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The nature of criticality in ionic fluids

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Abstract. Experiments on critical behaviour in certain electrolytes pose puzzling theoretical challenges. Some recent progress by the author and his co-workers in meeting these challenges through the study of the restricted primitive model (hard spheres carrying charges $\pm q$) is summarized briefly. However, basic questions regarding the universality class(es) of ionic criticality and the factors determining cross-over from mean-field to Ising behaviour remain unresolved.

In recent years, precise experiments by Pitzer and co-workers [1, 2] and by others [3–5] on phase separation and criticality in ionic fluids have suggested a sharp distinction between *solvophobic criticality*, displayed by non-ionic fluids and many electrolytes, that is associated with Ising-type exponents, $\beta \simeq 0.32$, $\gamma \simeq 1.24$ and $\nu \simeq 0.63$ when $t \equiv (T - T_c)/T_c \rightarrow 0$, and *Coulombic* (or *ionic*) *criticality* characterized by classical, van der Waals exponents, $\beta = 0.5$, $\gamma = 1$ and $\nu = 0.5$. See also the reviews [6–8]. Only earlier experiments on the sodium–ammonia systems [9] and more recent studies [10], especially by Narayanan and Pitzer [11, 12], seem to straddle this dichotomy: they show *cross-over* from classical to Ising behaviour close to T_c on characteristic cross-over scales

$$t_x = |T_x - T_c|/T_c \quad (1)$$

in the range $10^{-1.5}$ to $10^{-2.5}$. In contrast, typical (Ising-type) systems show no cross-over, corresponding, say, to $t_x \simeq 1-0.3$. On the other hand, if cross-over eventually occurs in Pitzer's original electrolyte [1, 2], one must have $t_x \lesssim 10^{-4}$ [6], which is beyond current limits of observation. These diverse results have presented rather profound challenges to theory.

Some of the earliest suggested explanations of the classical critical behaviour have proven to be untenable [13] or improbable [14, 15]. Thus it was claimed that a lattice model electrolyte in three-dimensional space could be mapped onto the standard, short-range spherical model and, hence, that the ionic system should display a gas–liquid critical point with coexistence curve exponent, $\beta = 0.5$ (and, it would follow, exponents $\alpha = -1$, $\gamma = 2$ and $\nu = 1$). However, there is no sound basis for that claim [6, 13].

Nor is there justification for a later suggestion that a Coulombic critical point is, somehow, of tricritical character [6, 7]. Nevertheless, the possibility that, in a suitably enlarged thermodynamic space, the observation of Coulombic criticality (or a very small t_x) might be associated with the vicinity of a multicritical point of some sort is a tempting scenario [6]. However, at this stage no concrete evidence has been adduced for it.

Simulation of appropriate lattice models, in particular a basic four-state model that allows for ionic association–dissociation, etc [6], might cast light on this. Currently such ($d = 3$)-dimensional lattice models seem to have escaped serious computational study.

A much more plausible and interesting suggestion [8, 16] is that the appearance of true classical or near-classical criticality in place of Ising behaviour in certain electrolytes might be associated with charge–cavity, ion–ion interaction potentials varying with distance as $1/r^4$. It can be shown [14, 15], however, that such forces should be strongly screened at non-zero ionic density, decaying as $\exp(-2\kappa r)/r^2$ when the direct, $1/r$ Coulomb coupling is screened, as usual, by the factor $\exp(-\kappa r)$. Within Debye–Hückel theory representing the ions as spheres of different dielectric constants does not change any thermodynamic parameters [14, 15]. Consequently, other explanations of the experiments still seem to be required.

