Criticality of ionic fields: The Ginzburg criterion for the restricted primitive model

LETTER TO THE EDITOR

Criticality of ionic fields: the Ginzburg criterion for the restricted primitive model

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Abstract. A Ginzburg criterion is employed to estimate the extent of the critical region for the restricted primitive model (RPM) of an ionic fluid. Mean-field critical amplitudes are calculated using the generalized mean-spherical approximation (GMSA) and other recently proposed theories. The resulting (reduced) Ginzburg temperature t_G is large and similar to that calculated for models of a one-component neutral fluid. This implies that crossover from mean-field to Ising-like critical exponents should not be expected for the RPM. The relevance of these results for the criticality of real ionic fluids is discussed.

Criticality of the liquid–vapour transition is generally assumed to be in the Ising universality class, since the order parameter for this transition is simply the difference in coexisting densities, i.e. a scalar. Accurate measurements for atomic and molecular fluids, including water and liquid metals, always yield Ising-like critical exponents [1, 2]. Mean-field (classical) exponents are not observed and any crossover to mean-field behaviour occurs so far from the critical point that power laws cannot be fitted. In such systems the effective interatomic or intermolecular forces are sufficiently rapidly decaying with distance that Ising-like behaviour is expected. For ionic fluids one might suppose that the long-ranged character of the Coulomb forces between ions could give rise to a different universality class, namely one with mean-field exponents. The counter argument to this idea is that counter-ion screening always occurs in a conducting system and, provided the corresponding screening length remains finite, criticality should still be Ising-like. Experimental work by Pitzer and co-workers [3] and by other groups [4, 2] showed that for a certain organic salt in a non-aqueous solvent the liquid–liquid consolute behaviour was mean-field-like for reduced temperatures $|t|$, where $t \equiv (T - T_c)/T_c$, as low as 10^{-4}. More recent turbidity measurements for a picrate salt in a series of non-aqueous solvents indicate that crossover from Ising to mean-field exponents increases from $t_x \sim (3–8) \times 10^{-3}$ to $\sim (1–4) \times 10^{-2}$ as the dielectric constant of the solvent is increased from 4.6 to 9.4 [5]. In such systems the extent of the critical region appears to be orders of magnitude smaller than in neutral fluids.

Understanding the nature of criticality for an ionic fluid poses a severe challenge to the theorist. The admirable reviews by Fisher [6] and Stell [7] summarize the key issues and describe what (little!) progress has been made. Most attention has been focused on determining the liquid–gas coexistence curve of the restricted primitive model (RPM), where the ions are modelled by equisized charged hard spheres of diameter a immersed in a structureless dielectric medium with dielectric constant ϵ. The pairwise potentials between ions are $\phi_{ij}(r) = \infty$, for $r < a$ and $\phi_{ij}(r) = Z_i Z_j e^2 / \epsilon r$ for $r > a$, with $Z_+ e = -Z_- e$ denoting equal and opposite charges and i, j referring to ionic species. Stillinger and

Lovett [8] first asserted that the RPM should show liquid–gas phase separation with its accompanying critical point. Recent computer simulations have confirmed that the model does exhibit coexistence between a very dilute vapour and a dense ionic liquid with the latest estimate of the critical point being $T_c^* \approx 0.053$ and $\rho_c^* \approx 0.025$ [9]. The dimensionless parameters are defined by $1/T^* \equiv \beta^* \equiv \beta(Z_+e)^2/\epsilon a$ and $\rho^* \equiv \rho a^3$ where $\beta \equiv 1/k_B T$ and ρ is the total number of ions per unit volume. Another Monte Carlo study finds, contrary to earlier results, that the vapour phase close to saturation is conducting and concludes that the RPM is likely to be a conductor throughout the fluid phase [10]. None of the simulations yield sufficient reliable data to allow estimates to be made of critical exponents. Several theories have been developed for the thermodynamic functions and the structure of the RPM—and there have been many recent attempts to improve upon earlier approaches by including ion pairing. Much of this work is reviewed in [6,7]. The theories which predict two-phase coexistence are all mean-field approximations and hence cannot account for Ising-like criticality—were this to be the correct behaviour for the RPM.

