NOTE ON THE CRITICAL BEHAVIOR OF
THE RESTRICTED PRIMITIVE MODEL

Q. ZHANG and G. STELL

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794-3400

ABSTRACT: We make precise an earlier argument that a fluid of symmetrically charged hard spheres, the restricted primitive model (RPM), has Argon-like critical behavior. By using a renormalized closure for the Ornstein-Zernike equation, it is shown that the RPM correlations are dominated by the same terms as those that dominates the critical behavior of a one-component simple fluid.

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Recently there has been considerable interest in the critical behavior of ionic solutions. Two sorts of experimental results have been reported. In some ionic fluids, the results appear to be consistent with mean-field behavior [1,2], while in others, the results are consistent with Argon-like critical behavior [3,4]. H. Weingärtner et al. atribute these different results to different types of unmixing—solvophobic unmixing and Coulombic unmixing [5]. Here we focus on a widely used ionic-solution model, the restricted primitive model (RPM), and give an argument that shows directly that only the Argon-like behavior can be expected in the RPM.

As one of us has discussed in earlier work [6,7], there are a number of important features of the Hamiltonians of real ionic solutions that are absent in the RPM, in particular, asymmetric features (such as different anion-cation charge numbers and diameters and different anion-solvent and cation-solvent interactions) as well as long-range r^{-4} terms due to ion-dipole interactions. We intend to precisely assess the effect of such feature in forthcoming work.

In a paper [6] summarying and extending earlier work in [7] which was based in turn on [8 − 10], one of the authors outlined an argument from which he concluded that the RPM is in the same universality class as a model of a simple non-ionic fluid such as Argon with respect to the liquid-gas critical point that one expects in both systems. That representation, however, does not lend itself to a direct determination of the critical exponents of either system. Here we consider a somewhat different representation that does so lend itself, and also facilitates a more precise comparison of the two systems. It is a variant of the representation recently introduced by one of the authors with Badiali to

treat an Argon-like simple fluid [11]. It enables one to make direct use of the field-theoretic arguments of refs. [12,13].

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

$$u(r) = q^2/\epsilon r, \tag{1}$$

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

One has an Ornstein-Zernike (OZ) equation relating the total correlation functions $h_{ij}(r)$ to direct correlation functions $c_{ij}(r)$ and a one-particle local density $\rho_n(r)$,

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \sum_n \int \rho_n(r_3) h_{in}(r_{13}) c_{nj}(r_{32}) d\mathbf{r}_3 \tag{2}$$

and a second independent relation expressing $c_{ij}(r)$ as $-\beta \varphi_{ij}(r)$ plus a functional that is fully determined by ρ_i, h_{ij} and r. Here $\beta = (k_B T)^{-1}$, T is the temperature and k_B is Boltzmann's constant.

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It is convenient for our purposes here to express $c_{ij}(r)$ as a term associated with the Coulombic potential plus a remainder,

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

where $\Phi_{ij}(r) = -\beta s_i s_j u(r)$. A boundary condition for this system is: $h_{ij}(r) = -1$ for $r \leq \sigma$, so we only need (3) for $r > \sigma$ [14].

When the d-dimensional Fourier transforms $h_{ij}(k)$ and $c_{ij}(k)$ are used, and $\rho_n(r) = \rho_n$, independent of r, eq. (2) can be rewritten as

$$h_{ij}(k) = c_{ij}(k) + \sum_n \rho_n h_{in}(k) c_{nj}(k) \tag{4}$$

from which we get

$$h_{aa}(k) = \frac{c_{aa}(k)\big(1 - \rho c_{bb}(k)\big) + \rho c_{ab}^2(k)}{\big(1 - \rho c_{aa}(k) + \rho c_{ab}(k)\big)\big(1 - \rho c_{aa}(k) - \rho c_{ab}(k)\big)} \tag{5a}$$

$$h_{ab}(k) = h_{ba}(k) = \frac{c_{ab}(k)}{\big(1 - \rho c_{aa}(k) + \rho c_{ab}(k)\big)\big(1 - \rho c_{aa}(k) - \rho c_{ab}(k)\big)} \tag{5b}$$

$$h_{bb}(k) = \frac{c_{bb}(k)\big(1 - \rho c_{aa}(k)\big) + \rho c_{ab}^2(k)}{\big(1 - \rho c_{aa}(k) + \rho c_{ab}(k)\big)\big(1 - \rho c_{aa}(k) - \rho c_{ab}(k)\big)} \tag{5c}$$

