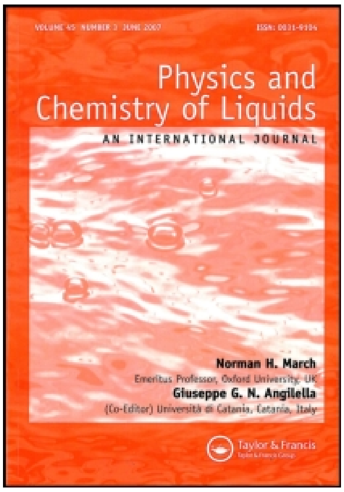

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Analysis of Liquid-Vapour Phase Transitions for Restricted Primitive Model of Ionic System in Mean Spherical Approximation

N. C. Tkachev[a]
[a] Institute of High-Temperature Electrochemistry of Russian Academy of Sciences (Ural Division), Ekaterinburg, Russia

To cite this Article Tkachev, N. C.(1996) 'Analysis of Liquid-Vapour Phase Transitions for Restricted Primitive Model of Ionic System in Mean Spherical Approximation', Physics and Chemistry of Liquids, 31: 2, 71 — 81
To link to this Article: DOI: 10.1080/00319109608029560
URL: http://dx.doi.org/10.1080/00319109608029560

Phys. Chem. Liq., 1996, Vol. 31, pp. 71–81
Reprints available directly from the publisher
Photocopying permitted by license only

ANALYSIS OF LIQUID–VAPOUR PHASE TRANSITIONS FOR RESTRICTED PRIMITIVE MODEL OF IONIC SYSTEM IN MEAN SPHERICAL APPROXIMATION

N. C. TKACHEV

Institute of High-Temperature Electrochemistry of Russian Academy of Sciences (Ural Division), S. Kovalevskaya str. 20, 620219 Ekaterinburg, Russia

(Received 3 May 1995)

Within the framework of MSA exact solution for charged hard spheres with equal diameters found by Waisman and Lebowitz for Coulomb part of free energy and Mansoori *et al.*, approximation for hard sphere contribution characteristics of evaporation phase transitions in terms of the equation of state have been estimated. The phase diagram has been evaluated and the behaviour of thermodynamic properties studied in a wide range of temperature and pressure for the example close to KF system. The position of the critical point is in accordance with the earlier determination of Telo da Gama, Evans and Sluckin using generalised MSA. Numerical values of the coefficients in the expansion of the relative deviation in pressure in powers of temperature and order parameter have been simply estimated near the critical region. Temperature and pressure dependencies of entropy and isothermal compressibility are typical enough for fluid systems, notwithstanding the collective nature of ionic interactions. In addition, the known Kauzman entropy paradox arises at low temperatures.

KEY WORDS: Restricted primitive model, mean spherical approximation, equation of state, evaporation, critical behaviour.

1 INTRODUCTION

The restricted primitive model (RPM) is the first meaningful model of an ionic system in which phenomena of mutual repulsion at short distances combined with Coulomb interaction of the ions are considered. It is not accidental that a number of theoretical and computer simulation studies has been devoted to the predictions and consequences of that model. RPM attracts a special attention, once Vorontsov-Vel'yaminov and Chasovskikh[1,2] and Stell, Wu and Larsen[3] (see also[4]) demonstrated the occurrence of liquid-vapour phase transitions. Also coexistence curve determinations have been carried out. In recent years significant progress was achieved in computer simulation estimations of RPM[5,6]. At the same time theoretical approaches have been evolved in which critical exponents for some simple variants of RPM were predicted, and the values established as classical or van der Waals ones. This phenomenon was suitably explained with the long-range acting character of the Coulomb tail of pair potential (see recent review of Fischer[7]). Models of Debye–Hückel type with

Bjerrum's modification show that the position of the critical point is surprisingly close to modern computer simulation studies. Detailed analysis of correlation function decay for GMSA RPM presented in[8] also confirms this mean-field picture. More complicated approximations based on the Poisson–Boltzmann equation reinforce these general points, at least for the order parameter behaviour[9].

The feasibility of the above problem, examined by means of an exact solution of mean spherical approximation (MSA) for charged hard spheres system, has demonstrated previously. As far back as 1972, Waisman and Lebowitz[10,11] deduced the Coulomb part of the RPM free energy according to MSA. Later Blum[12] succeeded in solving the problem in the general case of unequal sizes and charges by generalising Baxter's factorisation procedure. In Blum and Høye's work[13] it has been quoted that the general relations of the model could be applied either to aqueous electrolyte solutions or to ionic melts. Nonetheless, up to now a list of applications is full enough for the former class of ionic systems, whose thermodynamic behaviour (activity and osmotic coefficients) can be described by that theory up to concentrations about 1 mole/litre and even higher[14].