Our aim here is not to develop a theory which provides a more accurate estimate of the location of the critical point. Rather we consider a well-established theory of the RPM, the generalized mean-spherical approximation (GMSA), and determine the extent of the critical region using a Ginzburg [11] criterion. We compare our result with that obtained from the Debye–Hückel (DH) approximation and with those from some other recent treatments of the RPM. Comparison is also made with results for a square-well fluid, modelling a simple neutral fluid, treated in the random-phase approximation (RPA). We find that the Ginzburg (reduced) temperature of the RPM is $t_G \sim 1$, a value very similar to that for the square-well fluid. This implies that the critical regions for both models have a similar *large* extent. The results suggest that the RPM may have limited usefulness as a model system for understanding the criticality of real ionic fluids and we discuss its limitations.

Our reasons for choosing the GMSA for the analysis are threefold: (i) this is the simplest thermodynamically self-consistent integral equation approach for the RPM; (ii) correlation functions are given rather accurately; and (iii) unlike other integral equation closure approximations, such as the widely used hypernetted chain approximation (HNC), which fail to give a proper account of two-phase coexistence [12], the GMSA does yield a realistic, albeit mean-field, coexistence curve with accompanying spinodals [13, 14]. The GMSA was first introduced for ionic and polar fluids by Høye *et al* [15]. Subsequent workers [16, 17] laid out the procedure for determining the physical solutions to the self-consistent equations. The theory is defined by the equations

$$h_{ij}(r) = -1 \qquad \text{for } r < a \tag{1}$$

and

$$c_{ij}(r) = -\beta\phi_{ij}(r) + \frac{K \exp(-\tilde{z}(r/a - 1))}{r/a} \qquad \text{for } r > a \tag{2}$$

along with the (exact) Ornstein–Zernike equations for a binary mixture. Here $h_{ij}(r)$ is the total pairwise correlation function and $c_{ij}(r)$ is the direct correlation function between species i and j. Equation (1) is a statement of the exact hard-core exclusion condition. The approximation resides in the Yukawa form assumed for $c_{ij}(r)$ outside the hard core. K and $\tilde{z}$ are both (positive) functions of ρ and T, and are chosen so as to ensure consistency among the three routes to thermodynamic functions obtained from $h_{ij}(r)$, i.e. the virial, compressibility and internal energy routes. The procedure developed in [16] is valid everywhere in the mechanically stable region where the compressibility is positive. It fails in

the unstable region, between the spinodals, where $\tilde{z}$ becomes complex. However, since the Helmholtz free energy in the GMSA is simply the Carnahan–Starling hard-sphere free energy plus the free energy obtained from the MSA internal energy, this has a conventional mean-field form. Below T_c it has a van der Waals loop for the resulting pressure $p(\rho)$ and chemical potential $\mu(\rho)$. Spinodals are readily calculated and liquid–vapour coexisting densities can be determined very accurately using the standard procedure of equating chemical potential and pressure in the two phases. It follows that the order parameter critical exponent $\beta = \frac{1}{2}$. The critical amplitude B is defined by $\Delta\rho/\rho_c \sim B|t|^\beta$ for $t < 0$. Here $\Delta\rho \equiv (\rho_l - \rho_v)/2$, where $\rho_l(T)$ and $\rho_v(T)$ are the coexisting densities. The calculated value of B is given in table 1. The critical point was determined in two ways: (i) by locating the maximum of the coexistence curve; and (ii) by working in the single-phase region and ascertaining the highest temperature at which ξ^{-1}, the inverse correlation length for fluctuations in the total number density, vanishes (see below). Both methods yield, within numerical accuracy, $T_c^* = 0.0785769677$ and $\rho_c^* = 0.014485$. The GMSA critical temperature is about 50% higher than in simulation and the critical density is about 60% of the simulation value. Other thermodynamic critical exponents and amplitudes are easily obtained. The compressibility κ_T diverges as $\rho\kappa_T/\beta \sim C^\pm|t|^{-\gamma}$, with $\gamma = 1$. C^+ refers to $t > 0$ and C^- to $t < 0$ (along the coexistence curve). The calculated ratio $C^+/C^- = 2.00$, which is the standard mean-field value of the amplitude ratio. Along the critical isotherm ($t = 0$), $\beta_c(\mu - \mu_c) \sim D((\rho - \rho_c)/\rho_c)^\delta$, with $\delta = 3$ and the value of the critical amplitude D is given in table 1. Calculations were carried out sufficiently close to the critical point, typically in the range $10^{-8} \leqslant |T^* - T_c^*| \leqslant 10^{-5}$ and $10^{-4} \leqslant |\rho^* - \rho_c^*| \leqslant 10^{-3}$, to ensure that accurate power-law fits could be made to the numerical results.

