

Criticality in Ionic Fluids: Debye-Hückel Theory, Bjerrum, and Beyond

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Debye-Hückel (DH) theory predicts phase separation in the primitive model electrolyte: hard spheres of diameter a with charges $\pm q$. The coexistence curve (CC) is acceptable with $T_c^* \equiv k_B T_c a / q^2 = \frac{1}{16}$, which is roughly correct, but the critical density, $\rho_c^* \equiv \rho_c a^3 = 1/64\pi$, is far too low. Allowing for association into ideal dipolar pairs, following Bjerrum, improves ρ_c and leaves T_c unchanged but yields an unphysical CC. Extending DH theory to compute the dipole-ionic-fluid coupling yields a mean-field description with sensible CC and (T_c^*, ρ_c^*) close to Monte Carlo based estimates: $(0.057 \pm 15, 0.030 \mp 8)$.

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Seventy years ago Debye and Hückel (DH) published a theory of the thermodynamics of strong electrolytes [1]. The DH limiting laws for dilute solutions were subsequently proven to be exact [2]. Despite its fame, DH theory has unappreciated merits [3] relevant, we argue here, to the study of gas-liquid or liquid-liquid criticality in ionic systems. That topic is of renewed interest [4] because recent precise experiments [5,6] reveal two classes of electrolyte solutions [7]: In *solvophobic* systems, the phase separation is principally driven, as in nonelectrolytes, by the “dislike” of the (ionizable) solute for the solvent; critical exponents are standard, i.e., Ising-like, with $\beta \approx 0.32$, $\gamma \approx 1.24$, etc. By contrast, in *Coulombic* systems electrostatic interactions provide the driving force, phase separation occurs at very low concentrations, and the observed exponents are classical, i.e., van der Waals-like with $\beta \approx 0.50$ and $\gamma \approx 1.00$ [4–7].

In seeking to understand these facts the *restricted primitive model* (RPM) is basic: It consists [1] of $i=1, \dots, N \equiv \rho V$ hard spheres of diameter a with $\frac{1}{2}N$ carrying charge $q_i = +q$, the rest a charge $-q$. The solvent is represented by a dielectric constant, D , entering the pair potential $\varphi(r_{ij}) = q_i q_j / D r_{ij}$. Indeed, via the laws of corresponding states, Coulombic systems seem well approximated by the RPM [3,4,7]. Does this model exhibit phase separation and criticality? If so, what are the relevant physical mechanisms? Understanding these at a classical or mean-field level seems an important prerequisite for renormalization-group calculations that might reveal whether Coulombic systems truly represent a non-Ising-like universality class or whether, as seems plausible *a priori* [8], they merely have an anomalously small asymptotic critical region $\{|t| \equiv |T - T_c| / T_c < t_x \ll 1\}$ but would eventually exhibit crossover to Ising-like behavior [9]. In the latter case, however, a satisfactory theory must explain why t_x is so small.

In fact, Monte Carlo (MC) simulations [10] going back two decades suggest the existence of a critical point, but estimates of critical temperature T_c and density ρ_c have ranged widely. Thus in 1991 Valleau [10(b)] concluded $T_c^* \approx 0.070$ and $\rho_c^* \approx 0.07$, where $T^* = k_B T D a / q^2$

and $\rho^* = \rho a^3$, but our analysis of Panagiotopoulos' more recent data [10(c)] yields

$$T_c^* = 0.057 \pm 15, \quad \rho_c^* = 0.030 \mp 8. \quad (1)$$

We feel that Panagiotopoulos' data are more reliable since, in particular, while Valleau [10(b)] simulated only with $N=32$ ions, he used $N=512$ ions. Finite-size shifts of T_c should scale as $N^{-1/d\nu}$ with $\nu \approx 0.50-0.63$ so the difference is significant: Indeed the estimate for T_c in (1) may well be (3–6)% too high since finite size was not allowed for [4(c)].

The first thorough analytically based study of the RPM, by Stell, Wu, and Larsen [11], led to the contrasting estimates $T_c^* \approx 0.085$, $\rho_c^* \approx 0.011$. They utilized a range of series expansion and closure techniques, etc., but, as with the simulations, little physical insight seemed to be gained. The hypernetted chain, Percus-Yevick, and other integral equations from the theory of fluids have also been brought to bear on the RPM but again provide little insight. Furthermore, it has become increasingly clear that all these equations entail serious anomalies in the critical region [12]. Generally, indeed, they provide a much poorer description than do simple, traditional approaches following van der Waals (vdW) even though these cannot, of course, yield Ising-like critical exponents.