Perhaps the most fundamental issue raised is the *existence, location* and, especially, the *nature* of the long-heralded but still rather elusive gas–liquid transition and critical point in the continuum *restricted primitive model* (RPM): hard spheres all of diameter a but carrying charges $+q$ and $-q$ in equal proportions. Earlier theoretical work and Monte Carlo simulations have been reviewed [6]. Over the years, simulations by a succession of authors told a rather sad story: the estimated critical density dropped by factors of ten or more, while the apparent critical temperature has continually decreased, eventually by an overall factor of almost two! The most recent studies [17, 18] using larger systems and more sophisticated Monte Carlo techniques suggest, in reduced units, that

$$T_c^* \equiv Dk_B T_c a / q^2 = 0.052\text{--}0.056 \quad \rho_c^* = \rho_c a^3 = 0.023\text{--}0.035 \quad (2)$$

with $\rho = N/V$ for a total of N hard-sphere ions in a volume V of uniform dielectric constant D [19]†

In an effort to obtain a physically transparent, semi-quantitative description, the work of Debye and Hückel and its subsequent elaboration via Bjerrum’s concept of bound ion pairs has been revisited [6, 19, 20]. Unexpectedly, the original 1923 theory of Debye and Hückel (DH) (which allows explicitly for the hard-sphere diameter a) was found to predict phase

† Just before and at the Third Liquid Matter Conference held in Norwich, 6–10 July 1996, the author learned of progress in the next round of simulations aimed at understanding the critical region of the RPM made by J P Valleau (private communication, dated 20 June 1996) and by J M Caillol, D Levesque and J J Weis (private communication, dated 25 June 1996) respectively. Both studies were mentioned at the meeting.

Valleau uses his thermodynamic-scaling Monte Carlo approach [43] for $N = 32, 64, 128$ and 192 ions which allows extrapolation towards the thermodynamic limit, $N = \infty$. The data indicate $\rho_c^* \simeq 0.08$, significantly higher than the range indicated in equation (2), and, by extrapolation, $T_c^* \simeq 0.049\text{--}0.050$. Note that the higher value of ρ_c^* is reasonable in light of the 6–12% drop in the estimate for T_c^* because the diameter of the coexistence curve has a strong slope (see, e.g. [19, 20]). Furthermore, Valleau observes that the behaviour differs from that seen in simulations of the critical region of the simple hard-core-square-well and Lennard–Jones fluids, which exhibit Ising-type criticality (and then finite-size cross-over). Indeed, on first examination, the overall RPM critical behaviour looks rather classical with little sign of heat-capacity maxima near ρ_c^* , etc.

Caillol *et al* employ a grand canonical simulation of hard spheres on the surface of a four-dimensional hypersphere [44] and, in order to extrapolate on size, study systems with reduced volumes $V/a^3 = (1.5\text{--}10) \times 10^3$. To analyse the observed density and energy fluctuations they adapt the mixed-field finite-size scaling strategy of Bruce and Wilding [45]. Extrapolation of the data of Caillol *et al* suggests $\rho_c^* \simeq 0.070 \pm 0.005$ and $T_c^* \simeq 0.0488 \pm 0.0003$, similar to the estimates based on Valleau’s results. By contrast, however, on the basis of scaled energy and order-parameter distributions, Caillol *et al* conclude that the critical behaviour of the RPM is compatible with Ising-type character. This is in accord with the theoretical Ginzburg-criterion analysis reported below [33, 34] but seems to leave open the question of the magnitude of any classical-to-Ising crossover temperature. The use of finite-size extrapolation and scaling in both these studies is to be welcomed; but in terms of the linear system dimension (which is probably the most relevant parameter) a range of less than 1:1.9 has been spanned in the present calculations.

separation and criticality in the primitive model electrolyte [6, 20]. The coexistence curve proves to be strongly asymmetrical and in qualitative accord with the later simulations. The critical point at $T_c^* = 1/16$ is only about 15% above the best recent simulation estimates; but the predicted critical density $\rho_c^* = 1/64\pi \simeq 0.005$ is much too small. Because of the mean-field-like character of the DH theory, all critical exponents are classical [6, 19]; but that has no predictive value. Allowing also for direct hard-core exclusion effects reduces the values of T_c^* and ρ_c^* , but only slightly [6, 19, 20]. However, correction of the DH linearization of the Poisson–Boltzmann equation by including equilibrium *pairing* of positive and negative charges improves ρ_c^* significantly. Bjerrum’s 1926 theory of the crucial *chemical association constant*, $K(T)$, has been reviewed with a critical eye; Ebeling’s reformulation is to be strongly endorsed [19] (following [21, 22]), but makes negligible *numerical* difference in the critical region and below.

