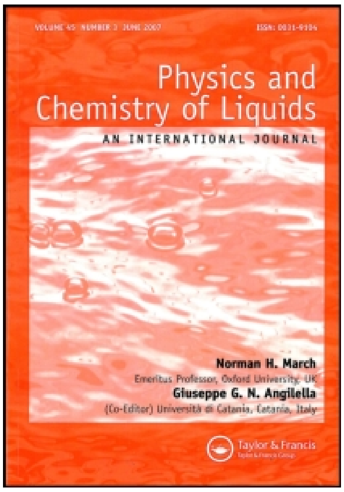

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Gas-Liquid Transition in Charged Fluids

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The connexion between the equation of state of a classical fluid of non-polarizable ions, the character of the screening, and the appearance of long range oscillations in the charge-charge radial distribution function is examined. While considerations of stability lead to the usual inequalities for the inverse static dielectric function and the compressibility of the charged fluid, the square of the inverse screening length k_s does not need to be positive for thermodynamic stability. Through a study of an approximate equation of state for a two-component fluid of charged hard spheres, the regions of negative and positive k_s^2 in the pressure-density plane are related to a liquid phase and to an ionized-gas phase, respectively. The model fluid displays a gas-liquid critical point, above which the transition between the two types of screening is continuous. This behaviour of the charged-hard-spheres fluid is contrasted with the transition of a real ionic liquid to the molecular gaseous phase.

1 INTRODUCTION

The classical one-component plasma on a uniform neutralizing background (OCP) is often taken as a prototype model for understanding the behaviour of real charged fluids. Some of the qualitative deficiencies of this model (the lack of a d.c. resistivity, for instance) are well known. Further concern has arisen from recent computer simulation work[1,2] showing that the "compressibility" of the OCP becomes negative with increasing plasma parameter Γ (defined as $\Gamma = e^2/(ak_BT)$ with $a = (4\pi n/3)^{-1/3}$ and n the particle density). At approximately the same value of Γ, oscillations are found to appear in the charge-charge radial distribution function $g_q(r)$. In fact, negative values of the "compressibility" had previously been obtained in approximate many-body theories for both the degenerate Fermi plasma at low density[3] and the OCP at high density.[4]

A negative value of the compressibility is commonly associated with a mechanical instability of the system,[5] although a full discussion of stability

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conditions for charged fluids seems to be lacking. A misleading feature of the OCP model is that its isothermal compressibility is defined[6] to coincide, apart from a trivial factor, with the square of its inverse screening length k_s, at least when the neutralizing background is not endowed with mechanical stiffness. One is thus tempted to suggest that the computer simulations of the OCP are merely observing a change in the character of the screening, from exponential to oscillatory, as Γ increases, while mechanical stability of the model is preserved through the boundary conditions imposed on the simulation runs.

These considerations have prompted us to examine the connexion between the equation of state and the character of the screening in a two-component charged fluid, where K_T and k_s^2 are naturally distinct quantities. We first discuss exhaustively the stability conditions for such a fluid, both on a microscopic scale and in the thermodynamic limit. We find in particular that a negative value of k_s^2, but not a negative value of K_T, is compatible with thermodynamic stability. To illustrate the behaviour of k_s^2 in relation to the equation of state, we then specialize the discussion to a classical fluid of charged hard spheres of equal diameters, adopting the analytic, albeit approximate, expressions for its thermodynamic properties derived by Waisman and Lebowitz[7] in the mean spherical approximation. We feel that this should suffice for the qualitative insight that we are seeking at present.

The main results are briefly summarized as follows. The isotherms of the model have the classical van der Waals shape with a liquid-gas critical point, in agreement with previous work[8] on the same model fluid. Below the critical pressure, the two phases are characterized by values of k_s^2 of opposite signs, that is negative for the high density (liquid) phase and positive for the low density (ionized gas) phase. These correspond, respectively, to an oscillatory and to an exponential asymptotic screening behaviour. The critical point is bracketed between the locus of points in the pressure-density plane where k_s^2 changes sign and the locus of points where oscillations in $g_q(r)$ appear, these "transitions" being continuous above the critical pressure. The gaseous phase in question is, of course, a fully ionized conducting fluid, although screening is strongly local except at the lowest densities, where the Debye–Hückel limit is recovered. Inclusion of electronic deformability would seem necessary to allow for the formation of molecular bound states.