Table 1. Mean-field critical amplitudes for various model fluids. LG refers to the lattice gas, vdW to the van der Waals equation of state and RPA to the random-phase approximation for a square-well fluid. The remaining results refer to the RPM treated in the approximations described in the text. DH and DHBj results are taken from [19, 20]. The correlation length amplitude ξ_0^+ is only available for four of the theories.

	B	C^+	D	ξ_0^+/a
LG	1.7321	0.5	0.6667	
vdW	2	0.4444	0.564	
RPA	2.447	0.3648	0.460	0.406
GMSA	6.904	0.8958	0.02342	0.75
DH	6.9282	1	0.02083	0.7329
DHBj	0.7617	0.10994	15.6773	0.7329
PMSA1	5.071	0.7177	0.05597	
PMSA2	5.286	1.0600	0.03486	
PMSA3	5.448	1.0645	0.03491	

Before discussing the Ginzburg temperature it is necessary to describe the picture of criticality which emerges in the GMSA treatment of the RPM [14]. The fluid is driven critical by fluctuations in the total density, i.e. the density–density total correlation function $h_s(r) \equiv \frac{1}{2}(h_{++}(r) + h_{+-}(r))$ has a diverging correlation length ξ at the critical point, but charge correlations remain non-critical and $h_D(r) \equiv \frac{1}{2}(h_{++}(r) - h_{+-}(r))$ has a finite correlation length. The Ornstein–Zernike equations for the Fourier transforms $\hat{h}_s(q)$ and $\hat{h}_D(q)$ have independent pole structure [14]. In the critical region the dominant pole of $\hat{h}_s(q)$ is pure imaginary $i\alpha_0^N$ and $rh_s(r) \sim A_N \exp(-r/\xi)$ as $r \to \infty$, with $\xi^{-1} \equiv \alpha_0^N$. $\alpha_0^N = 0$ defines the critical point and the spinodals. On the other hand, the dominant

poles of $\hat{h}_D(q)$ are a conjugate pair $\pm\alpha_1^Q + i\alpha_0^Q$, so damped charge oscillations are present: $rh_D(r) \sim A_Q \exp(-\alpha_0^Q r)\cos(\alpha_1^Q r + \theta_Q)$ in the vicinity of the critical point. Our numerical results for the charge pole at the critical point yield the values $a\alpha_0^Q = 2.132\,32$, $a\alpha_1^Q = 1.262\,46$ and $\theta_Q = 0.661\,64$, i.e. the charge correlation length $1/\alpha_0^Q$ is short, $\sim a/2$, while the wavelength of the oscillations $2\pi/\alpha_1^Q$ is long, $\sim 5a$. In this theory the charge correlations have no direct influence on the criticality. Their role is to determine, through the imposition of thermodynamic consistency, the indirect attraction that is necessary to drive the density–density correlations critical. This is achieved by imposing identical Yukawa tails (see (2)) on $c_{++}(r)$ and $c_{+-}(r)$. We would expect other self-consistent closure approximations to yield a similar picture of criticality [7] but we are not aware of any explicit results. It follows that within the GMSA, at least, the Ginzburg criterion should refer to correlations in the total density. The criterion is, therefore, equivalent to that for a single-component fluid.