Accordingly, our aim has been to uncover a simple theory which embodies as directly as possible the essential physical mechanisms. As we demonstrate, DH theory provides a suitable basis but requires extension: First, as realized by various authors [2,3,4(a)], one must allow, following Bjerrum [13], for the association of ions to produce neutral, dipolar pairs: This compensates for much of the error incurred in DH theory by the linearization of the Poisson-Boltzmann (PB) equation. Beyond that, however, we show it is essential to account for the interactions of a dipolar pair with the residual ionic fluid; this may be accomplished by extending the DH calculations.

We treat phase transitions systematically via the pressure, $p(T, \mu_a, \mu_b, \dots)$, as a function of the chemical potentials μ_j for species A, B, \dots, J, \dots , with number den-

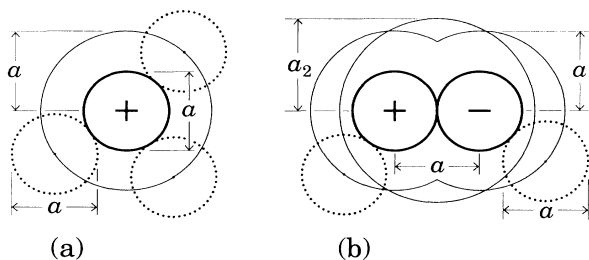


FIG. 1. Diagram illustrating boundary surfaces in the DH solution of the linearized PB equation for (a) a monopole and ion of diameter a and (b) a dipolar pair where $a_2 \geq \sqrt{\frac{3}{4}}a$ is an effective cavity diameter.

sities ρ_j . Coexisting phases are then described by multiple solutions $\{\rho_j\}_{k=1, \dots}$ of the extremal problem,

$$p = \max_{\rho_j} \left\{ f(T; \rho_a, \rho_b, \dots) + \sum_j \mu_j \rho_j \right\}, \quad (2)$$

where $f \equiv -F/V$ is the reduced Helmholtz free-energy density which we plan to construct as a *sum* of terms embodying relevant physical features. Note also that equilibrium under a chemical reaction, say, $\nu_A A + \nu_B B \rightleftharpoons \nu_C C$ is ensured by imposing $\nu_A \mu_a + \nu_B \mu_b = \nu_C \mu_C$, etc.

To start, each species requires an *ideal-gas* term $\beta f^{\text{Id}} = \rho_j - \rho_j \ln(\rho_j \Lambda_j^3 / \zeta_j)$, where $\beta = 1/k_B T$, $\Lambda_j(T)$ is the thermal wavelength, and $\zeta_j(T)$ the molecular partition function. *Hard core repulsions* may be included via the free-volume approximation

$$\beta f^{\text{HC}} = \left(\sum_j \rho_j \right) \ln \left(1 - \sum_j B_j \rho_j \right). \quad (3)$$

The B_j are chosen to yield appropriate maximal densities or to match high- T second virial coefficients [14]. Then vdW theory follows by adding attractive *second-virial* terms via

$$\beta f^{2V} = (A_{aa}\rho_a^2 + A_{ab}\rho_a\rho_b + \dots)/T, \quad A_{jk} > 0. \quad (4)$$

For simple nonionic fluids vdW theory is rather successful, predicting, e.g., T_c values and densities $\rho_c/\rho_{\text{max}} = \frac{1}{3}$ within (10–20)% of reality.