However, following Bjerrum by treating the uncharged (+, –) dipolar ionic pairs as ideal or electrically inactive, in accord with the original DH concepts, yields an unphysical coexistence curve [19, 20] resembling a tilted banana! To understand this, the actual nature and sizes of the associated (+, –) ion pairs in equilibrium must be examined quantitatively [19, 20]: in fact, Bjerrum’s famous cut-off length for dipolar ‘size’, namely,

$$R_{Bj} = \begin{cases} \frac{1}{2}b \equiv q^2/2Dk_B T & \text{for } T^* \leq \frac{1}{2} \\ a & \text{for } T^* \geq \frac{1}{2} \end{cases} \quad (3)$$

bears no relationship to any reasonable measure of the typical size of an ion pair [19]. The DH–Bjerrum theory can, nonetheless, be rather naturally extended by including the *solvation free energy* of a dipolar pair within the residual fluid of ‘free’ ions and this, in turn, can be calculated using the approach of DH theory [19, 20, 23]. The dipole–ionic (DI) contribution to the total free energy proves crucial and restores a reasonable shape to the coexistence curve. Overall, this DHBjDI theory (and its minor variants) currently provides the most physically accessible and quantitatively satisfactory description of the critical region of the RPM [6, 19, 20].

Furthermore, the temperature variation of the vapour pressure curve and of the density of neutral dipolar pairs is found to correlate rather well [19] with Gillan’s notable numerical analysis of ion clusters in the vapour at low T [24]. Improvements to allow for larger ion clusters and to represent the denser ionic liquid better below criticality are feasible [19]. However, if the DH approximation for the ionic part of the total free energy is replaced by the popular mean spherical approximation (MSA) (which is exactly soluble for $d = 3$), reasonable critical densities are generated but the MSA critical temperatures are all 40–50% *too high!* In addition, the predicted density of neutral clusters seems much too low near criticality and appears to decrease too rapidly (by an exponential factor) as does the vapour pressure line below T_c [19].

In order to understand the relative failure of the MSA and its improved version, the GMSA which satisfies various desirable sum rules [25, 26] (and reproduces the Kirkwood–Stillinger–Lovett charge–charge correlation oscillations at higher densities [26]), it is interesting to appeal to some of the rather few rigorous [27, 28] or near-rigorous [29] results available for the restricted primitive model. In 1939, Onsager [27] established the bound

$$u \equiv U_N(T, \rho)/N \geq -c_0(q^2/Da) \quad (4)$$

on the mean electrostatic energy per ion, with constant $c_0 = 1$. Both DH theory and the MSA satisfy this bound [30]. In the limit $\kappa a \rightarrow \infty$, where, as usual [6–8], the inverse

Debye length κ is explicitly given by

$$\kappa^2(T, \rho) = 4\pi q^2 \rho_1 / (Dk_B T) \quad (5)$$

with ρ_1 the total density of free ions, one finds that u_{MSA} approaches the Onsager bound with $c_0 = 1$. On the other hand, DH theory yields $u_{DH}(\kappa a \rightarrow \infty) = -\frac{1}{2}q^2/Da$. More recently, however, Totsuji [28] has improved the constant in (4) to $c_0 = 0.96$. Evidently, then, the MSA violates the Totsuji energy bound for large enough κa ($\gtrsim 1200$). One may suspect that the optimal constant in (4) is $c_0 \simeq 0.873779$, corresponding to NaCl ionic close packing: this is violated by the MSA for $\kappa a \gtrsim 104$ [30]. However, DH theory satisfies even this bound; but one might be happier if u_{DH} approached closer to the bound for large κa , since, energetically, the dense low-temperature fluid should probably resemble an amorphous NaCl crystal.