If we define the density–density correlation function as

$$G_s(r_1, r_2) \equiv \langle (\rho(r_1) - \langle \rho(r_1)\rangle)(\rho(r_2) - \langle \rho(r_2)\rangle)\rangle \tag{3}$$

where $\langle\ \rangle$ denotes a configuration average, then $G_s(r) = \rho^2 h_s(r) + \rho\,\delta(r)$, for a uniform fluid of average density ρ. The integral Ginzburg criterion [18] requires us to consider the dimensionless ratio

$$E_G \equiv \frac{\int_{V_\xi} dr\, G_s(r)}{\int_{V_\xi} dr(\Delta\rho)^2} \tag{4}$$

where the integrals are taken over a correlation volume V_ξ, for slightly subcritical temperatures. The correlation length, calculated along the coexistence curve, diverges as $\xi = \xi_0^-|t|^{-\nu}$, $t < 0$ (our numerical results confirmed that $\nu = \frac{1}{2}$ is the mean-field value). Note that the numerator in (4) is the integral of the mean square fluctuation of the density (order parameter) on length scales up to ξ. As $|t| \to 0$, $\xi \to \infty$, and we approximate the integral by its value over all space and employ the sum rule $\int dr G_s(r) = \rho^2\kappa_T/\beta$. The denominator in (4) is the integral over the same volume, of the square of the order parameter $\Delta\rho$, which is simply $4\pi\xi^3(\Delta\rho)^2/3$. Mean-field theory should be valid provided the numerator is much smaller than the denominator, i.e. fluctuation effects are small provided

$$E_G \approx \frac{3\rho^2\kappa_T}{\beta\,4\pi\xi^3(\Delta\rho)^2} \ll 1. \tag{5}$$

Using the mean-field critical exponents and amplitudes this condition can be expressed as

$$\frac{3C^-|t|^{-1/2}}{\rho_c\,4\pi(\xi_0^-)^3 B^2} \ll 1 \tag{6}$$

or

$$|t| \gg t_G \equiv \left(\frac{3C^-}{4\pi\rho_c B^2(\xi_0^-)^3}\right)^2 \tag{7}$$

which defines the Ginzburg temperature t_G. Other Ginzburg criteria, which give rise to the same ratio of amplitudes but different numerical factors in (7), can be defined but we feel

that (4) is the most appropriate ratio for a fluid; we return to this point in the discussion. The correlation length amplitude ξ_0^- was obtained from the imaginary (density) pole α_0^N calculated along the coexistence curve. For $t > 0$, $\xi = \xi_0^+ t^{-1/2}$ and the calculated ratio $\xi_0^+/\xi_0^- \approx 1.41$, in agreement with the standard mean-field value $\sqrt{2}$. The GMSA result for ξ_0^+ is given in table 1. Our GMSA estimate of the Ginzburg temperature is $t_G \approx 1.08$.

It is important to ask how sensitive t_G is to the choice of mean-field theory. Levin and Fisher [19] have obtained critical amplitudes for thermodynamic functions, and Lee and Fisher [20] have obtained correlation length amplitudes in the Debye–Hückel approximation (DH) [21] for the RPM, and their results are listed in table 1. It is remarkable that the DH approximation, which is based on a much cruder treatment of short-ranged correlations, should yield amplitudes that are rather close to those from the GMSA. However, since the critical density ρ_c^* is almost a factor of three smaller than the GMSA value ($\rho_c^* = 1/(64\pi)$, $T_c^* = \frac{1}{16}$ in DH) the resulting t_G is about eleven times larger for DH. Table 1 also lists the critical amplitudes calculated in [19, 20] using a modification of DH which includes some Bjerrum ion pairing (the DHBj of [21]). These amplitudes are completely different from the DH and GMSA results. Note that DHBj yields an unrealistic 'banana'-shaped coexistence curve [21]. González-Tovar and Outhwaite [22] have calculated the critical point of the RPM (and of an asymmetric model with an ionic size ratio of 2:1) using the modified Poisson–Boltzmann (MPB) and symmetric Poisson–Boltzmann (SPB) theories. The critical densities ρ_c^* are lower than in the GMSA, i.e. further from the simulation value, but T_c^* is slightly better than the GMSA value. Their calculated order-parameter critical exponent is $\beta = \frac{1}{2}$, within the accuracy of the power-law fitting. However, the corresponding critical amplitude $B \approx 0.56$ (MPB) and $B \approx 0.65$ (SPB) is an order of magnitude smaller than the GMSA and DH results of table 1. The authors do not report critical amplitudes for other quantities.