A first idea for RPM electrolytes is to replace f^{2V} by the DH *limiting law* $\beta f^{\text{LL}} = \kappa^3/12\pi \propto \rho^{3/2}/T^{3/2}$ [1,2], where the inverse Debye screening length is

$$\kappa(T, \{\rho_j\}) = \left[4\pi \sum_j q_j^2 \rho_j / Dk_B T \right]^{1/2}. \quad (5)$$

(Note f^{LL} is *independent* of the ionic diameter a .) But this LL theory gives $\rho_c^* \cong \rho_c/\rho_{\text{max}} = \frac{1}{3}$ and $T_c^* = 0.56 \dots$, both too large [11(a)] by factors of 9 to 10. Much more reasonable is to use the *full DH theory* which explicitly incorporates the ionic diameter in solving the linearized PB equation [see Fig. 1(a)] and thereby matches observations up to higher ionic strength [1,2]. Indeed, the DH result [1,2]

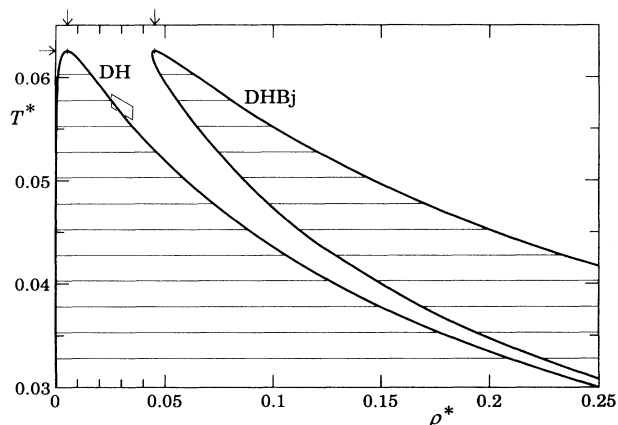


FIG. 2. Coexistence curves for the RPM electrolyte according to Debye-Hückel theory alone, DH, and as augmented by ideal Bjerrum pairing, DHBj. The parallelogram represents simulation-based critical point estimates [15].

$$\beta f^{\text{DH}} = [\ln(1 + \kappa a) - \kappa a + \frac{1}{2}(\kappa a)^2]/4\pi a^3, \quad (6)$$

combined *only* with f^{Id} yields a critical point [3] with $\kappa_c a = 1$, $T_c^* = \frac{1}{16}$, $\rho_c^* = 1/64\pi \cong 0.005$, and $\rho_c v_c / k_B T_c = 16 \ln 2 - 11 \cong 0.090$. The corresponding coexistence curve, $\rho_{\pm}^{\text{DH}}(T)$ (which seems to have been unexamined previously), is shown in Fig. 2: It has a parabolic peak so $\beta = \frac{1}{2}$, and, as to be expected, all the critical behavior is classical. Allowing for the hard cores by adding in βf^{HC} reduces T_c by 1% or 2%, and $\kappa_c a$ and ρ_c by 5% to 9%, while the coexistence curve narrows [15].

That this simple theory yields $T_c^* = 0.0625$, only 10% higher than the estimate (1), suggests that the DH description of the screened ionic fluid embodies much of the truth, but the critical density ρ_c^* is too small by a factor of 5 or 6. Why? The explanation lies in ideas advanced by Bjerrum already in 1926 [13]. At low temperatures many ions bind strongly into neutral (+, -) pairs, say, of density ρ_2 [2,3,4(a),13]; this reduces the density, $\rho_1 = \rho_+ + \rho_-$, of the free, unassociated ions which perform the screening and drive the transition. Hence a higher overall ionic density, $\rho = \rho_1 + 2\rho_2$, is needed to attain criticality.

Quantitatively, following Bjerrum [13] and many later workers, one treats the neutral pairs as an ideal species in equilibrium with the ions and so imposes $\mu_2 = \mu_+ + \mu_- \equiv 2\mu_1$ and invokes an *association constant* $K(T) \equiv \zeta_2/\zeta_+\zeta_-$, where, as above, ζ_2 , ζ_+ , and ζ_- are the internal pair and ionic partition functions. A natural physical postulate is [13]

$$K(T) = 4\pi \int_a^d e^{a/T^* r} r^2 dr \equiv 4\pi a^3 Q_b e^{b/b}, \quad (7)$$

where $b = 1/T^*$ and $Q_{16} = 1.3905$. For the necessary cutoff, d , we adopt Bjerrum's value $\frac{1}{2}ba$ [2,13,15]. [Despite contrary tendencies in the literature, the cutoff d

