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1996 J. Phys.: Condens. Matter 8 9329

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Phase separation in ionic fluids

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Received 15 July 1996

Abstract. The restricted primitive model is a complex fluid, compared to simple-fluid models such as Lennard-Jonesium. This is a result of the strong ionic association between anions and cations. Some ways in which this ionic association may contribute to the distinctive features of phase separation observed in RPM-like ionic fluids are noted.

1. Background

Over the past decade, the results of several experimental investigations of ionic liquids have raised a number of questions that have challenged our understanding of criticality and phase separation in fluids. Some of these ionic fluids have appeared to exhibit Ising-like criticality and some have appeared to exhibit ‘classical’ (mean-field) criticality [1]. Among the latter have been fluids (such as triethyl *n*-hexyl ammonium triethyl *n*-hexyl boride, N₂₂₂₆B₂₂₂₆, in diphenyl ether) that are regarded as being well-modelled by the restricted primitive model (RPM) of symmetrically charged hard-sphere anions and cations [2, 3]. These results seemed at odds with our conclusion, set forth in 1992 [4], that the RPM is Ising-like in its criticality. The disparity suggested that a reexamination of our 1992 arguments was in order. In particular, Fisher [5] questioned the assumption made in [4] that the charge–charge inverse correlation length Γ remains non-zero at criticality (where the density–density inverse correlation length κ is zero). This assumption greatly facilitated the development of our argument that the RPM is Ising-like (although as noted in section 3 below, there are strong arguments for Ising criticality in the RPM even if one were to assume $\Gamma = 0$). It was against this background that the extensions in [6] to our earlier discussion were developed. We pointed out in [6] that a strong justification for the $\Gamma \neq 0$ assumption lies in the argument of Kosterlitz [7] that for dimensionality d greater than 2, a Coulomb gas such as the RPM will be in a conducting state characterized by free ions at all temperatures T above zero. One expects on very general grounds that the presence of free ions is associated with charge screening, i.e., $\Gamma \neq 0$. If this is accepted, the condition $\Gamma = 0$ implies an insulating state with no free ions in the Kosterlitz sense. We refer to the appendix of [6] for further discussion of this issue; our conclusion was that there were as yet no convincing arguments against our original position that $\Gamma \neq 0$ or that the RPM should be expected to be in the Ising universality class.

In the meantime, the experimental picture began to change substantially, in part as a result of extremely precise measurements by Narayanan and Pitzer [8] on a family of ionic fluids that included RPM-like members. In general even in systems that have Ising criticality (including the Ising model itself) one sees thermodynamic behaviour that cannot

be differentiated from that of systems with mean-field criticality when one is sufficiently far from the critical point. But the RPM-like fluids examined by Narayanan and Pitzer show a ‘delayed’ crossover from mean-field-like behaviour to Ising criticality very much closer to the critical temperature T_c (in units of the dimensionless temperature variable $t = (T - T_c)/T_c$) and the critical density ρ_c (in units of $M = |(\rho - \rho_c)/\rho_c|$) than one finds in the nearest-neighbour lattice gas or in a simple liquid like argon. In this light, the earlier work by Singh and Pitzer [2] and by Zhang *et al* [3] on $N_{2226}B_{2226}$ that seemed fully consistent with mean-field behaviour should perhaps be interpreted instead as showing just such a delayed crossover rather than being more simply regarded as evidence of true mean-field behaviour. (In fact, the delayed-crossover possibility was already raised in the original data analysis in [2].) However, new experimental work on the turbidity of $N_{2226}B_{2226}$ by Wiegand *et al* [9] appears to be inconsistent with the earlier results in [3], with preliminary measurements revealing no deviations from Ising-like behaviour, thus bringing the status of the earlier $N_{2226}B_{2226}$ data into question. In any case, although the experimental consensus that is emerging is clearly still in flux, one finds that there is now substantial experimental evidence that fluids that can be faithfully modelled by the RPM are in the Ising class in their critical behaviour. But if this is the case, the central question that emerges is: why is the crossover behaviour in such systems so often different from that found in argon? It is a question that must be answered against a background that includes some recent RPM simulation results [10] that probe not only the critical-point location but the type of criticality as well. These simulation results are consistent with Ising criticality. Moreover, they do not reveal any sign of the ‘delayed crossover’ found in the experimental results described above. As will be seen, the magnitude of the delayed-crossover effect discussed in the next section is non-universal and system dependent; it could well be non-negligible in some real ionic fluids but negligible in the RPM and in other ionic fluids. (On the other hand, the effect of the dipole–dipole interaction discussed in section 3 can be expected to be of more universal relevance. Although it too is system dependent, its importance hinges on the simple observation that as long as the free-ion density is very small (or zero) at the critical point, one expects the criticality to be very much like that of a pure dipolar fluid.) The absence of any delayed-crossover effect in the simulation of [10] is no surprise, in the light of the fact that the simulation detects almost no free ions near criticality, while the delayed-crossover mechanism suggested in section 2 involves a prefactor of order ρ_C^2 , where ρ_C is free-ion density.