2 STABILITY OF AN IONIC FLUID AGAINST WEAK PERTURBATIONS

Let us consider first the electric stability of an ionic fluid in a weak external Coulomb potential $V_e(\mathbf{k}, \omega)$, at frequencies well below those of electronic excitations. The average dissipation of energy per cycle is $W = [\mathbf{F}_e \cdot \langle \mathbf{j} \rangle]_{av}$ where $\mathbf{F}_e$ is the external force acting on the ionic charges,

$$\mathbf{F}_e = \mathrm{Re}\left\{ -i\mathbf{k} \frac{V_e(\mathbf{k}, \omega)}{\varepsilon_\infty(k)} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \right\}, \tag{2.1}$$

and $\langle \mathbf{j} \rangle$ is the ionic current density, whose longitudinal component follows from the continuity equation,

$$\mathbf{k} \cdot \langle \mathbf{j} \rangle = \mathrm{Re}\{\omega \langle q(\mathbf{k}, \omega) \rangle \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t]\}. \tag{2.2}$$

We have taken into account the effects of electronic polarization formally through an electronic static dielectric function $\varepsilon_\infty(k)$ which screens the external field and the fields of ionic fluctuations. The ionic charge density $\langle q(\mathbf{k}, \omega) \rangle$ induced by the perturbation is thus related to the external potential by

$$\langle q(\mathbf{k}, \omega) \rangle = \frac{\chi_{qq}(k, \omega) V_e(\mathbf{k}, \omega)}{\varepsilon_\infty(k)} \tag{2.3}$$

where $\chi_{qq}(k, \omega)$ is the ionic-charge response function. The Poisson equation relates $\chi_{qq}(k, \omega)$ to the usual dielectric function $\varepsilon(k, \omega)$ of the system through

$$\frac{\varepsilon_\infty(k)}{\varepsilon(k, \omega)} = 1 + \frac{4\pi e^2}{k^2 \varepsilon_\infty(k)} \chi_{qq}(k, \omega). \tag{2.4}$$

Using the above equations and averaging over a cycle of the external field, we get

$$\begin{aligned} W &= -\frac{\omega}{2\varepsilon_\infty^2(k)} \mathrm{Im}\, \chi_{qq}(k, \omega) |V_e(\mathbf{k}, \omega)|^2 \\ &= -\frac{k^2}{8\pi e^2} \omega \,\mathrm{Im} \frac{1}{\varepsilon(k, \omega)} |V_e(\mathbf{k}, \omega)|^2, \end{aligned} \tag{2.5}$$

a result which in its latter form is well known[6] for a one-component plasma. This can also be written

$$W = \frac{k^2}{8\pi e^2} \omega \,\mathrm{Im}\, \varepsilon(k, \omega) |V_i(\mathbf{k}, \omega)|^2 \tag{2.6}$$

where $V_i(\mathbf{k}, \omega) = V_e(\mathbf{k}, \omega)/\varepsilon(k, \omega)$ is the potential inside the material.

The function $1/\varepsilon(k, \omega)$, being the response to the external perturbation which can in principle be varied at will, is necessarily causal and thus obeys the Kramers–Kronig relation

$$\mathrm{Re} \frac{1}{\varepsilon(k, \omega)} - \frac{1}{\varepsilon_\infty(k)} = P \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\mathrm{Im}[1/\varepsilon(k, \omega')]}{\omega' - \omega}. \tag{2.7}$$

From Eq. (2.5) and the inequality $W > 0$ for electric stability, we get

$$\frac{1}{\varepsilon(k, 0)} < \frac{1}{\varepsilon_\infty(k)}. \tag{2.8}$$

For $\varepsilon_\infty(k) > 0$, this inequality is compatible both with $\varepsilon(k, 0) > \varepsilon_\infty(k)$ and with $\varepsilon(k, 0) < 0$. On the other hand, if $\varepsilon(k, \omega)$ were to satisfy a Kramers-Kronig relation analogous to Eq. (2.7), one would obtain from Eq. (2.6) that the inequality (2.8) ought to be restricted to $\varepsilon(k, 0) > \varepsilon_\infty(k)$. As pointed out by several authors,[6,9,10] however, $\varepsilon(k, \omega)$ does not necessarily obey the requirements of causality, and examples of charged fluids with $\varepsilon(k, 0) < 0$ have recently been presented.[11]