must *not* be interpreted simply as the size of a typical ionic pair. See further below and note that no modification of (6) is called for at this stage.] Bjerrum's ansatz has been much debated and various alternatives (e.g., setting $Q_b \rightarrow Q_\infty \equiv 1$) has been advanced [2(b)]. However, Ebeling's careful analysis, based on defining $K(T)$ so as to yield the correct equation of state to order ρ^2 [2(b),3(c),16], implies that the error entailed for $T^* \lesssim \frac{1}{16}$ is less than 0.2% [15], amply adequate for us. The resulting "DHBj" theory still exhibits criticality with $\kappa_c a = 1$ and $T_c^* = \frac{1}{16}$ [17]; further, the critical density, $\rho_c^* = (1 + Q_{16} e^8 / 2^9) / 64\pi \approx 0.045$, is much improved being only $\sim 50\%$ larger than the MC estimate. [In more detail one has $\rho_c^* \propto K(T_c)(\rho_{1c}^*)^2$, yielding $(\rho_2^*/\rho_1^*)_c \approx 4.0$.] However, while all exponents remain classical, the coexistence curve, $\rho_{\pm}^{\text{DHBj}}(T)$, itself now assumes the peculiar "banana" shape [18] shown in Fig. 2.

This DHBj curve is surely unrealistic. To understand why, we observe via (2) that it differs from the DH curve only by an additive function $2\rho_0(T)$ [implying $\Delta\rho^{\text{DH}}(T) = \Delta\rho^{\text{DHBj}}(T)$]. Furthermore, $\rho_0(T)$ is just the density of ideal Bjerrum pairs at chemical potential $\mu_2^{\text{DHBj}}(T) = 2\mu_1^{\text{DHBj}}(T)$ where $\mu_1^{\text{DHBj}}(T)$ represents the pure DH phase boundary. It is clear physically that $\rho_0(T)$ increases exponentially fast when T falls as ever more free ions condense into neutral bound pairs, draining the free-ion fraction down to zero. Evidently, then, the assumed ideality of the neutral but strongly dipolar bound pairs is the major theoretical defect.

To advance further we use DH theory to compute the interaction of a dipolar pair with the fluid of free ions. Specifically, we solve the linearized PB equation for a pair of ions in close contact, as in Fig. 1(b); thence the mean energy of interaction of the paired ions with the ionic fluid is found, and, via the usual charging process [1,2,15], the incremental free energy is computed. To simplify the calculation we embed the dipolar charges in an *effective spherical cavity* of radius $a_2 \equiv (1 + s_2)a$: See Fig. 1(b).

Then, with

$$\omega_2(x) = 3[\ln(1+x + \frac{1}{3}x^2) - x + \frac{1}{6}x^2]/x^4 = \frac{1}{12} + O(x),$$

the dipole-ionic (DI) contribution is found to be

$$\beta f_{2,1}^{\text{DI}} = (\kappa^2 \rho_2 a^3 / a_2 T^*) \omega_2(\kappa a_2) \sim \rho_2 \rho_1 / T^2 \quad (8)$$

[15,17]. The sum of all higher-multipole terms can also be found [15] but in the region of interest amounts to less than 1% of the dipolar part.

As to a_2 , geometry implies $\sqrt{\frac{3}{4}} - 1 \leq s_2 \leq \frac{1}{2}$ while simple arguments indicate $s_2 = 0.1-0.25$; for convenience we adopt here the angular average value $\bar{s}_2 \approx 0.162$ [15]. Note also that Fig. 1(b) shows the dipolar ions in direct contact with centers separated by the minimum distance a . However, such a configuration has vanishing statistical weight and the Boltzmann factor embodied in the Bjerrum expression (7) implies, at low temperature, a some-

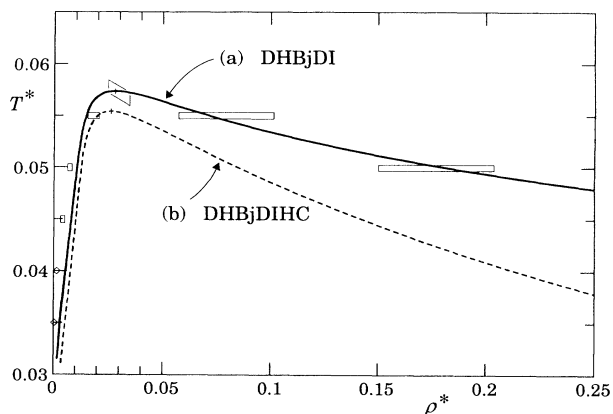


FIG. 3. Coexistence curves for the DHBj theory augmented [curve (a)] by inclusion of dipole-ionic coupling and [curve (b)] with further allowance for hard-core repulsions. The boxes represent the simulation data of [10(c)] and the suggested critical point.