2. Understanding the crossover behaviour

We believe that a possible explanation of the crossover behaviour lies in the presence of both free ions and associated ion clusters, such as ion pairs, in the critical region. The latter will behave much like dipolar dumbbells, so that there will be a charge-dipole term in the ion/ion-pair interaction potential. This will contribute a screened charge-dipole term $W_{CD}(r)$ to the ion/ion-pair potential of mean force, which will in turn contribute a term of the form $\langle W_{CD}^2(r) \rangle$ to the determinant $C_{\rho\rho}(r)$ of the density–density direct-correlation matrix. Here $\langle \rangle$ represents an average over the dipole orientations. The full functional dependence of $\langle W_{CD}^2(r) \rangle$ is not known, but its large- r form in the Debye–Hückel regime of low ion density provides useful information concerning the thermodynamic effect of its presence. As discussed in [6], Høye and Stell have found [11] that in this regime it has the form

$$(1 + \Gamma r)^2 e^{-2\Gamma r} / r^4 \quad (2.1)$$

times a spatially independent prefactor $(A\rho_C\beta q)^2$ where ρ_C is free-ion density, q is ion charge magnitude, $\beta = 1/kT$, and A depends upon the properties of the dipolar solvent formed by the ion pairs through the variables β , ρ_D , and μ , where ρ_D is ion-pair density and μ is ion-pair dipole moment. To lowest order, A is linear in $\rho_D\mu$. The thermodynamic behaviour of the system as $\kappa \rightarrow 0$ will depend upon the form of $C_{\rho\rho}(r)$ for $\kappa r < 1$. In the critical region we expect $\Gamma\sigma < 1$ where σ is the ion diameter, and probably even $\Gamma\sigma \ll 1$, because of substantial ion clustering into pairs and other larger neutral clusters that will deplete the free-ion population [12, 13]. When $\kappa\sigma \ll 1$ and $\Gamma\sigma \ll 1$ with $\kappa < \Gamma$, the term of (2.1) will contribute to mean-field-like behaviour, since for $\kappa r < 1$ it will be indistinguishable from an unscreened $1/r^4$ term, which would give rise to mean-field criticality. Very close to criticality, however, when κ becomes appreciably smaller than Γ , a crossover occurs because appreciable exponential decay of the $C_{\rho\rho}(r)$ -contribution now occurs over the range $\kappa r \ll 1$, revealing the (relatively) short-range nature of the term.

The thermodynamic details of the crossover are particularly subtle, because as $\kappa \rightarrow 0$, Γ is probably itself decreasing to a critical value Γ_c as a result of increasing ionic clustering. This means ρ_C is also probably decreasing. However this also means that ρ_D is increasing. Thus the prefactor $(A\rho_C\beta q)^2$ may well be changing (probably decreasing) and the inverse range, 2Γ , significantly decreasing, as $\kappa \rightarrow 0$: moreover, the prefactor is non-universal—it will depend upon the density ρ_D of the dipolar solvent in which the free ions are the solute (and also the ϵ of that solvent, through A). In the RPM, this solvent consists *only* of the clusters of ions formed by ionic association, but in real ionic fluids it will *also* include the solvent in which the ionic solute is dissolved.

The crossover that occurs when κ becomes smaller than Γ has no counterpart in the Ising model or argon, and we believe it may be significant in fluids in which there is appreciable ionic clustering. One way to study it is to use the Ginzburg criterion. Given a mean-field treatment of correlation, the criterion enables one to establish the values of the variables t and M below which the mean-field treatment ceases to be reliable as one approaches the critical point. These are the Ginzburg numbers t_G and M_G . The criterion has already been applied by Leote de Carvalho and Evans [14], by Fisher and Lee [15] and by Yeh and Stell [16] to a number of mean-field theories of RPM behaviour. In all cases, the Ginzburg numbers proved to be comparable to (or actually larger than) those for standard mean-field treatments of simple non-ionic fluids. In short, these studies have as yet not shed light on the delayed-crossover behaviour found in the experimental results cited above. However none of the versions of mean-field theory so studied have included either the ion/ion-pair term given by (2.1) or the effect of clustering beyond ion pairing as part of their description. The latter would presumably tend to lower both ρ_C and Γ as one approaches the critical point and possibly influence the effect of the ion/ion-pair term in a significant way.