For molten salts partial structure factors mainly were investigated according to this model[15,16] and the numerical computations carried out by solving the Ornstein–Zernike equation system with MSA closure. Though these authors used a liquid salt density as a parameter that was adjusted to the experimental data, since low-angle scattering functions were expressed in terms of compressibility. This approach matches aqueous electrolyte solutions behaviour to a greater extent, because of the concentration of charged particles in a mixture.

Telo da Gama *et al.*,[17] (see also[8]) performed the phase diagram calculation in terms of the generalised MSA and showed a reasonable picture in T–ρ plane corresponding to numerical values of critical parameters lying between the earlier prediction of Stell, Wu and Larsen[3] and the more recent computer simulation of Valleau[6]. However[17], was dedicated to a molten salt surface to a greater extent, and further considerations[8] have been concerned primarily with correlation function behaviour for this model. Some traditional thermodynamic applications were not pursued however by these authors. Besides, detailed analysis of the evaporation problem has not been carried out, especially using the equation of state although this model probably gives the most convenient analytical representation of the thermodynamic properties important for the practical problems.

Therefore, the aims of the present work are, first of all, to present a more detailed analysis of the evaporation problem according to the MSA RPM treatment by the Mansoori *et al.*,[18] approximation for hard sphere part of the fluid free energy including determination of nearby critical behaviour of the equation of state. Secondly, we shall estimate some important properties over a wide range of temperature and pressure, and shall discuss some quantitative aspects of MSA ionic system describing low temperature liquid phase thermodynamics as applied to alkali halide melts. In doing so, thermodynamic calculations are supplied for such properties as enthalpy, heat capacity at constant pressure and their dependence on pressure and temperature along the coexistence curve. Temperature dependence of entropy and isothermal compressibility for different pressures is also studied.

2 CHARGED HARD SPHERES RESTRICTED PRIMITIVE MODEL: THERMODYNAMICS

Waisman and Lebowitz[10,11] found a closed form for the Coulomb contribution in direct correlation functions and Helmholtz free energy and showed that the low-density limit coincided with the Debye–Hückel's theory of strong electrolytes at small concentrations. The MSA used in these studies is the closure of the Ornstein–Zernike equations by explicit expressions for direct correlation functions in the range of distances more than hard sphere diameters:$C_{ij}(R) = -Z_iZ_je^2/\varepsilon kTR^{-1}$, $R > d_{ij}$, where $Z_{i(j)}$ are values of ionic charges, e- electron charge, ε -dielectric constant of the medium, in which ions embedded, k- Boltzmann constant, T- absolute temperature. Pair distribution functions are equal to zero $g_{ij}(R) = 0$ for $R < d_{ij}$. For the RPM variant of the theory $d_{ij} = d$, where d is the only parameter characterising hard sphere repulsion at short distances, and charge values $Z_1 = -Z_2$ with magnitude equal to unity anywhere below.

The expression for the Coulomb part of the Helmholtz free energy per ion can be reduced to the following form (see, for example[11,13,19]):

$$\Delta F_{ch} = -\frac{e^2}{\varepsilon}\Gamma\frac{2+3\Gamma d}{(1+\Gamma d)^2}, \tag{1}$$

where Γ is the parameter of the inverse length defining the screening scale in the system at a given temperature and density. Blum has generalised this model to unequal sizes and charges of the constituent ions and has shown that Baxter's factorisation of the Ornstein–Zernike equation system leads to an algebraic equation relating Γ and density[12], namely $\Gamma^2 = \kappa_D^2 \sum_i X_i(Z_i^*)^2$ with $\kappa_D = \sqrt{4\pi e^2\rho/\varepsilon kT}$, where $\rho = N/V$ is numerical density and κ_D–the Debye inverse screening length x_i–ions' relative concentrations in binary system (in this event it is determined by electroneutrality condition, i.e. $x_i = 1/2$). It is convenient to follow Blum's formulation, because the expression for the screening characteristic of dense fluid includes only charge values "renormalization" (Z_i^*) regarding Debye's low-density limit. In the case of equal diameters the screening parameter becomes the root of a quadratic equation, namely:

$$\Gamma = (2d)^{-1}[\sqrt{1+2d\kappa_D} - 1]. \tag{2}$$

The Coulomb terms into internal energy and entropy are equal to

$$\Delta E_{ch} = -\frac{e^2}{\varepsilon}\Gamma(1+\Gamma d)^{-1} \quad \text{and} \quad \Delta S_{ch} = -k\frac{\Gamma^3}{3\pi\rho}. \tag{3}$$

