/\partial \rho \,|_{\beta} = 1 - \rho c_{\mathrm{S}}(k=0) = 1 - \rho R_{\mathrm{S}}(k=0) \tag{2.49}$$

which involve the "sum" functions introduced in (2.25). Before going further in the investigation of RPM criticality it is instructive to point out the way in which it is fundamentally different from that of systems in which the pair potential is given by (2.11). In Fourier space, (2.11a) becomes

$$\varphi(k) = \lim_{\gamma \to 0} f(k/\gamma) = \mathrm{const} \cdot \delta_{k,0} \tag{2.50}$$

where $\delta_{k,0}$ is the Kronecker delta, $\delta_{k,0} = 1$ for $k = 0$, and $\delta_{k,0} = 0$ otherwise, while for thermodynamic states that remain in a single phase it can be shown that

$$\lim_{\gamma \to 0} T(k; \rho, h] = T^{\mathrm{REF}}(k; \rho, h] \tag{2.51}$$

where T^{REF} is the tail function [defined in (2.15)] of the repulsive-core reference system evaluated at the ρ and β of the full system.

It is the behavior of $\Phi(k)$ that determines the (mean-field) critical exponents through (2.15), with $T^{\mathrm{REF}}(k; \rho, h]$ at $k = 0$ providing only the reference-system thermodynamics, which is wholly free of critical fluctuation.

The case of potentials of the power-law form given by (2.11b) is quite similar when $0 < p < d/2$. One has for small k

$$\varphi(k) \approx \mathrm{const} \cdot |k|^{p} \tag{2.52}$$

while $T(k; \rho, h]$ proves to be of higher power in k, as first shown by Stell;(54) its role is again limited to providing a background term $T(k=0; \rho, h]$ in the denominator $1 - \rho c(k)$ of (2.13) that determines the thermodynamics in the critical region, which is therefore again mean-field-like. From the result $1-\rho c(k)\approx\text{const}\cdot|k|^{p}$ that follows, the correlation-exponent relation $2-\eta=p$ is obtained, so the correlation-range behavior is not "mean-field-like" in the sense in which that term is sometimes used to describe the result $\eta=0$.

In the RPM, in contrast to the cases of the two long-ranged potentials just discussed, the T_S function is not just a passive background term—it is the whole story.

In considering this story, it is convenient to think of Eqs. (2.27), (2.29), (2.31), and (2.32) as describing the density–density correlations of a hypothetical equivalent one-species neutral system, with a c equal to c_S written not as (2.29) but as

$$c_S=\Phi^{\text{EQUIV}}+T^{\text{EQUIV}}=\Phi^{\text{EQUIV}}-\Phi^{\text{HS}}+R^{\text{EQUIV}} \tag{2.53}$$

where $-kT\Phi^{\text{EQUIV}}$ is the pair potential of this equivalent system. For $r>\sigma$ the Φ^{EQUIV} comes entirely from the h_D dependence of T_S in (2.31a) and it is therefore natural to identify T_S in which h_D is set identically zero as T^{EQUIV} and to define Φ^{EQUIV} through the relation

$$c_S[\rho,h_S,h_D]=\Phi^{\text{EQUIV}}+T_S[\rho,h_S,0] \tag{2.54}$$

which means, from (2.31a) and (2.33),

$$\Phi^{\text{EQUIV}}=\Phi^{\text{HS}}+R_S[\rho,h_S,h_D]-R_S[\rho,h_S,0] \tag{2.55}$$

One now can make the simple but important mathematical observation that $R_S[\rho,h_S,0]$ has exactly the functional dependence upon ρ and h_S that the R of a one-species system has on ρ and h. Hence one can also write

$$c_S[\rho,h_S,h_D]=\Phi^{\text{EQUIV}}-\Phi^{\text{HS}}+R[\rho,h_S] \tag{2.56}$$

It follows, for example, that if one discharges the RPM, the RPM $R_S=(R_{++}+R_{+-})/2$ becomes the hard-sphere R because $\Phi^{\text{EQUIV}}\to\Phi^{\text{HS}}$, $h_D\to 0$, and $h_S\to h^{\text{HS}}$. Or, if one puts into $R_S[\rho,h_S,0]$ the h_S of a one-species argonlike system with a hard-core potential having an attractive Yukawa tail, then $R_S[\rho,h_S,0]$ at this argon-like critical point will be the $R_S[\rho,h]$ of that system. For such a system, it can be verified that one expects, at criticality,

$$\begin{aligned} R(k;\rho,h]&=\text{const}\cdot k^{2-\eta}, && k\to 0\\ R(r;\rho,h]&=\text{const}\cdot h^{\delta}(r), && r\to\infty \end{aligned} \tag{2.57}$$

where η and δ are the critical exponents in standard notation. (This behavior of R was first given in ref. 54 and can readily be checked against known results for the Ising model.) Thus, in the formalism developed here, the critical behavior of the RPM hinges entirely on the properties of Φ^{EQUIV}, in which all of the effects of nonzero h_{D} sit. One of these effects is to bring into existence the critical point in the first place. One can get insight into how this must come about by looking at Φ^{EQUIV} in the Debye–Hückel limit, $\rho \to 0$, β fixed, where the dominant contribution to ϕ^{EQUIV} is given by

$$\Phi^{\mathrm{EQUIV}}(r) = -\beta\varphi^{\mathrm{EQUIV}}(r) = \Phi^{\mathrm{HS}}(r) + \tfrac{1}{2}h_{\mathrm{D}}^{2}(r) \tag{2.58}$$

This represents an attractive potential φ^{EQUIV} that is strongly ρ and β dependent. If one uses the expression of (2.40) for h_{D} in (2.58) and then obtains the resulting thermodynamic contribution of $\int \Phi^{\mathrm{EQUIV}}(r)\,d\mathbf{r}$, one finds it is of order Γ^3. It is exactly this term that is responsible for the celebrated Debye–Hückel limiting-law $\rho^{3/2}$ term $(=\Gamma_0^3/12\pi)$ in the free-energy density expression for the RPM.

The $\rho^{3/2}$ term becomes instead a $\rho_{\mathrm{F}}^{3/2}$ term, where ρ_{F} is free-ion density, if one takes explicit account of association, forcing the critical point to a considerably higher density. The h_{D} retains the form of (2.40c) for $r \gg \sigma$, but with Γ not equal to Γ_0. Instead Γ is equal to an inverse Debye length appropriate to *only* the free ions, so $\Gamma^2 = 4\pi\rho_{\mathrm{F}}\beta q^2/\varepsilon$. Moreover, an extra very short-ranged contribution $h_{\mathrm{D}}^{\mathrm{ASSOC}}(r)$ of h_{D} develops for r equal to σ and a bit larger than σ, which represents the contribution to h_{D} of associated pairs of ions and higher clusters. The part of h_{D} representing free ions is also short-ranged; it is exponentially damped for $\Gamma \neq 0$, and if one assumed $\Gamma = 0$, it would vanish because of the vanishing Γ_0^2 prefactor in the functional form of (2.40c). For $\Gamma = 0$, the only contribution to $h_{\mathrm{D}}(r)$ remaining would be from the part $h_{\mathrm{D}}^{\mathrm{ASSOC}}(r)$ representing fully associated clusters, which one expects to be at its maximum for $\sigma \leqslant r \leqslant 2\sigma$ and essentially zero for $r \gg 2\sigma$.

The $h_{\mathrm{D}}(r)$ that emerges from this phenomenological view of ionic association is an $h_{\mathrm{D}}(r)$ that would remain short-ranged even if $\Gamma \to 0$, and this continues to be the case when one superimposes association via the law of mass action upon theories that are more accurate for larger Γ_0 than the simple linearized Debye–Hückel theory. If $\Gamma \to 0$, the contribution to $h_{\mathrm{D}}(r)$ coming from free ions will vanish, while the contribution $h_{\mathrm{D}}^{\mathrm{ASSOC}}(r)$ from the clusters of associated ions will be negligible for $r \gg 2\sigma$. We note, however, that if this picture is taken seriously, $\Gamma = 0$ signifies the absence of free ions and hence would appear to be incompatible with the Stillinger–Lovett conclusion that $\varepsilon(0) = \infty$ and the Kosterlitz conclusion(63) that no states are insulating for $d > 2$ in Coulomb-gas models such as the RPM.