The MSA and, therefore, the GMSA treats hard-core repulsion rather accurately but does not properly take into account effects of ionic association. Recent simulation studies of the RPM [23] and of a Fumi–Tosi model of NaCl [24] confirm that pronounced association, into pairs, triplets and higher-order clusters, occurs for low densities and temperatures. Zhou *et al* [25], following earlier work by Zhou and Stell [26], have analysed improvements to the MSA which include contributions to the equation of state arising from unlike ionic pairs at contact. Three versions of this pairing MSA (PMSA) are described. PMSA 1, the simplest version, neglects the activity coefficient of the fully associated ion pairs. PMSA 2 includes the activity of these dipolar particles at the MSA level while PMSA 3 includes the effects of the dipolar particle (hard-dumbbell) cores. As the critical points (especially the critical densities) calculated from these theories are considerably closer to the simulation estimate than the GMSA result [25], it is of interest to investigate the magnitude of t_G for these new approximations. The pressure $p(\rho)$ and chemical potential $\mu(\rho)$ are given explicitly for all three theories [25], i.e. in each case the MSA equation of state is augmented by an ion-pairing contribution which depends on the association constant K_0. Van der Waals loops are obtained, leading to mean-field coexistence and criticality. We made accurate determinations of the critical points and the thermodynamic critical amplitudes using the same numerical procedures as for the GMSA. The results for the critical density and temperature are given in table 3 and those for amplitudes in table 1. The amplitudes were extracted using data† in the range $10^{-6} \leqslant |t| \leqslant 10^{-4}$ and $10^{-3} \leqslant |(\rho - \rho_c)/\rho_c| \leqslant 10^{-2}$. Their values, for

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† Note that K_0 is given by a series expansion in powers of β^* (see equation (2.13) of [25]). The series was truncated when the ratio of the mth term to the sum of the first m terms was smaller than 10^{-4}. Although this was shown to be sufficiently accurate for our purposes, the truncation might be the cause of the small discrepancies between the calculated values of DC^+ and B^{-2} given in table 1 for the PMSA results.

Table 2. The coefficients entering the LGW Hamiltonian (10) for various model fluids.

	$a_0\beta_c$	$u_0\beta_c$	$\bar{\gamma}\beta_c$
LG	2	0.1667	
vdW	2.25	0.1406	
RPA	2.74	0.115	0.452
GMSA	1.116	0.005 855	0.627
DH	1	0.005 2083	0.5372
DHBj	9.09573	3.919 32	4.8857
PMSA1	1.393	0.013 99	
PMSA2	0.9434	0.008 715	
PMSA3	0.9394	0.008 728	

all three versions of the PMSA, are similar to those obtained in the GMSA and Debye–Hückel approximation. Since there is no procedure for calculating correlation functions in the PMSA we estimated t_G using ξ_0^- obtained from our GMSA calculations. The results are collected in table 3. PMSA 1 yields a t_G that is a little smaller than the GMSA value, whereas the PMSA 2 and PMSA 3 values are somewhat higher. However, all four estimates agree to within a factor of two and we conclude that for the RPM $t_G \sim 1$.