where the symmetry relations $c_{aa} = c_{bb}$ and $c_{ab} = c_{ba}$ have been used. We can further decompose h_{ij} into a product of common function $\widetilde{\chi}(k)$ that is independent of charge species and a specific part $\widetilde{c}_{ij}(k)$ by writing $h_{ij}(k) = \widetilde{c}_{ij}(k)\widetilde{\chi}(k)$ with

$$\big[\widetilde{c}_{ij}(k)\big] = \begin{bmatrix} c_{aa}(k)\big(1 - \rho c_{bb}(k)\big) + \rho c_{ab}^2(k) & c_{ab}(k) \\ c_{ab}(k) & c_{bb}(k)\big(1 - \rho c_{aa}(k)\big) + \rho c_{ab}^2(k) \end{bmatrix}. \tag{6}$$

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The common part can be written as $\widetilde{\chi}(k) = \widetilde{\Gamma}^{-1}(k)$, where

$$\widetilde{\Gamma}(k) = \big(1 - \rho c_{aa}(k) + \rho c_{ab}(k)\big)\big(1 - \rho c_{aa}(k) - \rho c_{ab}(k)\big) \tag{7}$$

The Fourier transform of eq. (3) is in the form:

$$c_{ij}(k) = \Phi_{ij}(k) + R_{ij}(k, h_{ij}, \rho) \tag{8}$$

with $\Phi_{ij}(k) \sim 1/k^2$. In order to get the long-range behavior of $h_{ij}(r)$ through $h_{ij}(k)$, we need to focus on $k \to 0$. When eq. (8) is introduced in eqs. (5), the dominant term in both $\widetilde{c}_{ij}(k)$ and $\widetilde{\Gamma}(k)$ will be proportional to $1/k^2$ which diverges in the limit $k \to 0$. Therefore for small k, we further get

$$h_{ij}(k) = \mathbf{c}_{ij}(k)\chi(k), \qquad \chi(k) = \Gamma^{-1}(k), \tag{9a}$$

plus neglegible terms that vanish as $k \to 0$, where

$$\Big[\mathbf{c}_{ij}(k)\Big] = (2\rho)^{-1} \begin{bmatrix} \big(2\rho R_{aa}(k) + 2\rho R_{ab}(k) - 1\big) & 1 \\ 1 & \big(2\rho R_{aa}(k) + 2\rho R_{ab}(k) - 1\big) \end{bmatrix} \tag{9b}$$

and

$$\Gamma(k) = 1 - \rho R_{aa}(k) - \rho R_{ab}(k) \tag{10}$$

It is worth noting that the right-hand side of (7), which appears as the denominator in (5), is simply $\widetilde{c}_\rho(k)\widetilde{c}_q(k)$ where $n\widetilde{c}_\rho(k) = nc_\rho(k) - 1$ and $n\widetilde{c}_q(k) = nc_q(k) - 1$. Here $c_\rho(k)$ and $c_q(k)$ are the density-density and charge-charge direct correlation functions, respectively,

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given by the sum and difference terms. $c_\rho = (c_{aa} + c_{ab})/2$, $c_q = (c_{aa} - c_{ab})/2$, while $\tilde{c}_\rho(k)$ and $\tilde{c}_q(k)$ are the corresponding "modified" functions that include the "self" (*i.e.* ideal-gas) terms that are Kronecker deltas in k-space; $\rho\tilde{c}_{ij}(k) = \rho c_{ij}(k) - \delta_{ij}$, also $R_\rho(k) = c_\rho(k)$. The $\Gamma(k)$ of eq (10) is just $-n\tilde{c}_\rho(k)$; at $k = 0$ this is the inverse compressibility term $\beta\partial p/\partial n$ of the RPM, $p =$ pressure. Thus $\Gamma(0) = 0$ is the spinodal condition of criticality. We note from (7) that $\tilde{\Gamma}(k) = n\tilde{c}_q(k)\Gamma(k)$, so $\tilde{\Gamma}(k)$ would become zero in the presence of long-range charge-density waves, the signature of which is the condition $\tilde{c}_q(k) = 0$ at some $k = k_0$. Also $\chi(k) = \Gamma^{-1}(k)$ is just the density-density structure factor of the system,

$$\chi(k) = 1 + \rho h_{aa}(k) + \rho h_{ab}(k) = 1 + n h_\rho(k).$$

When $\Gamma(0) = 0$, one expects no singular behavior in the elements of $\mathbf{c}_{ij}(k)$, which can be replaced by $\mathbf{c}_{ij}(0)$ in analysing the long-range behavior of the $h_{ij}(r)$. At $\Gamma(0) = 0$, $\mathbf{c}_{ij}(0)$ becomes exactly

$$\left[\mathbf{c}_{ij}(0) \right] = n^{-1} \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \tag{11}$$