If one assumes a Néel-point singularity exists, one has (2.43) and $\frac{1}{2}h_{\mathrm{D}}^2(r)$ is no longer of short range. However, as already discussed, one expects this case to be associated with a λ-line of Néel points that would presumably bear an unmistakable signature, both experimentally and in simulation, that has not been observed in the vicinity of the Case I critical point. If one instead assumes that $h_{\mathrm{D}}(r)$ decays monotonically with increasing r, then the further assumption that $h_{\mathrm{D}}(r)$ is unscreened ($\Gamma = 0$) would require decay of the form

$$h_{\mathrm{D}}(r) \approx Dr^{-p}L(r), \qquad r \gg \sigma, \quad p \geqslant 5 \tag{2.59}$$

[times a term of $O(r^0)$ expressible in terms of logarithms in the borderline case of $p = 5$] in order for h_{D} to satisfy (2.39b). Although (2.59) represents unscreened decay, we see that it yields a $\frac{1}{2}h_{\mathrm{D}}^2(r)$ term of $O(r^{-10})$, which is quite short-ranged.

The *full* behavior of Φ^{EQUIV} is of course much less clear than that of the limiting form $\frac{1}{2}h_{\mathrm{D}}^2$. Using (2.55), one has a formally exact h_{D}-bond, h_{S}-bond, ρ-vertex cluster expansion of Φ^{EQUIV} from that of $R_{\mathrm{S}}[\rho, h_{\mathrm{S}}, h_{\mathrm{D}}] - R_{\mathrm{S}}[\rho, h_{\mathrm{S}}, 0]$, and if it is used with (2.42) or similarly plausible forms of h_{D} under the assumption $\Gamma \neq 0$, along with the expected homogeneous form for h_{S} near a critical point, $r \gg \sigma$,

$$h_{\mathrm{S}}^{\mathrm{H}} = f(\kappa_r)/r^{d-\iota} \tag{2.60}$$

then one finds that each term in the cluster expansion gives rise to a long-range contribution of range not greater than $\frac{1}{2}h_{\mathrm{D}}^2$ and none of these contributions vanishes more slowly than $\frac{1}{2}h_{\mathrm{D}}^2$. If one assumes $\Gamma \to 0$ at criticality, this is still true if one also assumes (2.59). Hence, no compelling evidence appears to emerge from such an analysis that Φ^{EQUIV} becomes long ranged even if one allows for the possibility that $\Gamma \to 0$ at criticality. As a result, it was concluded in ref. 53 that one can reasonably expect the RPM to be argonlike in its criticality.

Some additional remarks are pertinent:

(i) One cannot hope to get the properties of $R_{\mathrm{S}}[\rho, h_{\mathrm{S}}, h_{\mathrm{D}}]$ for $\kappa r \ll 1$ or $k/\kappa \ll 1$ directly from its h_{S}-bond, h_{D}-bond, ρ-vertex expansion. In ref. 52 and here, use was made of the fact that the difference $R_{\mathrm{S}}[\rho, h_{\mathrm{S}}, h_{\mathrm{D}}] - R_{\mathrm{S}}[\rho, h_{\mathrm{S}}, 0]$, which defines Φ^{EQUIV}, is amenable to a term-by-term analysis, from which it follows that Φ^{EQUIV} remains short-ranged under assumptions I regard as plausible. Of course this is clearly far from a *proof* that the RPM criticality is argonlike. Such a perturbative analysis is at its most convincing when used with an h_D that one can assume remains screened at the critical point with $\Gamma \neq 0$, and in ref. 52 it was simply assumed that $\Gamma \neq 0$ in the RPM without further discussion. As noted above, this assumption is a natural one in the context of the phenomenological picture in which $\Gamma = 0$ is identified with an absence of free ions and a resulting insulating state, which one does not expect at nonzero temperature in the RPM.(63)

(ii) There are alternative representations of $R_S(r)$ from which one can expect to get sharper results. One of them comes from extending the functional Taylor series used in ref. 54 to investigate nonionic criticality and in ref. 64 to treat wetting. Although particularly appropriate to the critical point, that representation has not been used here because its formal derivation raises some delicate questions concerning the introduction of single-ion chemical potentials which require further theoretical analysis. Another expansion that has some important advantages over the h-bond, ρ-vertex expansion is the hypervertex resummation of $R_S[\rho, h_S, h_D]$ obtained by extending the corresponding resummation of $R[\rho, h]$ discussed in ref. 33, Appendix. Its use suggests that Φ^{EQUIV} is in fact of significantly shorter range than the $O(r^{-10})$ estimate of $\frac{1}{2}h_D^2(r)$ given above. This representation in turn forms the starting point(57) of a renormalization group study of the primitive model being made by Qiang Zhang and the author. The results of that study lend strong support to the conclusion that the RPM is argonlike in its critical properties, and will be reported elsewhere.

(iii) The idea of regarding the g_S of a symmetric ionic fluid such as the RPM as the distribution function of a hypothetical one-species nonionic fluid can already be found in the work of Stillinger and his coworkers.(24, 25) Unlike the author's work using the decoupling of the Ornstein–Zernike equations for g_S and g_D as a basis, the approach of refs. 24 and 25 uses Kirkwood's charging-parameter hierarchy, in which an s-ion distribution function $g_{12\cdots s}$ is expressed as a functional of the $(s+1)$-ion distribution function $g_{12\cdots s+1}$. Plausible asymptotic estimates of g_{ij} and g_{ijk} yield in refs. 24 and 25 an integral equation for g_S involving an effective pair potential ψ_{ij} obtained from an integration of h_D over β. One of these estimates rests on the assumption that g_D is screened for all β. The resulting ψ_{ij} is argonlike.

2.2. The Asymmetric Case

In Section 2.1 an analysis of RPM criticality was given in terms of the Ornstein–Zernike formalism, in which it was shown that the extreme symmetry of the RPM makes it possible to consider the density–density correlations as if they belonged to a one-species fluid with an effective potential brought about the charge fluctuations. This is not true for the more general *unrestricted* primitive-model (UPM), in which there can be asymmetry as a result of the anions and cations having different charge numbers $|s_i|$ or different diamter σ_{ij}. The restriction to a single anion species A and a single cation species B shall be retained for simplicity. The treatment of the UPM below follows an unpublished development of Zhang and Stell.

In the UPM, Eqs. (2.18)–(2.23) of Section 2.1 still hold, but now in general the charge–charge correlation function h_q is given by

$$\rho^2 h_q = \sum_{ij} \rho_i \rho_j s_i s_j h_{ij} \tag{2.61}$$

while the density–density correlation function h_ρ is given by

$$\rho^2 h_\rho = \sum_{ij} \rho_i \rho_j h_{ij} \tag{2.62}$$

It is also natural to introduce a corresponding density–density generalization of the direct correlation function c_S and of R_S. We have

$$\rho^2 c_\rho = \sum_{ij} \rho_i \rho_j c_{ij} \tag{2.63a}$$

One can write (2.63a) as

$$\rho^2 c_\rho = \rho^2 R_\rho = \sum_{ij} \rho_i \rho_j R_{ij} \tag{2.63b}$$

since one has from change neutrality

$$\sum_{ij} \rho_i \rho_j \varphi_{ij}^{\mathrm{COUL}} = 0 \tag{2.64}$$

The Stillinger–Lovett moment conditions still hold$^{(65)}$ as

$$\lim_{k \to 0} [|s_a s_b|\, \rho + \rho^2 h_q(k)] = |s_a s_b|\, \rho k^2/\Gamma_0^2 \tag{2.65a}$$

or

$$\lim_{k \to 0} [1 + \rho h_q(k)/|s_a s_b|] = k^2/\Gamma_0^2 \tag{2.65b}$$

One can also write the second-moment condition as[60]

$$\sum_{ij} q_i q_j \rho_i \rho_j \int r^2 h_{ij}(r)\, d\mathbf{r} = -6 \sum_i \rho_i q_i^2 / \Gamma_0^2 \tag{2.65c}$$

and (2.39c) becomes

$$\frac{\varepsilon_0}{\varepsilon(k)} = 1 - \frac{\Gamma_0^2}{k^2}\left[1 + \frac{\rho h_q(k)}{|s_a s_b|}\right] \tag{2.65d}$$

In employing these relations, the identity which holds when $i = a, b$ and $j = a, b$

$$\sum_i \rho_i s_i^2 = \rho\, |s_a s_b| = -\rho s_a s_b \tag{2.66}$$

is useful to keep in mind.

