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Critical Point in a Fluid of Charged Hard Spheres

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Evidence is given for the existence of a heretofore undetected low-density critical point in a classical fluid of charged hard spheres.

We have found what we regard as compelling evidence for the existence of a critical point (cp) at a very low density in a classical fluid of charged hard spheres of equal diameter. To our knowledge this critical point has never before been described or discussed in the literature. The only specific reference to the possible existence of a charged-spheres critical point that we have seen is given in passing by Stillinger and Lovett,¹ and it is based upon the observation that a liquid-gas critical point is known to occur in certain real fused salts. However, that reference is to a cp, associated with a phase separation into a fused-salt-like concentrated fluid and its coexistent vapor, and anticipated at a density more than an order of magnitude higher than that of the point which we consider here. Furthermore, the Hamiltonian of a real fused salt, unlike that of a system of charged spheres, includes attractive dispersion terms that are enough to guarantee the existence of a cp even in the absence of a Coulombic term. Thus, the extrapolation from experimental fused-salt results to charged spheres in this connection requires special caution and qualification.

We consider in the thermodynamic limit the restricted primitive model (RPM), which consists of hard spheres of equal diameter R in a struc-

tureless continuum of dielectric constant ϵ . Negatively charged spheres have charge q_1 and number density ρ_1 , while positively charged spheres have charge q_2 and density ρ_2 , where $q_1 = -q_2 = q$ and $\rho_1 = \rho_2 = \rho/2$. Thus, the pair potential of two particles with centers separated a distance r is given, for $i = 1, 2$ and $j = 1, 2$, by

$$\varphi_{ij}(r) = \begin{cases} \infty & \text{for } r < R \\ (-1)^{i+j} q^2 / \epsilon r & \text{for } r > R. \end{cases} \quad (1)$$

The equation of state of this system is not known exactly; our quantitative results are based upon systematic procedures devised to eliminate the possibility that the cp which we find is an artifact of a particular approximation method. To this end, we have pursued three quite different routes to the thermodynamics. The first is via an equation of state developed by one of us (B.L.) to provide a good global fit to his Monte Carlo results.² It embodies the best overall "experimental" results currently available to us for a system of charged spheres.

The second route is via a Padé extrapolation procedure³ involving the first five terms in the exact Stell-Lebowitz⁴ expansion of the free energy per particle f in the parameter $\beta^* = \beta q^2 / \epsilon R$, where β is inverse temperature, $\beta = (kT)^{-1}$. The Padé approximant, f^p , is chosen to "saturate" as $\beta^* \rightarrow \infty$

so that it is of the appropriate asymptotic functional form $\beta f^p/\beta^* \rightarrow a_\infty(\rho)$, where $a_\infty(\rho)$ is a function only of number density ρ .⁵ From f^p an equation of state immediately follows.

The third starting point is the free energy associated with the lowest-order gamma-ordered approximation⁶ (LOGA) in a systematic approximation scheme^{4,7} based upon viewing q as a range parameter γ appearing in the Coulombic potential as $\gamma^3\varphi(\gamma r)$. It involves approximating the two-particle radial distribution function $g_{ij}(r)$ subject to the core constraint that the spheres are impenetrable, so that $g_{ij}(r) = 0$ for $r < R$. In the low-density region we shall consider, the LOGA result is numerically indistinguishable from that of the mean spherical approximation (MSA) to which it reduces when the Percus-Yevick approximation is used to assess the hard-spheres $g(r)$ that appear in the LOGA $g_{ij}(r)$. (There are several other approaches besides gamma-ordering that also lead one to the MSA.⁸) From the LOGA $g_{ij}(r)$ one obtains an approximation [via the internal energy as an integral over $g_{ij}(r)\varphi_{ij}(r)$] for the equation of state that we shall refer to as the $\Gamma 1$ approximation.