what larger, T -dependent average separation $a_1 = (1 + s_1)a$. Hence in (8) the factor a^3 would better read aa_1^2 . However, the approximation $s_1 \approx Q_b T^* (1 + 8T^*)$ proves reasonable [15] and yields $s_1 \lesssim 0.13$ for $T^* \lesssim \frac{1}{16}$. For simplicity, therefore, we accept $s_1 = 0$ here [15,19].

The new coexistence curve implied by this augmented DHBj or "DHBjDI" theory is shown in Fig. 3 [curve (a)] together with the MC observations [10(c)]. The critical parameters are $\kappa_c a \approx 1.13$ and $T_c^* \approx 0.0574$, $\rho_c^* \approx 0.0280$, which fall squarely within the MC range (1). Naturally all exponents remain classical. If, further, one allows for the hard core by adding (3) with $B_1 = \frac{1}{2} B_2 = 4/3\sqrt{3}$ (corresponding to an anticipated bcc or CsCl crystal packing), the curve shifts downwards yielding $\kappa_c a \approx 1.03$ and $T_c^* \approx 0.0554$, $\rho_c^* \approx 0.0260$; see Fig. 3 [curve (b)]. Then T_c lies on the border of the MC-based estimates although ρ_c is still within the uncertainties. Considering the conceptual simplicity of the augmented theory, the agreement is remarkable: We conclude that the overall physical picture is now essentially correct.

Doubtless, considering the approximations made, the numerical results are somewhat too good. Thus, T_c^* is roughly proportional to $1/a_2$; e.g., $s_2 = 0.100$ with the same $B_1 = \frac{1}{2} B_2$ gives $T_c^* \approx 0.058$ and $\rho_c^* \approx 0.025$ [still consistent with (1)]. Beyond that, tetramers ($2+, 2-$), and higher-order clusters [4(a),20] must play a role when T falls further below T_c . They can be included in the same way and should improve the description of the low-density vapor [4(a)]. However, our calculations suggest that their contribution in the critical region should be fairly small. These effects and, e.g., the screened dipole-dipole attractions can be represented in an *ad hoc* way by adding a vdW term (4): $A_{2,2}$ of order 0.1 (in reduced units) proves reasonable; at lower T , the liquid free energy is improved, instead, by a small $\rho^{4/3}$ term which mirrors the static crystal [1,15,21].

Finally, of course, there is no allowance for nonclassi-

cal critical fluctuations. Nor is an estimate of a putative nonclassical region ($|t| < t_x$) provided. Both issues will be addressed elsewhere [8,15] but as regards the latter, perhaps our values $\kappa_c a \approx 1.0$ to 1.13 could provide a hint. The Ginsburg criterion yields $t_x \propto (a/R_0)^6$ (for three dimensions), where R_0^2 is, say, the mean square range of the effective *density-density* attractive potential. If one guesses that this varies as $e^{-\kappa r}/r$ (mirroring the *charge-charge* screening), one might conclude $t_x \lesssim 0.15 t_x^{LJ}$, where t_x^{LJ} corresponds to a Lennard-Jones (6,12) potential [15]. That would point to a somewhat smaller nonclassical regime for the RPM and its real analogs [4-7,9]. However, (i) other factors enter the Ginsburg definition of t_x and (ii) the density-density correlations demand separate investigation. Nevertheless, we believe that the picture we have expounded here of Debye-Hückel-Bjerrum theory augmented by the dipole-ionic fluid couplings provides a sound basis for further progress.

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[17] Note only the free, unassociated ions (or *charged* trimers, etc.) enter the definition (5) of κ .

[18] Friedman and Larsen [11(b)] report this graphically as what appears to be a sharply pointed "marlin spike" (with $\rho_{liq} > \rho_{vap} > \rho_c$ for *all* $T < T_c$) instead of the correct rounded form shown in Fig. 2. Reference [10(c)] reproduces this marlin-spike shape but with a misplaced critical density.

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