One also has a somewhat stronger zeroth-moment condition associated with summation over the charges of only *one* of the particle pairs,

$$\lim_{k \to 0}\left[\sum_i \rho_i s_i h_{ij}(k)\right] = -s_j \tag{2.67}$$

The equations for the charge–charge and density–density correlation functions do not in general decouple as they do in the RPM (for which h_q and h_ρ become the h_{D} and h_{S} introduced in Section 2.1). As a result, the general algebra relating the h_q and h_ρ to the R_{ij} and Φ_{ij} is much more complicated. It simplifies considerably in the special case

$$\rho_a[1 - \rho_a R_{aa}(k)] = \rho_b[1 - \rho_b R_{bb}(k)] \tag{2.68}$$

for which an OZ equation for h_q decouples from the rest of the OZ equations. Equation (2.68) is obviously true in the RPM by symmetry, but it seems unlikely to be realized for all k otherwise. If one could tune the charge numbers s_a and s_b as continuous variables, one might expect to have (2.68) satisfied at the critical point (at least for $k = 0$) for some set of charge numbers and diameters that include the RPM values $s_a = -s_b$, $\sigma_{ij} = \sigma$. We shall refer to the case in which (2.68) is satisfied, at least for $k = 0$, as the case of special symmetry (SS) and cases in which it is not satisfied for any k as cases of ordinary asymmetry (OA).

It is useful to introduce the following auxiliary functions of the R_{ij}:

$$X(k) = 1 - \rho_a R_{aa}(k) - \rho_b R_{bb}(k) + \rho_a \rho_b R_{aa}(k)\, R_{bb}(k) - \rho_a \rho_b R_{ab}^2(k) \tag{2.69}$$

In the RPM, $X(k)$ factors into a product of charge–charge and density–density terms

$$X(k) = [1 - \rho c_S(k)][1 - \rho R_D(k)] \tag{2.70}$$

and vanishes at $k=0$ at critical [because $1 - \rho c_S(k=0) = 0$]. In the OA case, there is no such factoring and one can show that $X(k=0) \neq 0$ at criticality.

One introduces also

$$Y(k) = \rho - \sum_{ij} \rho_i \rho_j R_{ij}(k) \tag{2.71a}$$

From (2.63b) one sees that

$$Y(k) = \rho[1 - \rho c_\rho(k)] \tag{2.71b}$$

Thus, as in the RPM, the condition $Y(k=0)=0$ is the condition of criticality even in the asymmetric case.

In terms of the functions just introduced one has

$$\rho + \frac{\rho^2 h_q(k)}{|s_a s_b|} = \frac{Y(k)\,\Phi^{-1}(k)}{Y(k) + X(k)\,\Phi^{-1}(k)} \tag{2.72}$$

$$\rho + \rho^2 h_\rho(k) = \frac{N(k)}{Y(k) + X(k)\,\Phi^{-1}(k)} \tag{2.73a}$$

Here for notational simplicity we introduce the *positive* term

$$\Phi(k) = \Gamma_0^2/\rho k^2 \tag{2.73b}$$

(which reduces to $-\Phi_D(k)$ in the symmetric case) and

$$N(k) = \rho^2 + \{\rho - \rho_a \rho_b [R_{aa}(k) + R_{bb}(k) - 2R_{ab}(k)]\}\,\Phi^{-1}(k) \tag{2.73c}$$

There appears to be nothing in the structure of the R_{ij} that suggests that $N(k=0)=0$, so $N(k=0) \neq 0$ will be assumed. In the SS case, one can factor $X(k)$,

$$X(k) = Y(k)\,Z(k) \tag{2.74}$$

where

$$4\rho_a\rho_b Z(k) = \rho - \rho_a^2 R_{aa}(k) - \rho_b^2 R_{bb}(k) + 2\rho_a\rho_b R_{ab}(k) \tag{2.75}$$

Hence in the SS case the $Y(k)$ can be factored out of the denominator of (2.72), canceling the $Y(k)$ in the numerator, leaving

$$\rho + \frac{\rho^2 h_q(k)}{|s_a s_b|} = \frac{\Phi^{-1}(k)}{1 + Z(k)\,\Phi^{-1}(k)} \tag{2.76}$$

The denominator of (2.73) becomes $Y(k)[1 + Z(k)\,\Phi^{-1}(k)]$, with the $1 + Z(k=0)\,\Phi^{-1}(k=0)$ expected to remain nonzero. In the RPM case, there is further simplification, and

$$\rho + \rho^2 h_\rho(k) = \rho^2 / Y(k) \tag{2.77}$$

where $\rho Z(k) = 1 - \rho R_{\mathrm{D}}(k)$ and $Y(k) = \rho[1 - \rho c_{\mathrm{S}}(k)]$.

Away from the SS case, the story is very different. Since (2.72) and (2.73a) share the same denominator, h_q and h_ρ will have the *same* correlation length. But as we shall see the $Y(k)\,\Phi^{-1}(k)$ in the numerator of (2.72) not present in (2.73) gives rise to a factor not found in h_ρ that tends to strongly attenuate $h_q(r)$ for large r as the critical point is approached. Moreover, the $\Phi^{-1}(k)$ represents a k^2/Γ_0^2 term in the denominators of (2.72) and (2.73a) as a result of the Coulombic interaction that can be expected to yield mean-field-like behavior. To see these things, it is useful to introduce a small-k representation for $Y(k)/\rho$ $[= 1 - \rho c_\rho(k)]$ that captures its behavior at critical (i.e., $\kappa = 0$) as well as its near-critical dependence on κ as $k \to 0$. To this end we use a Fisher–Burford-type representation$^{(66)}$ and write

$$Y(k)/\rho = 1 - \rho c_\rho(k) = a_0(\kappa^2 + k^2)^{t/2} + \cdots \tag{2.78}$$

Here $a_0\kappa^t$ is $1 - \rho c_\rho(k=0)$, the dimensionless factor $\partial\beta p/\partial\rho$ that describes the inverse isothermal compressibility of the system, while κ is the inverse correlation length. The power t in (2.78) is the critical exponent $2 - \eta$, which is a bit less than 2 in argon; the value 2 typically gives rise to mean-field behavior. Inserting (2.78) into (2.72) yields the small-k result

$$\rho + \frac{\rho^2 h_q(k)}{|s_a s_b|} = \frac{\rho a_0 \kappa^t k^2/\Gamma_0^2 + \cdots}{a_0(\kappa^2 + k^2)^{t/2} + X(0)\,k^2/\Gamma_0^2 + \cdots} \tag{2.79}$$

[which manifestly satisfies the zeroth- and second-moment conditions given by (2.65)]. If one retains only terms through order k^2, one finds for $\kappa r \gg 1$

$$\frac{\rho h_q(k)}{|s_a s_b|} \approx -\frac{\Gamma^4}{\Gamma_0^2} \frac{e^{-\Gamma r}}{r} \tag{2.80}$$

where

$$\Gamma^2 = \kappa^2 / [t/2 + \kappa^{-t} X(0)/a_0 \Gamma_0^2] \tag{2.81}$$

Equation (2.80) is exactly the form (2.42a) one was led to expect in Section 2.1 on a similar level of approximation in the RPM. Here, as in the corresponding RPM expressions, attenuation represented by the Γ^4 in (2.80) is forced by the Stillinger–Lovett condition, which requires a second moment of $h_D(r)$ that remains bounded (and in fact, fully prescribed) as $\Gamma \to 0$ [see (2.39b) and (2.65c)]. The manifest coupling between Γ and κ found in (2.81), however, is completely absent in the RPM. As one takes into consideration the effect of the higher powers of k neglected in (2.79) one finds greater complexity of functional form, including the expected possibility of oscillatory behavior associated with a dominant pole in complex k space that is complex.