The inequality (2.8) thus expresses the condition for stability of the ionic system against a weak electric perturbation. If we notice that it is equivalent to the inequality

$$-\chi_{qq}(k, 0) > 0, \tag{2.9}$$

its extension to the full set of stability conditions is immediate: the matrix of the negatives of the static response functions (that is, in the classical limit, the matrix of the partial structure factors) must be positive definite.

Instead of proving this statement, as can be done by the same line of argument used above to derive Eq. (2.9), let us consider in detail the long wavelength limit, which is of special interest for what follows. We can use in this limit the standard procedure[5] for the derivation of thermodynamic stability conditions, which requests that the thermodynamic potential ought to be a minimum against small changes of state at constant temperature and chemical potentials. That is, considering for simplicity a two-component ionic fluid,

$$\delta e - T\delta s - \frac{P\delta\rho}{\rho^2} - \left(\frac{4\pi e^2}{k^2\varepsilon_\infty} + \mu\right)\delta q > 0 \tag{2.10}$$

where δe, δs, $\delta\rho$ and δq are the changes in densities of internal energy, entropy, mass and charge, and

$$\mu = \frac{m_+ m_-}{m_+ + m_-}(\mu_+ - \mu_-) \tag{2.11}$$

with μ_+ and μ_- the chemical potentials of the two components per unit mass. Expanding δe for small changes of state up to quadratic terms in δs, $\delta\rho$ and δq, we obtain the usual inequalities

$$C_v > 0, \qquad K_T > 0 \tag{2.12}$$

as well as the inequality

$$\frac{1}{k^2} + \frac{1}{k_s^2} > 0 \tag{2.13}$$

with

$$k_s^2 = \frac{4\pi e^2}{\varepsilon_\infty} \bigg/ \left(\frac{\partial \mu}{\partial q}\right)_{P,T}. \tag{2.14}$$

The equivalence between Eq. (2.13) and Eq. (2.9), as well as the identification of k_s^2 with the square of the inverse screening length, follow from the long-wavelength expression[12] for the static charge response function,

$$\lim_{k \to 0} \chi_{qq}(k, 0) = -\frac{\varepsilon_\infty k^2}{4\pi e^2}\left(1 + \frac{k^2}{k_s^2}\right)^{-1}. \tag{2.15}$$

In the case of a neutral mixture, the term $1/k^2$ is absent in Eq. (2.13) and the fluctuation δq coincides with the concentration fluctuation δc, so that Eq. (2.13) becomes the usual inequality $(\partial\mu/\partial c)_{P,T} > 0$ for stability against phase separation. In the charged fluid, on the other hand, the inequality (2.13) is always satisfied in the thermodynamic limit ($k \to 0$), irrespectively of the sign of $(\partial\mu/\partial q)_{P,T}$. Obviously, separation of the two ionic components is prevented by the Coulomb interactions. We conclude that the "screening length" defined by Eq. (2.14) may well become imaginary in a charged fluid. This behaviour would correspond to asymptotic oscillations of the screening charge density around a point-like impurity of (weak) charge Ze,

$$\lim_{r \to \infty} \langle \delta q(r) \rangle = \frac{Z|k_s^2|}{4\pi r} \cos(|k_s| r) \quad (k_s^2 < 0) \tag{2.16}$$

in place of the exponential decay to which one is accustomed from the low-density Debye–Hückel theory,

$$\lim_{r \to \infty} \langle \delta q(r) \rangle = -\frac{Z k_s^2}{4\pi r} \exp(-k_s r) \quad (k_s^2 > 0). \tag{2.17}$$

Notice also that Eq. (2.16), although strictly inapplicable for values of r of the order of ionic dimensions, indicates that the first pile-up of screening charge occurs at $r \simeq \pi/|k_s|$ rather than on top of the impurity. In an ionic liquid at very high densities this distance should correspond to near contact between the point-like impurity and its neighbour ions of opposite sign, and thus we may expect in this limit $k_s^2 \sim -\pi^2/R^2$, R being of the order of the ionic size.[13]