If we accept this conclusion we should then enquire whether this value is substantially different from the corresponding estimate for a neutral fluid. To this end we calculated the critical point and critical amplitudes for the square-well fluid, described by the pairwise potential

$$\phi(r) = \infty \qquad r < a$$
$$\phi(r) = -\epsilon \qquad a < r < 3a/2 \qquad\qquad (8)$$
$$\phi(r) = 0 \qquad r > 3a/2$$

with a the hard-sphere diameter, using the RPA, i.e. the direct correlation function was approximated as

$$c(r) = c_{hs}(r) - \beta\phi_{att}(r) \qquad\qquad (9)$$

and the attractive potential $\phi_{att}(r)$ was taken to be $-\epsilon$ for $r < 3a/2$ and zero otherwise. The Percus–Yevick approximation was used for the hard-sphere $c_{hs}(r)$. Thermodynamic functions were calculated from the compressibility route and the correlation length from the pure imaginary pole of $\hat{h}(q)$, obtained from the Ornstein–Zernike equation for a pure fluid. It is well known [27, 28] that the RPA yields a reasonable (mean-field) coexistence curve and sinodals. The critical point can be determined analytically and for the square-well fluid $T_c^* \equiv k_B T/\epsilon = 1.266\,6781\,22$ and $\rho_c^* \equiv \rho_c a^3 = 0.245\,735$. Our results for the critical amplitudes, calculated by the same procedures as those used for the RPM, are listed in table 1. We verified that the numerical results from the RPA agree with the standard mean-field amplitude ratios. The thermodynamic amplitudes are considerably different from those obtained for the RPM but they are similar to the amplitudes calculated for the lattice gas (LG) and for the van der Waals (vdW) equation of state—see table 1. It is clear that the values of the critical amplitudes do reflect the type of fluid. The correlation length amplitude, ξ_0^+/a, for the square-well fluid is about half that for the RPM. Again we obtain $\xi_0^+/\xi_0^- = \sqrt{2}$. In spite of the differences between the amplitudes, the calculated value $t_G \approx 1.6$ is similar to that obtained for the RPM. The size of the critical region in the neutral, square-well fluid is close to that estimated for the RPM of an ionic fluid.

The starting point for renormalization group treatments of critical fluctuations is usually the Landau–Ginzburg–Wilson (LGW) Hamiltonian. Using the results of microscopic liquid-state theories we can determine the coefficients in this Hamiltonian:

$$\beta H = \beta \int \frac{\mathrm{d}r}{a^3} \left(\frac{\tilde{\gamma}}{2} (\nabla m(r))^2 + \frac{a_0}{2} t m^2(r) + u_0 m^4(r) - \Delta\mu\, m(r) \right) \quad (10)$$

where $m(r)$ is the order-parameter density, $\Delta\mu$ is its conjugate field, and we restrict consideration to three dimensions ($d = 3$). For a fluid we set $m \equiv (\rho - \rho_c)/\rho_c$, and $\Delta\mu \equiv \mu - \mu_{co}$, where $\mu_{co}(T)$ is the chemical potential along the coexistence curve. Minimizing (10) for a uniform fluid yields the standard mean-field exponents, and the critical amplitudes, defined previously, are:

$$B = \left(a_0/4u_0\right)^{1/2} \qquad C^+ = \left(\beta_c a_0\right)^{-1} \qquad D = 4u_0\beta_c \quad (11)$$

Using our earlier results for B and C^+, a_0 and u_0 can be determined. The values are listed in table 2 for the various theories. Note that (11) implies the relationship $DC^+ = B^{-2}$. Our numerical results for the amplitudes do satisfy this, which provides a further check on their accuracy. The order-parameter correlation function is easily calculated from (10) and the amplitude of the correlation length is $\xi_0^+ = (\tilde{\gamma}/a_0)^{1/2}$. Thus, the coefficient of the square gradient term can be obtained from the microscopic results for ξ_0^+. Alternatively one can obtain $\tilde{\gamma}$ using the general result from density functional theory [29] $\beta\tilde{\gamma} = (\rho/6) \int \mathrm{d}r\, r^2 c(r)$, with the direct correlation $c(r)$ (or $c_s(r)$ for the RPM) evaluated at the critical point. The same results are found from both schemes, attesting to the self-consistency and numerical accuracy of the calculations. $\tilde{\gamma}$ takes on similar values in the GMSA and the DH treatments of the RPM and these are not substantially different from the RPA result for the square-well fluid—see table 2. On the other hand, the coefficient of the quartic term in the Hamiltonian, u_0, is 20 times smaller for the RPM, reflecting the fact that $\Delta\mu$ on the critical isotherm has a much smaller amplitude. In terms of the Landau coefficients the Ginzburg temperature (6) transcribes to