It should be noted that the term $X(0)\,k^2/\Gamma_0^2$ in the denominator shared by both $h_q(k)$ and $h_\rho(k)$ in (2.72) and (2.73) has no counterpart in an Ising or Lennard-Jones system. In the Lennard-Jones case, for example, one expects the term beyond the $a_0(\kappa^2 + k^2)^{t/2}$ in (2.79) to be of order k^3, coming from the dispersion term $\sim r^6$ in the Lennard-Jones potential. In the Ising case, one expects the term to be of considerably higher order in k. If $t = 2$ in (2.79), one would expect mean-field critical behavior. Suppose instead that in the OA case one had an argonlike t of 39/20 or so. The competing k^2 singularity would still give rise to apparent mean-field behavior if $X(0)/\Gamma_0^2$ were substantial in size, with $X(0)$ expected to increase as the degree of asymmetry does and Γ_0^{-2} increasing rapidly with Debye length. However, it seems likely that the presence of the k^2 singularity might well dictate the absence of a k^t term with $t < 2$ altogether in the $\kappa \to 0$ limit. In an Ising or argonlike model, the only k^2 term present in a Landau–Ginsburg treatment in three dimensions is one coming from short-range interactions; upon renormalization the whole k^2 term shifts when $\kappa = 0$, to become a k^t term, $t < 2$. The presence of the k^2/Γ_0^2 term in (2.79) that cannot be so shifted appears to inhibit the fluctuations that are necessary to give rise to the shift in the first place. The precise degree of this inhibition is now under investigation by Zhang and myself; our preliminary result indicates that there is no shift, so that $t = 2$.

In the RPM, the charge–density correlation function

$$\rho^2 h_{q\rho}(k) = \sum_{ij} s_i \rho_i \rho_j h_{ij}(k) \tag{2.82}$$

is identically zero. In the OA case, however, it is not; it has an amplitude factor

$$A = \rho_a s_a [\rho_a R_{aa}(k=0) - \rho_b R_{bb}(k=0) - (\rho_a - \rho_b) R_{ab}(k=0)] \tag{2.83}$$

that vanishes with vanishing asymmetry, and $h_{q\rho}(k)$ shares the $Y + X\Phi^{-1}$ denominator with $h_q(k)$ and $h_\rho(k)$. In that case the expression corresponding to (2.80) for h_q is

$$\rho^2 h_{q\rho}(r) \approx \frac{-A\kappa^2}{4\pi\Gamma_0} \frac{\exp^{-\Gamma r}}{r} \tag{2.84}$$

It is of interest to study the crossover from OA to SS behavior as the asymmetry factor

$$w(k) = (\rho_a - \rho_b) - \rho_a^2 R_{aa}(k) + \rho_b^2 R_{bb}(k) \tag{2.85}$$

goes to zero. For this purpose it is convenient to introduce the difference between the function $X(k)$ and the function $Y(k)\, Z(k)$ into which it factors in the SS case,

$$W(k) = X(k) - Y(k)\, Z(k) \tag{2.86}$$

which in fact turns out to be just the square of $w(k)$ times a trivial factor

$$4\rho_a \rho_b W(k) = -w(k)^2 \tag{2.87}$$

$W(k=0)$ itself can be regarded as the asymmetry parameter in the problem; as such a parameter should be, it is invariant under the interchange of the labels a and b. In terms of $W(k)$, we have the small-(W/Y) expansion

$$\rho + \frac{\rho^2 h_q(k)}{|s_a s_b|} = \frac{\Phi^{-1}(k)}{1 + Z(k)\,\Phi^{-1}(k)} - \left[\frac{\Phi^{-1}(k)}{1 + Z(k)\,\Phi^{-1}(k)}\right]^2 \frac{W(k)}{Y(k)} + O\left(\frac{W(k)}{Y(k)}\right)^2 \tag{2.88}$$

The fact that the W appears always in the combination W/Y here illuminates the nonuniform nature of the crossover. For any nonzero W, no matter how small, $W(k=0)/Y(k=0)$ becomes arbitrarily large as criticality is approached [i.e., $Y(k=0) \to 0$]. Hence, sufficiently close to critical, the full form of (2.72) must be used and the effects of asymmetry that have been discussed here will appear. But the smaller the asymmetry, the closer one must come to the critical point to see them.

3. SOLVENT-DOMINATED CRITICALITY

The case of solvent-dominated criticality seems to be characterized by a quite different set of mechanisms than those considered in Section 2. In this case, in which some ions are introduced into a solvent that is already at or near criticality, there are several nontrivial problems to be resolved even *before* the ions are added. Since the best and most common solvents for ionic solute are dipolar, a central problem is whether the dipole–dipole interaction introduces any significant change in the sort of liquid–gas critical point one would have in a nonpolar fluid such as argon. More precisely, one can ask whether one expects the critical point to be in the same universality class as that of argon. In a 1974 study(67) I concluded that the answer is "Yes," and this answer appears to be consistent with the best experimental evidence (e.g., ref. 68).

One can also inquire into the way the addition of a strong dipolar interaction can be expected to change the critical parameters and the shape of the coexistence curve of a simple argonlike fluid. For this purpose, a model fluid with a Stockmayer pair potential is especially useful; it consists of a Lennard–Jones potential plus an ideal dipole–dipole term. In a pair of studies(69, 70) it was found that for the Stockmayer potential, lowest-order thermodynamic perturbation theory in the strength of the dipole–dipole interaction is inadequate, but that a Padé approximation that includes both the second-order and third-order terms appears to give satisfactory results. (The first-order term is identically zero for reasons of symmetry.) The Padé is constructed to give the expected linear response(33) to increasing dipole–dipole strength for large values of this strength.

There is another important issue concerning fluid criticality that hinges on the presence of dipole–dipole interactions and is of crucial importance experimentally even for polarizable systems in which there are only induced dipole–dipole terms in the pair potential and no permanent dipole moment. This is the critical behavior of the dielectric susceptibility (i.e., the dielectric constant and the index of refraction) at the critical point. Its practical importance lies in the fact that modern methods of measuring the critical exponents [especially β, which describes the coexistence curve shape, $\rho - \rho_C \approx \text{const}(T_0 - T)^{\beta}$] use laser optics to measure the index of refraction $\varepsilon(\omega)^{1/2}$ (ω is the optical frequency) and typically assume a Lorentz–Lorenz-type law to relate $\varepsilon(\omega)$ and ρ. If $\varepsilon(\omega)$ were to have a significant critical anomaly itself, it would introduce an important error into the results of this approach unless the Lorentz–Lorenz relation were suitably corrected. I investigated this question with Hocken(70) and with Høye(71) and found that $\varepsilon(\omega)$ shares the singularity of the internal energy at the critical point so that it remains finite as the critical point is approached, but its temperature derivative shares the weak "α singularity," const $|T - T_C|^{-\alpha}$, of the specific heat at constant volume. (In earlier work of Bedeaux and Mazur, it was concluded that the singularity would be stronger, with exponent $2\beta - 1$.(72) Our results were derived for the case of nonpolar fluids in which the molecules carro no permanent dipole moment, but these conclusions can be shown to hold for polar fluids as well. Later work(73) using a purely thermodynamic approach further established a correspondence between the singularities of ε and energy density, confirming the α singularity found by Høye and Stell. [The singularity turns out to have a sufficiently weak amplitude in most fluids to be negligible in the relation between ρ and $\varepsilon(\omega)$ in the critical region.]