3 SCREENING AND EQUATION OF STATE FOR A CHARGED-HARD-SPHERES FLUID

We have seen in the preceding discussion that an imaginary screening length does not conflict with stability criteria and is in fact suggested at high densities. The OCP simulation work[1,2] that we have discussed in the introduction indicates that this effect arises at densities considerably lower than those met in molten-salt liquids. To explore the behaviour of k_s^2 in a two-component charged fluid and its relation to the equation of state, we resort in the following to the model of a fluid of charged hard spheres of equal diameters, which has been solved in the mean spherical approximation by Waisman and Lebowitz.[7]

The equation of state of this approximate model is given analytically as

$$P = 2nk_BT\frac{1+\eta+\eta^2}{(1-\eta)^3} + \frac{k_BT}{4\pi\sigma^3}[x + x(1+2x)^{1/2} - \tfrac{2}{3}(1+2x)^{3/2} + \tfrac{2}{3}] \tag{3.1}$$

where n is the number of ion pairs per unit volume, $\eta = \frac{1}{3}\pi n\sigma^3$ is the packing fraction, σ is the hard-sphere diameter, and $x = k_0\sigma$ with k_0 the Debye–Hückel inverse screening length,

$$k_0 = \left(\frac{8\pi ne^2}{\varepsilon_\infty k_BT}\right)^{1/2}. \tag{3.2}$$

Similarly, an analytic expression for k_s^2 can be obtained from the low k expansion of the charge-charge structure factor $S_{qq}(k)$, defined as

$$S_{qq}(k) = \tfrac{1}{2}[S_{++}(k) + S_{--}(k) - 2S_{+-}(k)], \tag{3.3}$$

if we use the fluctuation-dissipation theorem to relate $S_{qq}(k)$ to the response function $\chi_{qq}(k, 0)$,

$$S_{qq}(k) = -\frac{k_BT}{2n}\chi_{qq}(k, 0), \tag{3.4}$$

and compare the result of the expansion with Eq. (2.15). The result of this lengthy but straightforward calculation is

$$(k_s\sigma)^2 = x^2[\tfrac{1}{2} - \tfrac{1}{3}x - \tfrac{1}{12}x^2 - \tfrac{1}{6}x(1+2x)^{1/2} + \tfrac{1}{2}(1+2x)^{1/2}]^{-1}, \tag{3.5}$$

with the limiting values $k_s = k_0$ for $x \to 0$ and $k_s^2 = -12/\sigma^2$ for $x \to \infty$.

The behaviour of k_s/k_0 as a function of the variable x is reported in Figure 1. Starting from the low values of x (that is, low density or high temperature), and with reference to Eqs. (2.16) and (2.17), the screening cloud is becoming more rapidly localized with increasing x than predicted by the Debye–

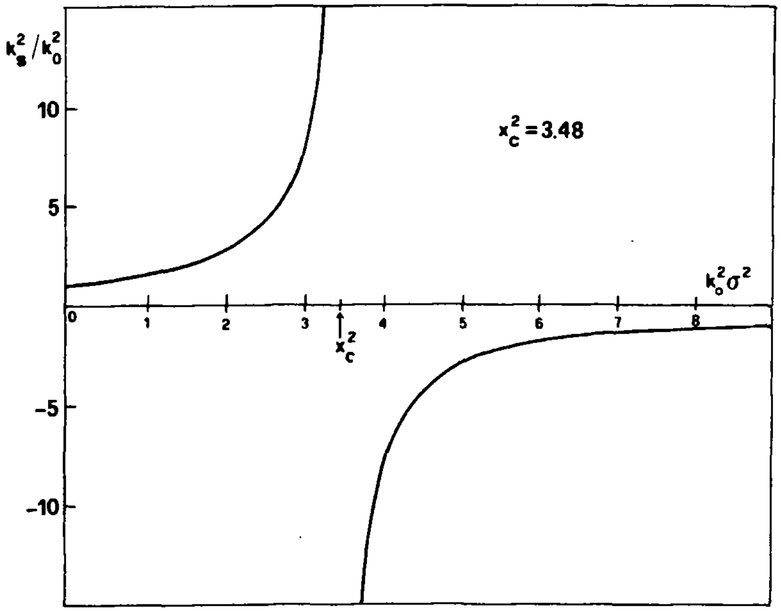

FIGURE 1 The function k_s^2/k_0^2 versus $k_0^2\sigma^2$ for a charged-hard-spheres fluid in the mean spherical approximation.