All three of the equations of state that we have just summarized (i.e., the Larsen, Padé, and $\Gamma 1$ equations) yield low-density critical points denoted as the L, P, and $\Gamma 1$ results in Fig. 1. These three approaches are fundamentally different enough from each other for the appearance of the cp in all three cases to suggest that the cp is not

simply an artifact of a particular approximation scheme. These same differences account for the rather considerable spread in the locations of the three points. (Note, however, that there is a relatively small spread in temperature of only about $\pm 5\%$ around $T_c^* = 78 \times 10^{-3}$, where $T^* = 1/\beta^* = \epsilon kTR/q^2$. All three equations of state are lacking an exact "second ionic virial coefficient" B_2 , which is the first nontrivial coefficient appearing in a systematic cluster expansion of the function S , which is $-\beta\rho f$ minus its ideal-gas contribution,⁹

$$S = \frac{\kappa^3}{12\pi} + \sum_{n=2} B_n \rho^n; \quad \kappa^2 = 4\pi\beta q^2 \rho / \epsilon. \quad (2)$$

This expansion appears to converge too slowly⁹ to directly provide a good approximation scheme in itself, even at the very low density $\rho^* \approx 10^{-2}$ ($\rho^* = \rho R^3$) in which we are interested. But at such densities, one *can* hope to improve substantially such approximation as the Padé and $\Gamma 1$ expression for S by taking the union of the B_2 terms and any such result—in other words, by adding to such a result the piece of B_2 that it is lacking. The results for P and $\Gamma 1$, denoted as PUB_2 and $\Gamma 1UB_2$, are also shown in Fig. 1. (The Larsen equation, because it hinges upon Monte Carlo results, does not lend itself to ready formation of LUB_2 in the way the P and $\Gamma 1$ equations do.)

By taking the union of P or $\Gamma 1$ with B_2 , this improves those approximations by yielding a βf that remains exact through $O(\rho^{*2})$ no matter how large β^* is—a desirable feature for probing the

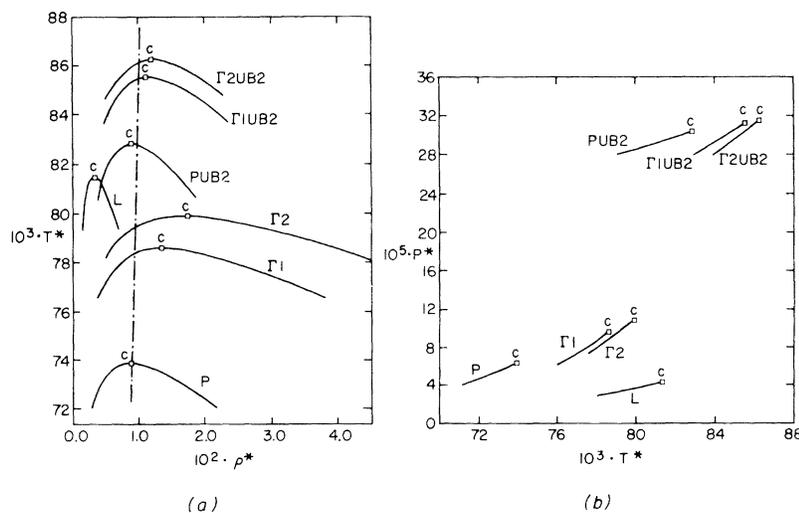


FIG. 1. (a) Coexistence curves in the neighborhood of their critical point for the restricted primitive model in the various approximations that we discuss. The straight line is the locus of points marking the onset of long-range charge-density oscillations in the lowest-order gamma-ordered approximation. (b) Phase diagrams in the same approximations in the same critical region.

large β^* , small ρ^* regime in which the critical point is found. One can also systematically improve $\Gamma 1$ through higher-order terms in β^* by means of gamma-ordering, and we have computed the next-order result [which includes all terms of $O(\beta^{*2})$] to obtain the results labeled $\Gamma 2$ in Fig. 1 as well as the $\Gamma 2 \cup B_2$ result, also shown. The P result [which already includes all terms of $O(\beta^{*3})$ and is designed to have the correct behavior for $\beta^* \rightarrow \infty$ as well] cannot so readily be extended in this direction.

The $\Gamma 1 \cup B_2$, $P \cup B_2$, and $\Gamma 2 \cup B_2$ results are likely to be our most accurate results, and it is gratifying that they cluster quite closely together about the values $T^* = 0.085$ and $\rho^* = 0.011$ (and $P^* = 31 \times 10^{-5}$, where $P^* = \epsilon P R^4 / q^2$ and P is the pressure) which represent our best current estimate of the location of the cp. Only the T^* value can be regarded as precise to within 10% or so; we believe the ρ^* and P^* could be off by as much as 50% in either direction. Nevertheless, we regard these results as strong evidence that only the precise location of the cp, rather than its existence, remains in doubt.