I move on now to a consideration of what happens when one adds ions to a solvent at or near its critical point. Nabutovskii *et al.*(74) concluded on the basis of a Landau–Ginsburg analysis that for a certain range of values of the Landau–Ginsburg parameters, one can have a very dramatic effect—the critical point would be lost, and in what had been the critical region one would have charge-density waves instead. Høye and the author(75) reanalyzed the problem using a molecular theory and confirmed this possibility, and were further able to give a molecular interpretation to the Landau–Ginsburg parameter appropriate to an ionic solution. We found that such an effect could be expected to occur only if there were strong and strongly asymmetric ion–solvent association. To describe this mathematically is a bit tedious, even if one stays on the phenomenological Landau–Ginsburg level, but the physical picture seems clear enough: To support solvent-dominated criticality, one needs solvent-particle clustering over a wide range of length scales. If a substantial fraction of the solvent particles have ions of one charge sign adhering to them, but few or no ions of the other sign, then the like-charge repulsion that would be generated upon this cluster formation severely inhibits such formation, and hence inhibits criticality. Instead there is a tendency of the adhering ions of one sign and free ions of the other to position themselves so that around each "dimer" formed by a solvent particle and its adhering ion there is a layer of free ions of opposite charge, about which one can discern a further layer of dimers, etc. The result is a charge-density distribution that changes sign as it decays—i.e., charge-density waves.

To our knowledge, no such charge-density waves have been reported to be experimentally observed in ionic fluids. However, the approaches of Nabutovskii *et al.* and of Høye and Stell, suitably extended, seem well suited to investigating theoretically a number of less dramatic but nevertheless important phenomena associated with solvent-dominated criticality, such as the shift in critical parameters when salt is added to the pure solvent and the attendant disappearance of the α singularity in the heat capacity.(76) The approaches of refs. 74 and 75 have not been applied to these issues.

Høye and Stell(15) have already used their approach to consider the effect on solvent-dominated critical behavior of the charge–dipole interaction that is present when ions are added to a dipolar solvent. In the case of symmetric ions ($\sigma_{ij} = \sigma$, $s_i = -s_j$) with ion–solvent interactions that preserve certain symmetries, one can extend the analysis of Section 2.1.2 to include solvent averaging. The resulting $\Phi^{\mathrm{EQUIV}}(r)$ includes an averaged squared charge–dipole contribution, $\frac{1}{2}h^2_{q\mu}$, which is screened.(77, 78) In the Debye–Hückel limit one knows explicitly, from earlier Høye–Stell work,(78)

$$\tfrac{1}{2}h^2_{q\mu}(r) = Aq^2\mu^2[1 + \lambda r + \tfrac{1}{4}(\lambda r)^2]\, e^{-\lambda r}/r^4 \tag{3.1}$$

where A is a constant, μ is the dipole moment, and $\lambda = 2\Gamma_0$. One expects the same form to hold somewhat beyond the Debye–Hückel limit, but with Γ_0 replaced by the true inverse screening length Γ.(79)

In k space, the corresponding contribution to $\Phi^{\mathrm{EQUIV}}(k)$ is, for small k,

$$\Phi^{\mathrm{EQUIV}}_{q\mu}(k) \approx (Aq^2\mu^2\pi/k)[k\lambda - (\lambda^2 + 2k^2)\,\mathrm{arctg}(k/\lambda)] \tag{3.2a}$$

so

$$\Phi^{\mathrm{EQUIV}}_{q\mu}(k) \approx \begin{cases} -A\pi^2 q^2\mu^2 k, & \lambda \to 0, \quad k \text{ fixed} \\ -A\,5q^2\mu^2k^2/3\lambda, & k \to 0, \quad \lambda \text{ fixed} \end{cases} \tag{3.2b}$$

Thus as $\lambda \to 0$ one expects a crossover to the mean-field-like behavior characteristic of inverse-fourth-power potentials.

In the solvent-dominated case, λ will grow from zero as one adds salt to a dipolar solvent, but the magnitude of the resulting contribution from $\Phi^{\mathrm{EQUIV}}_{q\mu}$ to the thermodynamics of the solution will be negligible in the dilute-salt regime. However, the result indicates that in systems in which Γ is driven to be zero at a critical point (e.g., by asymmetry in

Coulomb-dominated fluids) the presence of charge–dipole terms may be a source of perceptible mean-field behavior when sufficiently large concentrations of both charges and dipoles are present.

4. DISCUSSION, CONCLUSIONS, AND THINGS TO DO

Of the several new results obtained in this work, perhaps the one with the greatest potential importance is the analysis pointing out the differences in critical behavior that can be expected in symmetric and asymmetric Coulomb-dominated criticality.

Imbedded in the more general unsymmetric primitive-model case, the RPM is seen to exhibit an "accidental" decoupling of the charge–charge and density–density correlations because of its high degree of symmetry. One knows that universality class of criticality depends crucially upon range, dimension, and symmetry of the potential fields associated with the order parameters; it therefore should come as no great surprise if one finds that the RPM and the OAPM are in different universality classes as a result of differences in symmetry. The Zhang–Stell results appear to offer compelling evidence that this is the case, and further lead to the conclusion that the OA case exhibits mean-field-like critical behavior, in contrast to the argonlike behavior that they predict in the RPM case.

The mean-field nature of the OAPM would be consistent with the intuition shared by a number of workers in the field that Coulombic Case I critical behavior should be mean-field-like, compared to the expected argonlike critical behavior of Case II or Case III systems, in the categorization introduced in Section 1. In light of this, it is somewhat ironic that the RPM has for years been assumed to epitomize the generic case of Coulombic phase separation and because of its special simplicity has been widely studied in this regard—one sees now that the very simplicity that makes it attractive as a model may rob it of its status as a prototype in the study of Case I criticality. The conclusion that OA systems rather than the RPM should be regarded as showing generic Case I behavior helps resolve the contradiction between the expected mean-field behavior of Case I systems and the argonlike behavior of the RPM that seems to emerge from its theoretical treatment.

In the primitive model, if the size and charge number of anions and cations are equal one has $W(k) \equiv 0$, where $W(k)$ is the asymmetry factor introduced in Section 2.2. But in real Coulombic fluids one can have asymmetry even if the size and charge numbers of the anions and cations are the same. In particular, symmetry can be broken either with respect to permanent electric moments (dipole, quadrupole,...) or polarizability. (For example, one such asymmetry would result from a positional asymmetry in which the distance between the charge center and volume center is different in the anion and cation. This would give rise to a dipole-moment disparity.) Although we have not explicitly included ion–solvent interactions in our formalism here, a straightforward extension of our treatment that includes such terms shows that any disparity between anion–solvent and cation–solvent interactions will similarly give rise to contributions to the anisotropy parameter $W(k=0)$. It seems worthwhile to scrutinize Coulombic fluids that show mean-field behavior but have no size or charge-number asymmetry for such "hidden" asymmetries, which can be large in magnitude. In particular, the N2226, B2226 organic salt investigated by Singh and Pitzer(2) and Zhang *et al.*(7) is worth checking for any such asymmetries, in light of its well-documented mean-field-like criticality.

In addition to providing a potential key to the differences between argonlike and mean-field behavior in Case I criticality, the difference between the RPM and OA behavior brings to the fore some fuzziness in our current phenomenological understanding of insulating and conducting states as well as some gaps in their formal description. As noted in Section 2.1, the Stillinger–Lovett result $\varepsilon(k) \to \infty$ for $k \to 0$ signifies that one has a conducting system. Phenomenologically, one expects this to imply the presence of free charges, which in turn implies screening, so that $\Gamma \neq 0$. This picture appears to be confirmed by the Kosterlitz renormalization-group argument(63) that there is no insulating state for nonzero temperature in a Coulomb gas above two dimensions. Our conclusion that in the unsymmetric case the inverse charge–charge screening length Γ goes to zero at criticality forces us to reappraise the phenomenological argument, since one still has the SL result $\varepsilon(k) \to \infty$ for $k \to 0$, which implies a conducting system. Hence one would again expect free charges and screening. But this would contradict our conclusion $\Gamma \to 0$.