This means that in the case of RPM, $\mathbf{c}_{ij}(k)$ is universal at the critical point and $h_{ij}(k)$ can be simply expressed for small k near critical as $h_{ij}(k) \approx \chi(k)/n$. But $\chi(k)/n \approx h_\rho(k)$ near critical, so $h_{ij}(k)$ can be effectively replaced by $h_\rho(k)$ in assessing its critical and near critical behavior, which is determined by $\Gamma(k)$ in eq. (10).

To evaluate the $R_{ij}(k)$ of (10) we shall follow ref. [11] in constructing a perturbation theory in which the reference system consists of the molecules enclosed in an isolated sphere $S(1, \lambda)$ of radius $\lambda = \Lambda^{-1}$, which we take to be large compared to a molecular diameter

but small compared to the density-density correlation length. The system in $S(1, \lambda)$ is held at the same chemical potentials and temperature as the infinite system, which we shall examine at its critical point. Under these condition the finite reference system in $S(1, \lambda)$ will not be at the critical; it will be at $\beta = \beta_c$, but at some expected density $\rho^{\Lambda 1}(r)$, where $\rho^{\Lambda 1}(r) = \rho_\Lambda$ for $r \in S(1, \lambda)$, $\rho^{\Lambda 1}(r) = 0$ for r outside $S(1, \lambda)$. This system has its own correlation functions $h_{ij}^{\Lambda 1}$ and $R_{ij}^{\Lambda 1}$, which are short-ranged on the scale of λ. Introducing the reference system also enables us to define a useful set of longer-ranged h_{ij}^{Λ}-function, given by eq. (2) with c_{ij} and c_{nj} replaced by $c_{ij}^{\Lambda 1}$ and $c_{nj}^{\Lambda 3}$, respectively, and $\rho_n(r_3)$ replaced by $\rho_n^{\Lambda 3}(r_3)$ (rather than $\rho_n^{\Lambda 1}(r_3)$, as in the case of $h_{ij}^{\Lambda 1}$). Thus h_{ij}^{Λ} is the sum over all chains of $c_{ij}^{\Lambda l}$-bonds and $\rho^{\Lambda l}$-vertices while $h_{ij}^{\Lambda 1}$ is the sum over all chains of $c_{ij}^{\Lambda 1}$-bonds and $\rho^{\Lambda 1}$-vertices. The relevant behavior of $h_{ij}^{\Lambda}(k)$ near the critical point will occur through the function $1 + \rho_\Lambda h_{aa}^{\Lambda}(k) + \rho_\Lambda h_{ab}^{\Lambda}(k) = 1 + n_\Lambda h_\rho^{\Lambda}(k) = \Gamma^{\Lambda}(k)$ $(n_\Lambda = 2\rho_\Lambda)$ which we expect (and can verify) to be of the Gaussian-approximation form $(A exp - m_2 r)/r^{d-2}$ for $r > \lambda$.

We now need a way of breaking $c_\rho(r)$ and $R_\rho(r)$ into parts $c_\rho^S(r)$ and $R_\rho^S(r)$ that are short-ranged (even at critical) plus comparatively longer-range remainders. We do this by extracting from $h_\rho(\mathbf{k})$ the Ornstein-Zernike term $h_\rho^{OZ}(\mathbf{k}) = A/(k^2 + \kappa^2)$ associated with the poles $\pm i\kappa$ of $h_\rho(\mathbf{k})$ nearest the origin in complex Fourier space, for h_ρ off (but near) critical. This $h_\rho^{OZ}(\mathbf{k})$ term has a well-defined critical-point limit as $\kappa \to 0$ even though the pole loses its identity at the critical point in a branch-point confluence of the other singularities. We shall denote the parts of $c_\rho(r)$ and $R_\rho(r)$ associated with this $h_\rho^{OZ}(r)$ through the Ornstein-Zernike equations as $c_\rho^S(r)$ and $R_\rho^S(r)$, since they are short-ranged, and write $c_\rho = c_\rho^S + c_\rho^L$ and $R_\rho = R_\rho^S + R_\rho^L$. We also introduce the zeroth moment of $c_\rho(r)[= R_\rho(r)]$