$$t_G \equiv \left(\frac{3u_0}{2\pi\beta_c\rho_c(\xi_0^-)^3 a_0^2} \right)^2 \quad (12)$$

which may be a more familiar form. All the results for t_G are summarized in table 3.

Table 3. The Ginzburg temperatures t_G and critical parameters for the square-well fluid treated in the RPA and for the RPM treated in the GMSA, DH and PMSA (the PMSA uses ξ_0^- from the GMSA).

	T_c^*	ρ_c^*	t_G
SqW(RPA)	1.2667	0.2457	1.57
GMSA	0.078 58	0.014 48	1.08
DH	0.0625	0.004 974	12.90
PMSA1	0.074 81	0.025 02	0.80
PMSA2	0.073 33	0.022 93	1.76
PMSA3	0.074 52	0.024 33	1.37

As mentioned earlier, other criteria have been employed to define a Ginzburg temperature or Ginzburg number Gi—see e.g. Anisimov *et al* [30] and references therein. One choice [30], based on the argument that the fluctuation contribution to the compressibility in the one-phase region should remain small, corresponds to Gi $\equiv t_G/2$, with t_G given by (12). Clearly t_G, or Gi, is very sensitive to the value of the correlation length amplitude ξ_0^-, so it is important to calculate this consistently from the same microscopic theory which determines the thermodynamic critical amplitudes. (The value of Gi ≈ 0.01 given in [30] for a van der Waals fluid is obtained from a crude estimate of ξ_0^+.)

The main result of our analysis is that t_G for the RPM taken on a similar value to that for a neutral square-well fluid. It follows that the critical regime of both types of fluid should be large in extent and there is no crossover expected from mean-field critical exponents to non-classical exponents. If one were to use the LGW Hamiltonian (10) to describe the RPM one would obtain (from a renormalization group perspective) Ising-like criticality with the critical regime extending to values of $|t|$ that are similar to those observed for neutral fluids. From this viewpoint the RPM is no different from a one-component, atomic fluid and therefore cannot account for the crossover behaviour that is observed in real ionic fluids. Such a viewpoint has, as its basis, the notion that charge correlations, $h_D(r)$, remain non-critical at the critical point. It is unlikely that this notion remains valid beyond mean-field theory and some weak singular behaviour in $h_D(r)$ is expected [6, 7]. Whether it is necessary to employ two order-parameter densities for describing criticality of the RPM and what consequences this would have, is not established. However, our intuitive feeling is that the RPM will fall into the Ising universality class.

What should be more relevant to the experimentalist is the nature of criticality for an asymmetric ionic fluid, i.e. one in which the ions have different sizes and/or charges. No real fluid can correspond precisely to the RPM. Stell [7, 25] has suggested that the presence of asymmetry could have a profound effect on the nature of criticality. When $c_{++}(r) \neq c_{--}(r)$ the Ornstein–Zernike equations have a rather different structure from in the RPM (see also [14]) and it is feasible that the renormalization group flow near the critical point could be of a different character from that in the RPM or in a neutral binary mixture. Stell and co-workers state that this should yield mean-field critical exponents for *any* asymmetric primitive models of ionic fluids. Indeed the simulation results of [24] for a model of NaCl are interpreted as being more consistent with mean-field behaviour than those for the RPM. However, crossover to Ising behaviour could occur close to the critical point and not be picked up in the simulations. Should Stell be correct and the RPM found to lie in a different universality class from any other ionic model, this would be a remarkable result which would certainly have significant repercussions for real ionic fluids. The degree of anisotropy between anion–solvent and cation–solvent interactions would also be relevant for criticality.

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