We note, first of all, that the Kosterlitz argument, at least as it stands, does *not* explicitly address the issue of Coulomb-gas criticality, nor does it immediately apply to the asymmetric case, leaning as it does on the simplicity of the full symmetry of the Coulomb gas. It is clearly important to investigate whether the critical state is automatically accommodated within the framework of the argument, and what it yields when extended to the asymmetric case.

With respect to the SL result, an explication of its status as $\Gamma \to 0$ would be helpful and perhaps could come from further development of the Kosterlitz argument. All the demonstrations and derivation of the SL result known to the author(23, 65, 80) impose conditions, implicit or explicit, that prevent it from directly serving as a reliable guide to the structure of $h_q(k)$ and $\varepsilon(k)$ when $k > \Gamma$, and of $h_q(r)$ when $\Gamma r < 1$, $\Gamma \to 0$. On the other hand, the SL condition yields a sharp result for any nonzero Γ, no matter how small, on the second moment of $h_q(r)$, prescribing it as a finite quantity. This makes it attractive to embrace the conclusion that $h_q(r)$ must remain short-ranged as $\Gamma \to 0$, either in the sense of decaying more rapidly than r^{-5} as $r \to \infty$ or in the sense of having oscillating decay, so that there is cancellation between positive and negative contributions to yield a finite second moment. This line of thought, when applied optimistically, pertains not just to $k \ll \Gamma$ and $\Gamma r \gg 1$, but to all k and r such that $\sigma k \ll 1$ and $r \gg \sigma$. Such optimistic application underlies Eq. (2.59) as well as Fisher's discussion of his Eq. (A.5), and it leads one to conclude that one should take the SL condition seriously at a critical point, even if $\Gamma = 0$ there, by continuity. A more conservative approach is to reserve judgment on $h_q(k)$ and $\varepsilon(k)$ when $k < \Gamma$ and $h_q(r)$ when $\Gamma r < 1$, and to be prepared for a crossover from conducting to insulating behavior as $\Gamma \to 0$. Such an approach is not inconsistent with the conclusion that $\Gamma \neq 0$ at the RPM critical point and $\Gamma \to 0$ in the asymmetric case, and it keeps open the provocative possibility of an insulating state at criticality in the asymmetric case. Renormalization-group arguments appear to offer the most promising way to get into the small-Γr, large-k/Γ regime as $\Gamma \to 0$.

As pointed out in Section 2.1, one expects a tricritical point at the end of a λ-line of Néel points in the spin-1 Ising antiferromagnet with a short-ranged antiferromagnetic exchange interaction $J(r)$. What happens when one considers the off-lattice analog—the Yukawa RPM—and lets the range of the Yukawa interaction become infinite is of great interest, since this gives the RPM. The lattice-system version of this limit is of interest, too, but cannot be expected *a priori* to be a reliable guide to the continuum-space behavior. One can hope to gain considerable insight into the possibility of unscreened oscillating $h_q(r)$ raised in this article through a study of this limit by means of simulation and judiciously chosen approximations.

If the screening is strong (Γ large), the effect of the resulting cavity contribution could be lost as a result of the competition it faces from the other contributions to $S^{-1}(k)$. In ref. 53 it was noted that an unscreened term would face competition from as-yet-unassessed n-body solvent-averaged cavity terms, $n \geqslant 3$, which could cancel the effect of the asymptotic behavior of the two-body term. Høye and Stell(15) have subsequently found that this cancellation occurs.

APPENDIX: COMMENTS ON AN ANALYSIS OF M. E. FISHER

Much of the development of Section 2.1.2 leading to the conclusion that argonlike critical behavior rather than mean-field behavior can be plausibly expected in the RPM was already summarized in an earlier paper.$^{(53)}$ In an Appendix to ref. 37, Fisher has given a detailed critique of that paper. His remarks raise a number of interesting questions worth pursuing.

In ref. 53 it was asserted without further discussion that the inverse charge–charge correlation length Γ can be expected to be nonzero at the RPM critical point. Fisher criticizes the lack of justification of this assumption; I shall therefore elaborate here upon its basis, which is the conclusion (cogently argued by Kosterlitz$^{(63)}$) that for a d-dimensional Coulomb gas, of which the RPM is an example, one expects all of the thermodynamic states to be noninsulating at nonzero temperature for all $d>2$. I interpret this to mean that there is a nonzero concentration of free (unassociated) charges in the RPM at all such states, including the critical state. I further assume that whenever there are free ions there will be screening of the charges, so that the charge–charge inverse screening length Γ is not zero. The crucial point is that I do *not* exempt the RPM critical state from this conclusion—even though the density–density correlations indeed become unscreened, because the density–density and charge–charge correlations are not directly coupled in the RPM, as they more generally are.

Fisher argues that one must be suspicious of the statement that $\Gamma \neq 0$ at criticality in the RPM on the basis of our general understanding of criticality that has been built up from the investigation of a variety of models, which he sums up as a principle of "infection by the critical singularities" such that *all* the correlation functions of a system must display power-law decay at critical. In this connection, Fisher calls attention to the observation made in ref. 53 that the RPM internal energy U can be wholly determined from $h_D(r)$, the charge–charge correlation function. Since $c_V \sim \partial U/\partial T$ diverges as $(T-T_C)^{-\alpha}$ at criticality (with $\alpha = 0.11$ for argon), the h_D must therefore carry information concerning critical singularities in its structure. Moreover, Fisher observes, the specific heat c_V itself can be directly expressed in terms of a four-particle function $h(12;34)$ that must be expected to exhibit power-law decay in order for c_V to diverge. It is natural to assume that $h(12;34)$, like $h_D(r)$, has Γ as its inverse screening length, which leads one to conclude that $\Gamma = 0$ at criticality.

These arguments are surely food for thought. But perhaps they prepare one for what one might typically expect when special symmetries are not at work, and fall short of implying what one *must* expect, special symmetries or no. In particular, all one requires of $h_D(r)$ in order to get the $(T-T_C)^{-\alpha}$ singularity is that for fixed r such that $\kappa r \ll 1$, the difference between $h_D(r)$ and its critical value $h_D(r)_C$ goes like $(T-T_C)^{1-\alpha}$ as $T \to T_C$. Here κ is the inverse density–density correlation length. With respect to $h(12;34)$, one might reasonably expect its inverse screening length in the r_{12} direction to be Γ, but it does not seem obvious why one should expect its inverse screening length in the $|(\mathbf{r}_1+\mathbf{r}_2)/2-(\mathbf{r}_3+\mathbf{r}_4)/2|$ direction to be Γ rather than κ. Thus, on the face of it, power-law decay of $h(12;34)$ at criticality does not necessarily seem to imply $\Gamma=0$.

As discussed in Section 2.2, all of this is changed when one loses the special symmetry of the RPM. In the asymmetric case that I have labeled the OA case, one finds from the same analysis that one can reasonably expect the critical behavior anticipated by Fisher with $\Gamma \sim \kappa$, so that $\Gamma \to 0$ at criticality.

I have noted in Section 2.1.2 that even if the RPM Γ were to go to zero at criticality so that $h_D(r)$ becomes unscreened, the Stillinger–Lovett relation (2.39b) would limit $h_D(r)$ to a negative power of r of at least 5 if $h_D(r)$ decayed monotonically, and the line of reasoning given there and in ref. 53 would yield argonlike behavior "to all orders" in the perturbation theory defined by the cluster expansion representation of $R_S[\rho, h_S, h_D]$. In his Appendix, Fisher acknowledges this, but goes on to point out that if one allows oscillatory forms such as his example

$$h_D(r) = J(\sin k_0 r)/r^{1+\eta(q)} \tag{A1}$$

then $h_D(r)$ will no longer be asymptotically dominated by $h_S(r)$ for large r in a way that permits the analysis of ref. 53 and Section 2.1.2 to go through. This is certainly true, but the form of (A1) is an example of our Eq. (2.43)—a special case that one expects to find associated with the λ-line of Néel points, as discussed in ref. 53. In responding to a suggestion by Kholodenko and Beyerlein[(62)] that one might have a tricritical point in the RPM associated with the intersection of such a λ-line and the coexistence curve, Fisher argues that such tricritical behavior is theoretically unlikely and moreover has a striking thermodynamic signature that has not been detected in either the experimental or simulation studies of Coulomb-driven phase separation. It seems to me that such behavior, the possibility of which Fisher assures us in his Section 3 can be safely ignored, is but another face of the same behavior that he cautions us in his Appendix to take seriously.