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and the second moment of $c_\rho^S(r)[= R_\rho^S(r)]; \Gamma = M^2 = \Gamma(k = 0) = 1 - \rho R_\rho(k = 0)$ and

$K = (\rho/2d) \int r^2 R_\rho^S(r) d\mathbf{r}$. We can neglect moments of R_ρ^S beyond the zeroth and second

for our purposes here and write

$$R_\rho(k) = -Kk^2 + R_\rho(k = 0) + R_\rho^L(k) - R_\rho^L(k = 0) \tag{12}$$

which, used in (10), yields

$$\Gamma(k) = Kk^2 + M^2 + 2\rho \left[R_\rho^L(k = 0) - R_\rho^L(k) \right] \tag{13a}$$

For $\kappa \ll \Lambda \ll \sigma^{-1}$ we can also neglect both $K - K^\Lambda$ and $R_\rho^{\Lambda 1, L}(k = 0) - R_\rho^{\Lambda 1, L}(k)$ in

the remaining analysis, and write simply [15]

$$\Gamma_\Lambda(k) = Kk^2 + M_\Lambda^2 \tag{13b}$$

For $\kappa \ll \Lambda \ll \sigma^{-1}$ we can prove $nM_\Lambda^2 \sim \Lambda^2$ in the reference system [11]. Introducing

$\Gamma_\Lambda(k) = \chi_\Lambda^{-1}(k)$, $\mathbf{c}_{ij}^{\Lambda 1}(k)$ can be written in terms of $\Gamma_\Lambda[= \Gamma_\Lambda(0)]$ as

$$\left[\mathbf{c}_{ij}^{\Lambda 1}(k) \right] = \frac{1}{(2\rho_\Lambda)} \left[\begin{matrix} (1 - 2\Gamma_\Lambda) & 1 \\ 1 & (1 - 2\Gamma_\Lambda) \end{matrix} \right] \tag{14}$$

This follows from evaluating the *l.h.s.* of (9b) with $R_{ij} = R_{ij}^{\Lambda 1}$, using the fact that

$\mathbf{c}_{ij}^{\Lambda 1}(k)$ can be approximated here by $\mathbf{c}_{ij}^{\Lambda 1}(0)$.

The critical behavior of our system is clearly determined by the critical behavior

of the function $\Gamma(k)$, which describes the two-particle density-density correlations. The

evaluation of $\Gamma(k)$ in turn requires the evaluation of R_ρ. To determine the behavior of R_ρ as a functional of the ρ_i and h_{ij} at and near the critical point, where $\rho_i = \rho_c$ and $h_{ij} = h_{ij}^c$, we can evaluate R_ρ at $\rho^{\Lambda 1}$ and $h_{ij} = h_{ij}^\Lambda$ in terms of a functional Taylor-series expansion of R_{ij} about $R_{ij}^{\Lambda 1}$ in the independent function h_{ij} expanded about h_{ij}^Λ. This brings in the functional derivatives $\delta R_{ij}^{\Lambda 1}/\delta h_{kl}^\Lambda$, $\delta^2 R_{ij}^{\Lambda 1}/\delta h_{kl}^\Lambda \delta h_{mn}^\Lambda$, etc., which can be systematically re-expressed in terms of the functional derivatives $\delta \widetilde{c}_{ij}^\Lambda/\delta \rho_k = \widetilde{c}_{ijk}$, $\delta^2 \widetilde{c}_{ij}^\Lambda/\delta \rho_k \delta \rho_l = \widetilde{c}_{ijkl}$, etc.. The expansion can be conveniently represented as a sum of graphs with bonds representing the $h_{ij}^\Lambda - h_{ij}^{\Lambda 1}$ and reference-system hypervertices representing $R_{ij}^{\Lambda 1}$ and the functional derivatives. We can then relate the expansion of $R_\rho[\rho^{\Lambda 1}, h_{ij}^\Lambda]$ to $R_\rho[\rho^c, h_{ij}^c]$ by means of a renormalization-group argument. This argument and its conclusion follows closely the analysis in [11] of a non-ionic one-species system, and a few observatives concerning the correspondence between quantities appearing here and in that analysis will facilitate contact with its results.