As soon as one begins to entertain seriously the notion of a cp in the RPM, one sees that it is to be expected in three dimensions on the basis of any reasonable thermodynamic description that duly takes into account the Debye-Hückel limiting law (which insures a negative contribution to the pressure of order $\rho^{3/2}$) as well as the effect of the hard core (which insures a positive and rapidly increasing contribution to the pressure at increasing densities). The competition between these two terms alone generates a cp in the same way that the positive core term and negative ρ^2 term generates a cp in a van der Waals fluid. Experience has shown that for many systems the simple mean-field description obtained by neglecting all but such key terms yields an essentially correct picture in three dimensions, but in our case it gives the values $T_c^* = 0.327$, $\rho_c^* = 0.123$, and $P^* = 790 \times 10^{-5}$, which are very different from our best estimates.

Below the critical point, we would expect the rarer fluid phase to be rich in pairs of oppositely charged ions that are bound sufficiently tightly to each other to be regarded as neutral diatomic dipolar molecules. (In the denser phase, the ions of opposite sign perhaps shield each other according to the usual Debye picture in a way that inhibits pairing. We are doing further model calculations to elucidate this point.) In the point-charge limit of the RPM in which $R \rightarrow 0$, one indeed sees

a well-defined phase transition associated with this pairing in two dimensions, where the thermodynamics is exactly known in this limit.¹⁰ Unfortunately, in the limit one also loses the independence of the two parameters β^* and ρ^* and has only a single plasma parameter ($\beta^* \rho^{*(d-2)/d} = q^2 \beta \rho^{(d-2)/d}$ in d dimensions). This degeneracy, along with the difference in dimensionality, precludes direct contact with our results. The phase separation recently found by Hansen and Vieillefosse¹¹ in a two-component plasma of positively charged point particles in a uniform negative background is likewise an effect that we cannot directly relate to the two phases which we find. On the other hand, the equal-density mixture of positively charged hard spheres and negatively charged points studied by Gillan *et al.*¹² may well be sufficiently closely related to the RPM to show similar behavior. Gillan *et al.* found numerical evidence for polymerization in this model but made no systematic search for evidence of a phase separation.

Some time ago, Friedman¹³ discussed and extended experimental results on electrolyte solutions that unmix to form two liquid phases. We believe our charged-spheres model embodies all the essential features pertinent to an understanding of such unmixing in real systems. Friedman's own theoretical discussion, which relates the phase separation to an increasing dielectric constant of the system as a result of ion pairing, can be given within the framework of our charged-spheres model, as can the much more recent discussion of possible first-order phase transitions and critical points in metallic vapors by Gitterman and Steinberg.¹⁴ In addition to the high-density first-order phase transition that is expected for all T^* in the RPM even when $q = 0$, our LOGA will exhibit a much weaker form of ordering at a distinguished value, 1.229, of $\kappa R = (4\pi \rho q^2 \beta / \epsilon)^{1/2} R$ that is associated with the onset of pronounced long-range oscillations of the charge distribution function $g_{11}(r) - g_{12}(r)$. These oscillations signal the onset of long-range layering of positive and negative charges about each ion.¹⁵ The locus of points associated with the onset is shown in Fig. 1(a) along with the approximate coexistence curves; one sees that it bears a striking resemblance to the locus of transition points shown by Gitterman and Steinberg in their Fig. 2. We intend to investigate the possibility of strong low-density ordering in approximations for charged spheres of one sign in both dense-point and uniform neutralizing backgrounds; there is already

experimental evidence for such ordering in dispersions of charged polystyrene spheres¹⁶ as well as theoretical evidence for it in a one-component plasma of point ions in a uniform neutralizing background.^{17,18}

Further details of our RPM results will appear elsewhere.¹⁹

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¹F. Stillinger and R. Lovett, *J. Chem. Phys.* **48**, 3858 (1968). The reference is found in the caption of their Fig. 1, which shows a cp.