Fisher has justified reservations concerning the cluster-sum representations of $R(r;\rho,h]$ and $R_S(r;\rho,h_S,h_D]$. They cannot be expected to directly yield reliable information about R or R_S for $\kappa r = \ll 1$, as he points out. However, in ref. 53 and here, I have not attempted to use these representations to give direct information about either function for $\kappa r \ll 1$, but rather have used them to extract information about the range of the difference between $R_S(r;\rho,h_S,h_D]$ and $R(r;\rho,h_S]$. This strategy is indeed perturbative with no pretense of rigor—its chief function is to probe for the appearance of a physically describable mechanism that could lead to mean-field behavior. None has emerged. On the other hand, in a parallel investigation of the unsymmetric case in Section 3 here such a mechanism *does* emerge on the basis of plausible assumptions concerning the R_{ij}.

The obvious next step is to seek representations of the R_{ij} that *can* directly yield small-κr and small-κ/k information and so test our assumptions and well as provide specific details of criticality that our approach here cannot do. To this end we have initiated a renormalization-group study of the R_{ij} with Qiang Zhang. Our preliminary RPM results yield argonlike behavior; they are consistent with $\Gamma \neq 0$ at criticality, but do not rule out $\Gamma \sim \kappa^p$, $p < 1$. They also confirm $\Gamma \sim \kappa$ and mean-field behavior in the OA case; a report on our progress in this work is in preparation.

I turn briefly to a second item in ref. 53 that Fisher considers. It is the claim there that in more realistic models than the RPM, $1/r^4$ repulsive ion–ion terms arising from solvent-averaged ion–dipole–ion interactions will tend to prevent true criticality, although competing $1/r^4$ terms that can suppress this effect will in general also be present and remain to be evaluated. Fisher raises the question of whether screening will alter this result. One expects to find such screening in charge–dipole correlations as well as charge–charge correlation as pointed out by Kirkwood(77) and subsequently examined in detail by Høye and Stell.(78)

As discussed in ref. 53, such a $1/r^4$ already appears in the so-called cavity model, which differs from the primitive model in one important way. The primitive model can be regarded as a model of charged hard spheres immersed in a uniform dielectric continuum of dielectric constant ε that uniformly permeates the interiors of the spheres as well as the space exterior to them. In the cavity model,(81) the continuum does not permeate the interiors of the spheres. These are the cavities—which are characterized instead by the dielectric constant ε_0 of the vacuum. There are no explicit charge–dipole terms in the cavity model, which is the model considered in ref. 53. Instead the $1/r^4$ "cavity term" comes from polarization effects associated with an induced charge–cavity interaction. The conventional treatments of the cavity model(81) have not delved into the question of screening, which was neglected in ref. 53 also. However, in an extension of their earlier work on charge–dipole and dipole–dipole screening, Høye and Stell(15) have established that $h_q(r)$ will indeed be screened in the cavity model by regarding the model as an appropriately scaled limit of a model in which one has a solvent of dipolar particles. The screening will introduce a rounding at $k = 0$ of the term proportional to k in the inverse structure factor $S^{-1}(k)$ that comes from the cavity term. However, if the screening is weak (Γ small), this will not alter the effect of this term, which is to shift the minimum of $S^{-1}(k)$ from $k = 0$ to some $k_0 \neq 0$; $S^{-1}(k)$ at k_0 will be insensitive to the details of $S^{-1}(k)$ at $k=0$. In particular, in the OA case, in which one can expect $\Gamma \rightarrow 0$ as criticality is approached, screening is unlikely to be a significant factor.

NOTE ADDED IN PROOF

The screening has also been found by direct computation in the cavity model by M. E. Fisher, Y. Levine, and X.-J. Li, *J. Chem. Phys.* **101**:2273 (1994). See also X.-J. Li, Y. Levine, and M. E. Fisher, *Europhys. Lett.* **26**:683 (1994).

ACKNOWLEDGMENTS

The author gratefully acknowledges the Norsk Hydro for its support of the Lars Onsager Professorship, which he held while preparing this manuscript at the Norwegian Institute of Technology. He is also grateful to the National Science Foundation for its support of his work at Stony Brook, where this manuscript was completed. He thanks his many coworkers who contributed to the work described herein, especially his long-term collaborators, Bjørn Hafskjold and Johan Høye, and his postdoctoral associate, Dr. Qiang Zhang. Correspondence and conversations with Prof. M. E. Fisher, Prof. H. L. Friedman, Dr. F. Raineri, and Dr. F. H. Stillinger have been particularly stimulating. He is especially grateful to Prof. Fisher for his probing questions and for sending him a copy of ref. 37 before publication, which made possible a response here to Fisher's critique of ref. 53.

REFERENCES

1. R. R. Singh and K. S. Pitzer, *J. Am. Chem. Soc.* **110**:8723 (1988).
2. R. R. Singh and K. S. Pitzer, *J. Chem. Phys.* **92**:6775 (1990).
3. M. L. Japas and J. M. H. Levelt Sengers, *J. Phys. Chem.* **94**:5361 (1990).
4. K. S. Pitzer, *Acct. Chem. Res.* **23**:333 (1990).
5. H. Weingärtner, T. Merkel, U. Maurer, J.-P. Conzen, H. Glasbrenner, and S. Käshammer, *Ber. Buns. Phys. Chem.* **95**:1579 (1991).
6. H. Weingärtner, S. Wiegand, and W. Schröer, *J. Chem. Phys.* **96**:848 (1992).
7. K. C. Zhang, M. E. Briggs, R. W. Gammon, and J. M. J. Levelt Sengers, *J. Chem. Phys.* **97**:8692 (1992).
8. J. M. H. Levelt Sengers and J. A. Given, *Mol. Phys.* **80**:899 (1993).
9. J. P. Valleau, *J. Chem. Phys.* **95**: 584 (1991).
10. A. Z. Panagiotopoulos, *Fluid Phase Equilib.* **76**:97 (1992).
11. G. Orkoulas and A. Z. Panagiotopoulos, *J. Chem. Phys.* **101**:1452 (1994).
12. J. L. Caillol, *J. Chem. Phys.* **100**:2161 (1994).
13. B. Widom and J. S. Rowlinson, *J. Chem. Phys.* **52**:1670 (1970); D. Ruelle, *Phys. Rev. Lett.* **27**:1040 (1971).