The function $R_\rho^L(k = 0) - R_\rho^L(k)$ appearing in (13) can also be written as $c_\rho^L(k = 0) - c_\rho^L(k)$. In the one-species case with a short-range potential, it is exactly the corresponding term $c^L(k = 0) - c^L(k)$ that appears in the expression for the inverse structure factor $\Gamma(k)$. The dependence of $R_\rho^L(k = 0) - R_\rho^L(k)$ upon $h_{ij}^\Lambda - h_{ij}^{\Lambda 1}$, $R_\rho^{\Lambda 1}$, and the functional derivatives of $R_\rho^{\Lambda 1}$ in turn correspond to the dependence of $c^L(k = 0) - c^L(k)$ as a functional of $h^\Lambda - h^{\Lambda 1}$, $c^{\Lambda 1}$, and the derivatives of $c^{\Lambda 1}$ for the one-component non-ionic fluid considered in [11]. The reference-system quantities can be seen to have the same asymptotic behavior in the two systems, and the crucial question is whether the $h_{ij}^\Lambda - h_{ij}^{\Lambda 1}$ here has the same asymptotic behavior as the corresponding $h^\Lambda - h^{\Lambda 1}$ in the non-ionic case. We can decompose $h_{ij}^\Lambda - h_{ij}^{\Lambda 1}$

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into the products $c_{ij}^{\Lambda l}\chi_\Lambda - c_{ij}^{\Lambda 1}\chi^{\Lambda 1}$ and using (14) we see that $c_{ij}^{\Lambda l} = c_{ij}^{\Lambda 1}$. We can replace $c_{ij}^{\Lambda 1}$ by the constant n^{-1} in considering $R_\rho[\rho^{\Lambda 1}, h_{ij}^\Lambda]$ through $O(\Lambda^2)$. So we let $c_{ij}^{\Lambda l}\chi_\Lambda - c_{ij}^{\Lambda 1}\chi^{\Lambda 1} \approx (\chi_\Lambda - \chi^{\Lambda 1})/n$. But this is just $h^\Lambda - h^{\Lambda 1}$, as in the non-ionic case. (Only this lowest-order result in Λ is needed in our analysis.) The net result of the above observation is that the analysis of [11] for a non-ionic system can be applied step-by-step to the RPM without change and with no change in the conclusions. Thus the critical behavior to be expected is exactly that of the non-ionic one-species fluid (*e.g.* Argon). This is the conclusion already reached in ref. [6] and earlier in [7] on the basis of a very similar argument. The primary difference between that argument and the one given here lies in the representation used for R_{ij}. In [6], a representation was used that did not lend itself to direct determination of critical exponents and similar technical features. The representation used here does. Since they have already appeared in ref. [11], we shall not repeat all the steps in that determination. Instead we note certain differences in notation between the discussion here and in ref. [11] to help the reader interested in following the full determination of the critical behavior given there. First the h and c with which the analysis is begun in [11] would be denoted ρh and ρc in the notation used here. The h and c there are then rescaled by a factor K. We have not done that rescaling here. The reference-system ρh is denoted δh_Λ there rather than the $\rho_\Lambda h^{\Lambda 1}$ that would be consistent with our notation here. Finally, the long-range h_Λ-bonds in [11] should, strictly speaking, be $(h_\Lambda - \delta h_\Lambda)$-bonds. (The subtracted δh_Λ term is of short-range and can be completely neglected for $r > \lambda$).

We conclude with a final observation concerning the behavior of h_ρ and h_q determined by eq. (9) near but off the critical point ($M^2 \neq 0$). For $\kappa r \gg 1$ we find $h_\rho(r) = (1 -$

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$M^2)\chi(r)/n$ (consistent with Argon-like behavior) and $h_q(r) = M^2\chi(r)/n$. Thus the charge-charge correlation function varies sensitively with M for large r. A more detailed account of the application of the field-theoretic analysis of [11] to the primitive model is in preparation.

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[14] More generally, when one has a hard-core potential, it is convenient to take R_{ij} outside the core as the difference between c_{ij} and $-\beta\varphi_{ij}$, where φ_{ij} is the full pair potential outside the core. This was the definition of R_{ij} used in [6].

[15] If we were working with a model in which $\varphi_{ij}(r) \sim r^{-(d+s)}$ for $s < 2$, we could not write (13b). See [11].