In a different direction, Gillan [29] obtained in a convincing, albeit non-rigorous, manner an *upper bound* on the free energy of the RPM at general T and ρ . He found that the MSA seriously violates this bound at low temperatures, roughly $T^* \lesssim 0.095$, and low densities, $\rho^* \lesssim 0.03$. The domain of violation reaches the critical region (2) and encloses most of the vapour side of the coexistence curve. However, the pure DH free energy violates the bound in a very similar region [30]! Gillan's argument is based on the idea that ion pairing is important at low T . Indeed, one finds [30] that, if ion pairing is introduced (following [19, 20]), Gillan's bound is satisfied *throughout* the interesting regions of small T^* and ρ^* [30]; but this is true equally of the simple DHBj and MSABj theories as it is of the more sophisticated theories allowing for dipole-ionic coupling, direct hard-core repulsions, etc [30]! Thus the crucial importance of ion-pairing is confirmed, but little further guidance is provided for preferring DH theory.

Of course, the mean-field character of the DH-based theories (and equally of those based on the MSA) implies the neglect of all large-scale charge and density fluctuations. As such, these theories can provide no direct understanding of the reasons for the observation of classical rather than Ising-type critical behaviour. An appealing conjecture, seemingly consistent with the current experimental situation [1–15], is that the simple RPM with only hard-core and Coulombic interactions displays classical critical behaviour, or perhaps has $t_x \lesssim 10^{-5}$, but that the introduction of further, more realistic interactions, van der Waals forces, ionic polarizability, etc (see, for example, [31–33]) would yield Ising-type criticality with increasing values of t_x , ultimately becoming of order unity. To test this possibility, the Ginzburg criterion was proposed as a guide to the magnitude of the mean-field-to-Ising reduced cross-over temperature t_x and roughly applied [20]. However, a proper implementation of the Ginzburg criterion requires knowledge (at the mean-field level) of the *density–density* correlation length, $\xi(T, \rho)$; this, of course, is quite distinct from the charge–charge correlation or Debye screening length $\xi_D(T, \rho) \approx 1/\kappa(T, \rho)$, which is all that is provided by the previous DH-based theories.

One option for estimating $\xi(T, \rho)$ is to employ the GMSA [26, 34] which provides both charge and density correlation functions. However, in the light of the strong violations of the Gillan free-energy bound discussed above [29, 30] (owing to the failure to allow for ion-pairing), the GMSA results [34] must be regarded with suspicion. As has also been remarked, the GMSA estimates for T_c are significantly too high and, furthermore, it transpires that the behaviour of $\xi(T, \rho)$ predicted by the GMSA when $\rho \rightarrow 0$ is quite erroneous [35, 36].

Happily one can, instead, meet the challenge of estimating $\xi(T, \rho)$ by *generalizing* DH theory (and all its ion-pairing, dipole-ion and hard-core extensions [19, 20]) by allowing for *non-uniform* ionic and dipolar-pair densities in the basic formulation [35]. The resulting

GDH theories are conceptually simple and yield explicit expressions for the second-moment density–density correlation length $\xi(T, \rho)$. Furthermore (in contrast to the GMSA), the predicted low-density divergence, namely,

$$\xi(T, \rho) = \frac{1}{4}[b/(36\pi\rho)]^{1/4}\left[1 + \frac{1}{8}\kappa b + O(\rho^*)\right] \quad (6)$$

(with $b = q^2/(Dk_B T)$ as in (3)) is seen to be *universal* (that is, independent of a) and, indeed, appears to be asymptotically *exact* [35–37] in the same way that standard DH theory predicts the correct universal limiting law

$$\xi_D(T, \rho) \approx 1/\kappa(T, \rho) \approx 48\xi^2/b \quad \text{as } \rho \rightarrow 0 \quad (7)$$

for the charge–charge correlation length. (Note that $\rho_1/\rho \rightarrow 1$ in (5) as $\rho \rightarrow 0$.) The last part of the relation (7) demonstrates that, although divergent when $\rho \rightarrow 0$, the density fluctuations decay on a *shorter* scale than do the charge fluctuations.