14. H. Xu, H. L. Friedman, and F. O. Raineri, *J. Solution Chem.* **20**:739 (1991).
15. J. S. Høye and G. Stell, SUSB College of Engineering and Applied Sciences Report 679 (1993); J. S. Høye and G. Stell, *J. Stat. Phys.* **78**:1171 (1995); *J. Chem. Phys.*, in press.
16. D. Wei and G. N. Patey, *Phys. Rev. Lett.* **68**:2043 (1992).
17. D. Wei and G. N. Patey, *Phys. Rev. A* **46**:7783 (1992).
18. J. J. Weis *et al.*, *Phys. Rev. Lett.* **69**:913 (1992).
19. J. J. Weis and D. Levesque, *Phys. Rev. E* **48**:3728 (1993).
20. E. Lomba et al., *Phys. Rev. E* **49**:5169 (1994); E. Lomba, J. J. Weis, and G. Stell, *Phys. Rev. E*, in press.
21. D. A. McQuarrie, *J. Phys. Chem.* **66**:1508 (1962).
22. H. L. Friedman, *J. Phys. Chem.* **66**:1595 (1962).
23. F. H. Stillinger, Jr., and R. Lovett, *J. Chem. Phys.* **48**:3858 (1968).
24. F. H. Stillinger, J. G. Kirkwood, and P. J. Wojtowicz, *J. Chem. Phys.* **32**:1837 (1960).
25. F. H. Stillinger, Equilibrium theory of pure fused salts, In *Molten Salt Chemistry*, Milton Blander, ed. (Interscience, New York, 1964).
26. P. N. Vorontsov-Veliaminov, A. M. El'yashevich, L. A. Morgenshtern, and V. P. Chasovshikh, *Teplofiz. Vys. Temp.* **8**:277 (1970) [*High Temp. (USSR)* **8**:261 (1970)].
27. V. P. Chasovshikh, P. N. Vorontsov-Veliaminov, and A. M. El'yashevich, *Dokl. Akad. Nauk Tadzhiksko SSR* **16**(10):23 (1973).
28. V. P. Chasovshikh and P. N. Vorontsov-Veliaminov, *Teplofiz. Vys. Temp.* **14**:199 (1976) [*High Temp. (USSR)* **14**:174 (1976)].
29. G. R. Stell, K. C. Wu, and B. Larsen, *Phys. Rev. Lett.* **37**:1369 (1976).
30. G. Stell and J. L. Lebowitz, *J. Chem. Phys.* **49**:3706 (1968).
31. G. Stell and K. C. Wu, *J. Chem. Phys.* **63**:491 (1975).
32. J. C. Rasaiah, B. Larsen, and G. Stell, *Mol. Phys.* **33**:987 (1977).
33. G. Stell, Fluids with long-range forces: Toward a simple analytic theory, In *Modern Theoretical Chemistry*, Vol. 5A: *Statistical Mechanics*, Bruce Berne, ed. (Plenum, New York, 1977).
34. E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **56**:3086 (1972).
35. J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **144**:251 (1966).
36. G. Stell and B. Larsen, *J. Chem. Phys.* **70**:361 (1979); see also E. W. Montroll and J. L. Lebowitz, eds., *Studies in Statistical Mechanics*, *Fluids Volume* (North-Holland, Amsterdam, 1982).
37. M. E. Fisher, *J. Stat. Phys.* **75**:1 (1994).
38. N. Bjerrum, *Kgl. Danske Vidensk. Selsk. Mat.-Fys. Medd.* **7**:1 (1926).
39. H. L. Friedman and B. Larsen, *J. Chem. Phys.* **70**:92 (1979).
40. W. Ebeling, *Z. Phys. Chem.* (Leipzig) **247**:340 (1971).
41. W. Ebeling and M. Grigo, *Ann. Phys.* (Leipzig) **37**:21 (1980).
42. M. J. Gillan, *Mol. Phys.* **49**:421 (1983).
43. A. Tani and D. Henderson, *J. Chem. Phys.* **79**:2390 (1983).
44. K. S. Pitzer and D. R. Schreiber, *Mol. Phys.* **60**:1067 (1987).
45. J. A. Given and G. Stell, *J. Chem. Phys.* **96**:9233 (1992).
46. M. E. Fisher and Y. Levin, *Phys. Rev. Lett.* **71**:3826 (1993).
47. J. S. Høye and K. Olaussen, *Physica* **104A**:435, 447 (1980); **107A**:241 (1981).
48. V. McGahay and M. Tomozawa, *J. Noncryst. Solids* **109**:27 (1989).
49. V. McGahay and M. Tomozawa, *J. Chem. Phys.* **97**:2609 (1992).
50. M.-C. Justice and J.-C. Justice, *J. Solution Chem.* **5**:543 (1976); **6**:819 (1977).
51. P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953), Chapters 12 and 13.

52. P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979), especially Section IV.3.
53. G. Stell, *Phys. Rev. A* **45**:7628 (1992).
54. G. Stell, *Phys. Rev. B* **1**:2265 (1970).
55. G. Stell, *Phys. Rev. Lett.* **20**:533 (1968).
56. G. Stell, Correlation functions and their generating functionals, In *Phase Transitions and Critical Phenomena*, Vol. 5B, C. Domb and M. S. Green, eds. (Academic Press, London, 1976).
57. Q. Zhang and J. P. Badiali, *Phys. Rev. Lett.* **67**:1598 (1991); *Phys. Rev. A* **45**:8666 (1992).
58. B. Larsen, *Kgl. Norske Vidensk. Selsk.* **2**:1 (1979).
59. C. W. Outhwaite, Equilibrium theory of electrolyte solutions, In *Specialist Periodical Reports: Statistical Mechanics*, Vol. 2, K. Singer, ed. (Chemical Society, London, 1975).
60. R. Lovett and F. H. Stillinger, *J. Chem. Phys.* **48**:3869 (1968).
61. G. Stell, SUSB College of Engineering and Applied Sciences Report 608 (August 1991).
62. A. Kholodenko and A. L. Beyerlein, *Phys. Lett. A* **175**:366 (1993).
63. J. M. Kosterlitz, *J. Phys. Chem.* **10**:3753 (1977).
64. Y. Zhou and G. Stell, *J. Chem. Phys.* **92**:5533, 5544 (1990).
65. F. H. Stillinger and R. Lovett, *J. Chem. Phys.* **49**:1991 (1968).
66. M. E. Fisher and R. J. Burford, *Phys. Rev.* **159**:583 (1967).
67. G. Stell, *Phys. Rev. Lett.* **32**:286 (1974).
68. J. M. H. Levelt Sengers and S. C. Greer, *J. Heat Mass Transfer* **15**:1865 (1974); see also J. V. Sengers and J. M. H. Levelt Sengers, *Ann. Res. Phys. Chem.* **37**:189 (1986), and references therein.
69. G. Stell, J. C. Rasaiah, and H. Narang, *Mol. Phys.* **23**:393 (1972)**27**:1393 (1974).
70. R. Hocken and G. Stell, *Phys. Rev. A* **8**:887 (1973).
71. G. Stell and J. S. Høye, *Phys. Rev. Lett.* **33**:1268 (1974).
72. D. Bedeaux and P. Mazur, *Physica* **67**:23 (1973).
73. J. V. Sengers, D. Bedeaux, P. Mazur, and S. C. Greer, *Physica* **104A**:573 (1980).
74. V. M. Nabutovskii, N. A. Nemov, and Yu. G. Peisakhovich, *Sov. Phys. JETP* **52**:1111 (1980) [*Zh. Eksp. Teor. Fiz.* **79**:2196 (1980); *Phys. Lett.* **79A**:98 (1980); *Mol. Phys.* **54**:979 (1985).
75. J. S. Høye and G. Stell, *J. Phys. Chem.* **94**:7899 (1990).
76. J. M. H. Levelt Sengers, C. M. Everhart, G. Morrison, and K. S. Pitzer, *Chem. Eng. Comm.* **47**:315 (1986).
77. J. G. Kirkwoord, *J. Chem. Phys.* **2**:351 (1934).
78. J. S. Høye and G. Stell, *J. Chem. Phys.* **67**:1776 (1977); **68**:4145 (1978); **71**:1985 (1979); *Faraday Disc. Chem. Soc.* (*Ion–Ion Ion–Solvent Interactions*) **64**:16–21 (1978); see also C. W. Outhwaite, *Mol. Phys.* **31**:1345 (1976).
79. G. Stell, G. N. Patey, and J. S. Høye, *Adv. Chem. Phys.* **48**:183 (1981).
80. D. J. Mitchell, D. A. McQuarrie, Attila Szabo, and J. G. Groeneveld, *J. Stat. Phys.* **17**:15 (1977); J. S. Høye and G. Stell, *J. Chem. Phys.* **67**:1776 (1977); D. Chan, D. Mitchell, B. Ninham, and B. Pailthorpe, *J. Chem. Phys.* **69**:691 (1978); M. Baus and J. P. Hansen, *Phys. Rep.* **59**:1 (1980); Ph. A. Martin and Ch. Gruber, *J. Stat. Phys.* **31**:691 (1983).
81. S. Levine and G. Bell, In *International Symposium on Electrolytes*, G. Pesce, ed. (Pergamon Press, New York, 1962); S. Levine and D. K. Rozenthal, In *Chemical Physics of Ionic Solution*, B. E. Conney and R. G. Barradas, eds. (Wiley, New York, 1966).