3. The role of ion-pair/ion-pair interactions

The effect of the ion-pair/ion-pair term also appears to be of great importance in determining the critical behaviour of RPM-like fluids, and we believe this issue also deserves further study. One of its implications is in connection with the conclusion we drew in section 2.2 of [6] that in the unsymmetric PM (UPM) the charge–charge inverse correlation length Γ may well be constrained to vanish at criticality along with κ , the density–density inverse correlation length. The formally exact analysis that leads to this conclusion revealed a significant difference in the density–density structure factor when one compares the RPM and the UPM, with the UPM structure factor of non-Ising form. On the other hand, if Γ does go to zero at criticality in the UPM, one can reasonably argue that in three dimensions the

resulting critical system will look very much like a system of ions that have been completely associated into neutral dipolar clusters. (For example, if the anion–cation asymmetry is one of size rather than charge number, the critical system will look much like a collection of heteronuclear dipolar dumbbells.) But we expect such a system of dipolar particles to be in the Ising universality class, which is what we also expect of the RPM despite the formal difference in density–density structure factors. In the case of the RPM, where we expect Γ non-zero but relatively small, the same line of reasoning leads us to conclude that at criticality, the system will look very much like a system of homonuclear dipolar dumbbells plus a relatively small concentration of free ions. Even if we were wrong to assume that $\Gamma \neq 0$ at criticality in the RPM (so that Γ is instead zero, and we have only neutral clusters such as the dipolar dumbbells), we would again expect Ising critical behaviour from such a system of dipolar particles. Our conclusion is that the presence of a significant population of ion pairs at criticality in both the RPM and UPM gives rise to similarity in critical behaviour that would not necessarily be found in the absence of ionic association.

To explore these ideas in a more precise and quantitatively accessible form, we advocate using the formalism developed by Høye and Stell to investigate solutions of ions in dipolar solvents. The formalism is quite general and was used by us to investigate the screening found in the ion/ion, ion/dipolar-particle, and dipolar-particle/dipolar-particle correlation functions [17]. We subsequently used it [18] to extend the Landau–Ginzburg analysis of Nabutovskii *et al* [19] in investigating the effect of adding ionic solutes to a dipolar solvent in its critical region. In the problem we are discussing here, the dipolar species is formed through ionic association rather than independently existing as a molecular species, but when adjusted for this feature (which requires the use here of a mass-action law that does not enter [17] or [18]) the existing formalism is very well suited to the problem at hand. In fact, the expression given by (2.1) for the charge-dipole part of the ion/ion-pair contribution to the direct-correlation matrix was first obtained by Høye and Stell in the context of the ion/dipole-solvent mixture [11].

The dominant role of ionic pairing and the resulting ion-pair/ion-pair interaction in determining the quantitative features of the liquid–gas coexistence curve in the RPM appears to have received striking confirmation from recent simulation results of Shelley and Patey [20]. They compared the coexistence curves of the RPM with that of a system of homonuclear dipolar dumbbell molecules, each consisting of a hard-sphere anion and a hard-sphere cation bearing point charges at their centres, with each ion pair held in rigid tangential contact, so that the distance between the charges q and $-q$ is a sphere diameter σ . (Shelley and Patey refer to these dumbbells with extended point dipoles as charged dumbbells.) They found that the two coexistence curves were very similar in shape and in the location of their critical points. On the other hand, they found the coexistence curve of a system of ideal-dipolar dumbbells (hard-sphere dumbbells, each bearing an ideal dipole at the tangency point of hard-sphere contact) to be very different. This result suggests that we incorporate into our treatment of the RPM the new approximation procedures that we have been developing to treat chemically associating liquids and interaction-site liquids. One such application we have made of these procedures (to highly asymmetric electrolytes) has proved very successful [21].

4. The self-consistent Ornstein–Zernike approach (SCOZA)

Some time ago, Høye and Stell [22] suggested using self-consistency between the compressibility relation and the relation for the internal energy, both of which involve the pair correlation function $h(r)$, to obtain a closure for the Ornstein–Zernike integral

equation for $h(r)$ that one might expect to accurately predict thermodynamics around the critical point as well as far from it. For the three-dimensional nearest-neighbour lattice gas, for which precise estimates of exact results are available, Dickman and Stell [23] have for the first time comprehensively solved the non-linear partial differential equation that arises from the self-consistency condition. They find that the procedure yields remarkably accurate predictions (less than 3% error over most of the temperature range) for the correlation length, compressibility, specific heat, and the coexistence curve. Critical temperatures agree to within 0.2% (and other critical properties to within 1 to 2%) of the best numerical estimates. We have begun the development of versions of SCOZA that are appropriate to the RPM.

Acknowledgment

We gratefully acknowledge the support of the National Science Foundation.

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