Hückel theory, till k_s diverges for a critical value $x_c \simeq 1.8$. Obviously, in the neighbourhood of x_c higher order terms in the low k expansion of the response function will become important, and Eqs. (2.16) and (2.17) will lose their validity. At larger values of x, screening is oscillatory, with a wavelength which is eventually determined only by the ionic size. Typical values of x for molten salts near freezing at atmospheric pressure are of the order of 80, much larger than x_c.

The two screening regimes that we have just seen to exist in the present model fluid are related to an ionized-gas phase at low densities and to a liquid phase at high densities. This is borne out in Figure 2, where we report the equilibrium curve of the two phases in the pressure-volume plane as well as the locus of points (curve K) where k_s^2 changes sign. The equilibrium curve was determined by the usual Maxwell construction from the isotherms calculated from Eq. (3.1), which are seen to have the classical van der Waals shape with a critical point. Below the critical pressure, curve K runs within the region of densities that are excluded for a stable homogeneous phase, implying that the transition in screening behaviour will be met on crossing the interface between the liquid and the ionized gas, as the density changes from its value deep in the liquid to its value in the gas.

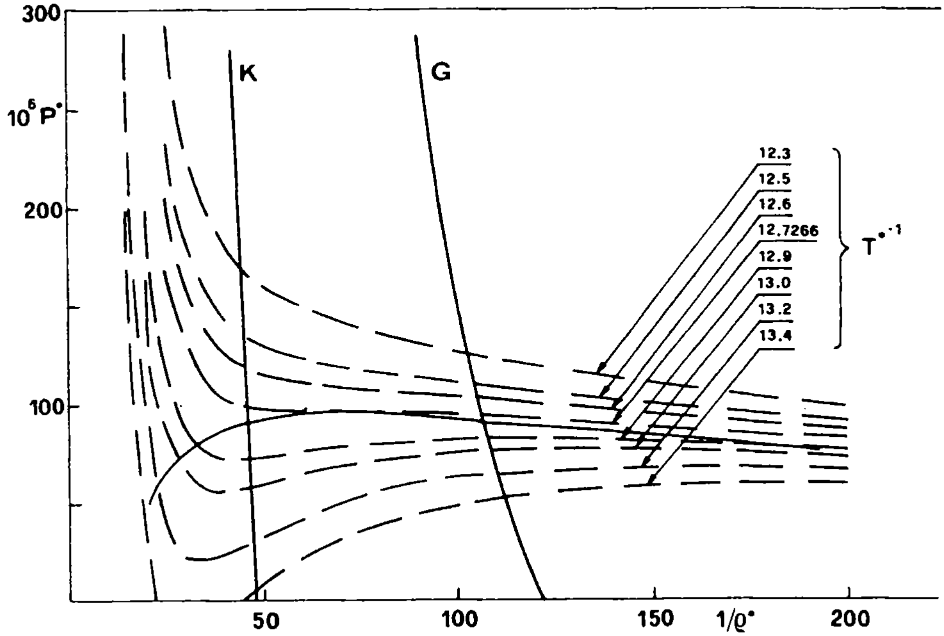

FIGURE 2 Isotherms (broken lines) and coexistence curve (full line) of the model. Curves K and G give, respectively, the locus of points where k_s^2 changes sign and the locus of points where oscillations in $g_q(r)$ appear.

Curve K crosses the equilibrium curve near the critical point of the model: we see no basic reason to expect the intersection to occur exactly at the critical point, although the difference may well be within the imprecision brought in by the mean spherical approximation. Above the critical pressure, the transition between the two screening regimes in the homogeneous fluid is, of course, continuous. On the low-density side of curve K, screening is very strongly local ($k_s \gg k_0$) but still consistent with the usual Debye–Hückel picture of Eq. (2.17), while on the high-density side of curve K a definite structuring of the screening cloud into shells of positive and negative ions has set in.