²B. Larsen, *Chem. Phys. Lett.* **27**, 47 (1974), and to be published. In G. Stell and K. C. Wu, *J. Chem. Phys.* **63**, 491 (1975) the equation is misprinted with $b(\eta)$ instead of $b(\eta)\Gamma^{1/2}$, $4^{1/3}7\eta/12$ instead of $4^{1/3}7\eta^{2/3}/12$, and Γ missing a $2\eta^{1/3}$ factor.

³Stell and Wu, Ref. 2.

⁴G. Stell and J. L. Lebowitz, *J. Chem. Phys.* **49**, 3706 (1968).

⁵This (unique) Padé approximant that uses all five of the known terms in the Stell-Lebowitz expansion and at the same time is linear in β^* for $\beta^* \rightarrow \infty$ can be written as $\beta f - a_0 = a_{3/2}\beta^{3/2}(1 + b_{1/2}\beta^{1/2})/(1 + d_{1/2}\beta^{1/2} + d_{1/2}\beta^*)$ with the a_i , b_i , and d_i being functions only of ρ . See Ref. 3 for further details.

⁶G. Stell, *J. Chem. Phys.* **55**, 1485 (1971).

⁷J. L. Lebowitz, G. Stell, and S. Baer, *J. Math. Phys.* (N.Y.) **6**, 1282 (1965).

⁸See, e.g., J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **144**, 251 (1966); J. K. Percus and G. Yevick, *Phys. Rev.* **136B**, 290 (1964). The MSA for the RPM was solved by E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **56**, 3086, 3093 (1972).

⁹H. L. Friedman, *Ionic Solution Theory* (Wiley, New York, 1962). Unlike the virial coefficients of an un-

ionic fluid, the $B_n(T^*, \rho^*)$ are functions of $\rho^* = \rho R^3$ as well as temperature.

¹⁰E. H. Hauge and P. C. Hemmer, *Phys. Norv.* **5**, 209 (1971); C. Deutsch and M. Lavaud, *Phys. Rev.* **9**, 2598 (1974).

¹¹J. P. Hansen and P. Vieillefosse, *Phys. Rev. Lett.* **37**, 391 (1976).

¹²M. Gillan, B. Larsen, M. P. Tosi, and N. H. March [*J. Phys. C* **9**, 889 (1976)] treat the related "sphere-point" case of $R_2 = 0$, but with $\rho_2 = \rho_1$ and $q_2 = -q_1$.

¹³H. L. Friedman, *J. Phys. Chem.* **66**, 1595 (1962).

¹⁴M. Gitterman and V. Steinberg, *Phys. Rev. Lett.* **35**, 1588 (1975).

¹⁵There is a considerable literature in ionic solution theory concerning the onset of these oscillations in the RPM, which are best described in terms of the singularities of the Fourier or Laplace transforms of $g_{11}(r) - g_{12}(r)$. For a good review, with many references, see C. W. Outhwaite's contribution to *Specialist Periodical Report in Statistical Mechanics* (The Chemical Society, London, 1975), Vol. 2.

¹⁶Judith C. Brown, P. N. Pusey, J. W. Goodwin, and R. H. Ottewill, *J. Phys. A* **8**, 664 (1975), and references therein.

¹⁷J. P. Hansen, *Phys. Rev. A* **8**, 3096 (1973).

¹⁸We anticipate that solidification could suppress the incipient critical behavior at low densities in these models, in contrast to the RPM, because their mutually repulsive ions will tend to order themselves at sufficiently low temperatures, rather than to form dimers. The approximations we use for the RPM cannot be expected to show solidification in such models, however. In particular, the MSA shows a critical point for charged spheres in both uniform and dense point neutralizing backgrounds when its free energy for these two cases is evaluated by extending the analysis given by E. Waisman and J. L. Lebowitz in *J. Chem. Phys.* **56**, 3093 (1972) and by R. G. Palmer and J. D. Weeks in *J. Chem. Phys.* **58**, 4171 (1973), respectively.

¹⁹B. Larsen, J. Rasaiah, and G. Stell, to be published; K. C. Wu, thesis, State University of New York at Stony Brook, 1976 (unpublished). Larsen *et al.* use a Padé based upon a series in which the coefficient of the β^{*3} term is evaluated according to a slightly different approximation scheme than used here. Their quantitative results differ slightly from our results here as a consequence.