Armed with the GDH approach, one can estimate the amplitude of divergence of $\xi(T, \rho)$ at the mean-field level when the (mean-field) critical point is approached. This is the essential ingredient, beyond the equation of state itself (obtained from the DHBjDI theories), needed to implement the Ginzburg criterion [20, 33]. What does one find? Surprisingly, and perhaps sadly, the conjectured classical (or near-classical) critical behaviour of the RPM is *not* supported by the estimates found for t_\times [33] (in agreement with the GMSA conclusions [34]). Indeed, by calibrating the Ginzburg approach via the hard-core square-well fluid [33, 34] one finds, if anything, that the RPM should cross over to Ising-type behaviour relatively *further* from T_c ! Of course, the Ginzburg criterion is not definitive and one may speculate [33] that the high asymmetry of the RPM critical region or other factors will change the picture (see, for example, [38]). At this point, however, other routes to understanding must be sought.

In a quite distinct attempt to gain analytical insight, the DH theory for the restricted primitive model has been extended to *general dimensionality* d [39, 40]. The Coulombic potential should be taken as

$$\varphi_{ij}(r) = q_i q_j (r^{-\epsilon} - a^{-\epsilon})/\epsilon \quad \text{for } \epsilon = d - 2 \neq 0 \quad (8)$$

but when $\epsilon = 0$ or $d = 2$, one has

$$\varphi_{ij}(r) = -q_i q_j \ln(r/a). \quad (9)$$

Explicit results include Bjerrum association of the positive and negative ions and also the dipole–ionic solvation energy [39, 40]. For all $d > 2$, a critical point terminates coexistence between a conducting liquid and a conducting vapour. One finds that the critical density, $\rho_c^* = \rho_c a^d$, falls as d decreases, but $T_c^* \equiv k_B T_c a^{d-2}/q^2$ rises! When $d = 2$, an *insulating* vapour with no free ions suddenly appears when T drops below $T^* = \frac{1}{4}$. However, this temperature is, in fact, just the well known Kosterlitz–Thouless point. The insulating vapour phase is found to be separated from the conducting high-temperature fluid by an infinite-order critical line ending at a *tricritical* point at $\rho_{tri} = \rho_c(d \rightarrow 2) \simeq 0.004$, $T_{tri}^* = T_c(d \rightarrow 2) \lesssim \frac{1}{4}$. For $\rho^* > \rho_{tri}^*$, the transition is of first order [39, 40]. At present, however, it is not clear whether this tricritical point, which has a quite novel, exponentially sharp character, will survive in more accurate theories.

Nevertheless, the DHBjDI theory for $d = 2$ provides an effective counter-example [41] to startling speculations by various authors to the effect that *above* the standard Kosterlitz–Thouless (KT) transition at $T_{KT}^* = \frac{1}{4}$ (when $\rho \rightarrow 0$) there should be an *infinite sequence* of subsidiary, multiple unbinding transitions commencing (for $\rho = 0$) as T^* falls below $T^* = 2T_{KT}^* = \frac{1}{2}$. In fact, one can show [41] that this dramatic scenario is without any serious foundation!

Beyond that, it proves possible to extend the DHBjDI theories in a natural and *systematic* way that embodies the crucial KT concept of the effective Coulombic interactions that bind the larger dipolar ion pairs, being *renormalized* by smaller dipoles: Bjerrum's chemical-equilibrium picture extends simply to describe a *family* of dipolar pairs of varying sizes from $r = a$ to ∞ . Preliminary calculations [40] indicate that the original KT results for low densities are reproduced (and extended), but a sharp tricritical point remains at a surprisingly low density. If this is, in fact, correct it will be very hard to check, even by the best simulations [42] since the first-order transition near the tricritical point appears to remain exponentially weak. Finally, however, the original challenge to theory posed by the experiments revealing van der Waals or classical critical behaviour in bulk, three-dimensional electrolytes still remains unresolved!

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Note. The following list of articles in no way corresponds to a full list of relevant references: rather it mainly focuses on works by the author and his co-workers. However, detailed references to the literature are to be found in these papers and others cited, particularly [6–8, 15, 19, 35]. This report itself represents an expanded and updated version of an extended abstract prepared for the *Proceedings of the Hayashibara Forum '95, International Symposium on Coherent Approaches to Fluctuations*, organized by Professor Masuo Suzuki and held in Kyoto in July 1995, edited by M Suzuki and N Kawashima and published in 1996 (Singapore: World Scientific).

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