We report in Figure 2 also the locus of points (curve G) where the charge-charge radial distribution function $g_q(r)$,

$$g_q(r) = \frac{1}{(2\pi)^3 n} \int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{r}}[S_q(k) - 1], \qquad (3.6)$$

acquires long range oscillations. This function can be represented through a sum of exponentials with exponents determined by the poles of the Laplace transform[7] of $rg_q(r)$, and its asymptotic behaviour at large distance is

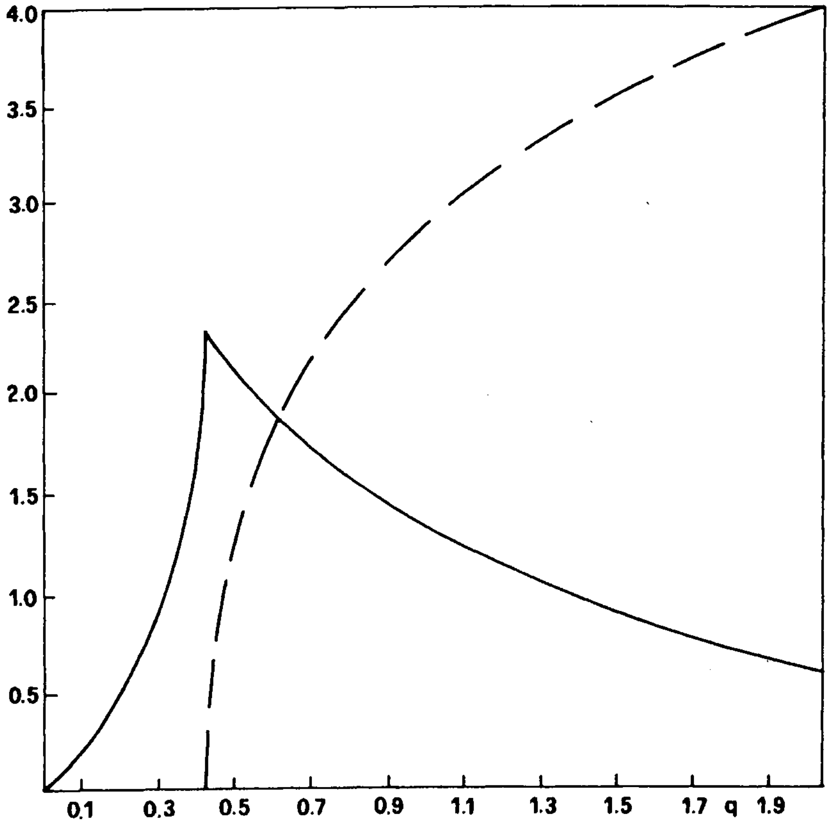

FIGURE 3 Negative of the real part (full line) and imaginary part (broken line) of the first pole in the Laplace transform of $rg_q(r)$, versus $q = \frac{1}{2}[\sqrt{1 + 2x} - 1]$.

determined by the pole having a real part which is closest to the imaginary axis. In fact, this pole is on the real axis for low values of x, but acquires an imaginary part at a critical value $x_c \simeq 1.2$, as shown in Figure 3. This transition corresponds to the onset of a structuring of the liquid around any given ion into shells of unlike and like ions. As seen in Figure 2, curve G lies on the low-density side of curve K, the discrepancy between the two curves being associated apparently, with the relevance of higher terms in the low-k expansion of $S_q(k)$ as k_s^2 becomes very large. Taken together, these two curves bracket the critical point of the model. Below the intersection with the equilibrium curve, curve G runs in the region of excluded densities, implying that the transition in behaviour of $g_q(r)$ will be met on crossing the interface between liquid and gas. The Fowler approximation[14] on the pair correlation functions across the interface is thus necessarily inappropriate in calculations of surface tension for charged liquids, as discussed exhaustively in recent work by Pastor and Goodisman.[15]

4 DISCUSSION

In this last section we wish to address ourselves to three main points, in an attempt to explore the relevance of the preceding discussion to the properties of the charged-hard-spheres fluid on one side, and to the behaviour of real ionic fluids on the other.

The first question has to do with the accuracy with which the approximate treatment of the charged-hard-spheres liquid in the mean spherical approximation (MSA) used in the preceding section predicts the location of its critical point (because of the MSA, there is no point in asking about critical indices). The presence of a critical point in this fluid was first reported by Stell *et al*[8] on the basis of various approximate equations of state, including one that had been deduced from a global fit of Monte Carlo simulation data.[16] In the reduced units adopted by these authors, $T^* = \varepsilon_\infty k_B T\sigma/e^2$, $\rho^* = 2n\sigma^3$ and $P^* = \varepsilon_\infty P\sigma^4/e^2$, the present calculation yields the critical point at $T^* = 0.079$, $\rho^* = 0.014$ and $P^* = 9.65 \times 10^{-5}$. Stell *et al.*[8] report two main sets of results, one obtained from the Monte Carlo equation of state and from some approximate expansions of the free energy, and the other obtained by refining the equation of state to give a better account of the second virial coefficient. The first set of results, with which ours should be compared, are $T^* = 0.078 \pm 5\%$, $\rho^* \sim 0.005 \div 0.02$ and $P^* \sim (4 \div 10) \times 10^{-5}$. Account of the second virial coefficient brings these values to their best estimates of $T^* = 0.085$, $\rho^* = 0.011$ and $P^* = 31 \times 10^{-5}$, the main effect clearly being a large increase in the critical pressure. We would thus conclude that the MSA yields good values of the critical temperature and density for the charged-hard-spheres fluid, and yields instead a value of the critical pressure that is too low when compared with the best available estimates.

The next question concerns the relevance of the results for a charged-hard-spheres fluid to predictions on the behaviour of real ionic fluids, typically the molten alkali halides, near and above the critical point. Two features of the model are clearly called in question: (1) the infinitely steep hard core repulsion, against the soft nature of the Born–Mayer repulsion in the real fluid; (2) the absence of electronic polarizability effects, that would favour molecular bound state at low densities and temperatures. Taking NaF as typical of alkali halides with nearly equal cation and anion radii, our results yield, with $\sigma \simeq 2$ Å and $\varepsilon_\infty \sim 2$, $T_c = 3300$ K, $\rho_c = 0.06$ g cm^{-3} and $P_c = 70$ atm. An estimate of the location of the critical point for several alkali halides has been given by Gillan[17] on the basis of a significant structures model, which in essence represents the partition function of the liquid as a superposition of partition functions for solid and gas. His values for NaF are $T_c = 4251$ K, $\rho_c = 0.213$ g cm^{-3} and $P_c = 361$ atm. The discrepancies between the two sets of results are uncomfortably large.

It is possible to correct the MSA results for a finite steepness of the repulsive interactions by allowing for a dependence of the ionic diameters on temperature and density.[18] While the dependence on density is at present unknown, the dependence on temperature at constant pressure has been determined[19] only in a narrow temperature range near freezing, through a fit of isothermal compressibility data. Reasonable extrapolations to higher temperatures show that this effect has a major influence on the coexistence curve and on the location of the critical point. Although we feel unable to present quantitative estimates at the present time, it appears that this effect could lead to values of the critical temperature, density and pressure for NaF that are in the region of Gillan's estimates reported above.

Let us, finally, comment briefly on the question of electronic polarizability. As we have stressed earlier, the charged-hard-spheres model describes the equilibrium between an ionic liquid and an ionized-gas phase, rather than a molecular gas phase. Well below the critical pressure or temperature, the alkali halide vapour consists of alkali halide molecules, whose binding derives to a significant extent[20] from induced ionic dipoles. Electronic polarization is thus very important for the gaseous phase, but not so relevant in the liquid phase[21] where structuring of the liquid into spherical ionic shells occurs around each ion.

The effect will thus be to stabilize the gaseous phase to higher densities, shifting the gas side of the equilibrium curve in Figure 2 towards the left and leading probably to higher values of ρ_c and P_c. Above but not too far from the critical point, the fluid presumably consists of a mixture of bound molecules and free ions in varying concentration, and it is interesting to ask whether a sudden transition in the structuring of the total charge density still occurs in these conditions. This question, as well as a refined study of the critical parameters and of the behaviour of a real ionic fluid above the critical point, ought to be tackled by computer simulation techniques with polarizable-ion models.

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