Hence, if one chooses some approximation for the hard sphere part of the ionic system free energy, it would be conceivable to acquire one and all thermodynamic properties of interest. In the present work the approximation of Mansoori *et al.*,[18] has been applied for this purpose, because this approach is best suited to the computer simulation data for binary mixture of hard spheres with arbitrary diameter ratio. The excess Helmholtz free energy concerning the ideal gas in this approximation is the following:

$$\Delta F_{hs} = kT\frac{\eta(4-3\eta)}{(1-\eta)^2}, \quad \text{with} \quad \eta = a\rho \quad \text{and} \quad a = \frac{\pi}{6}d^3. \tag{4}$$

The excess entropy is simply equal to $\Delta S_{hs} = -\Delta F_{hs}/T$. The hard sphere term in the pressure of the system with equal diameters coincides with Carnahan–Starling formula. Thus the pressure expression for RPM under these approximations is as follows:

$$\frac{P}{kT} = \frac{\eta}{a}\left(\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}\right) - \frac{\Gamma^3}{3\pi}. \tag{5}$$

Using thermodynamics for heat capacity at constant volume one obtains:

$$c_v = \frac{3}{2}k + kd^3\frac{\Gamma^3(1+\Gamma d)}{12\eta(1+2\Gamma d)}, \tag{6}$$

since the hard sphere contribution to this quantity equals to zero. The isothermal compressibility χ_T is given by

$$\chi_T = \eta^{-1}\left(\frac{\partial\eta}{\partial P}\right)_T = (\eta kT)^{-1}\left[\frac{(1+2\eta)^2-\eta^3(4-\eta)}{a(1-\eta)^4} - \frac{\Gamma^3(1+\Gamma d)}{2\pi\eta(1+\Gamma d)}\right]^{-1}. \tag{7}$$

Likewise, one can derive for the isobaric bulk modulus:

$$\alpha_P = \eta^{-1}\left(\frac{\partial\eta}{\partial T}\right)_P = k\chi_T\left(\frac{P}{kT} + \frac{\Gamma^3(1+\Gamma d)}{2\pi(1+2\Gamma d)}\right), \tag{8}$$

and the heat capacity at constant pressure can be rewritten according to the familiar thermodynamic relation[20]: $c_P = c_V + (T/\rho)(\alpha_P^2/\chi_T)$.

To conclude this section we consider the high-temperature limit. As $T \to \infty$, $\eta \to 0$, from (3) one obtains $\Gamma \to \kappa_D/2$. Solving the resulting cubic equation with respect to the packing fraction gives rise to a branching point of three roots at infinite temperature, so it is necessary to select the only one matching the ideal gas asymptote, namely:

$$\eta \cong \frac{aP}{kT}\left(1 + x + \frac{1}{4}x^2 + \ldots\right) \quad \text{with} \quad x = \frac{\pi^{1/2}e^3P^{1/2}}{3\varepsilon^{3/2}(kT)^2}. \tag{9}$$

Isothermal compressibility, bulk modulus and heat capacities at constant volume and pressure vanish with increasing temperature too:

$$\begin{gathered}\chi_T \cong P^{-1}\left(1 + \frac{1}{2}x - \frac{1}{4}x^2 + \ldots\right), \quad \alpha_P \cong T^{-1}(1 + 2x - x^2 + \ldots), \\ c_V \cong \frac{3}{2}k\left(1 + x + \frac{1}{2}x^2 + \ldots\right), \quad c_P \cong \frac{5}{2}k + 4kx - \frac{3}{2}x^2 + \ldots\end{gathered} \tag{10}$$

At very high temperatures the theory must involve ions' excitations and this contribution has to be inserted into internal statistical sums of the constituent ions in explicit form. The examination carried out below deals with the solely non-degenerate energy ionic level, i.e. any ion still remains on the ground state at any temperature and pressure, and the internal sum over states is reduced to the Boltzmann factor. That is why we use energy quantities with reference to the cation and anion energies on the ground state.

3 ANALYSIS OF LIQUID-VAPOUR PHASE TRANSITIONS

In the theories of van der Waals' type, the contribution to the pressure relating to the attraction between particles depends on the square of the density, while the proportionality coefficient is independent on temperature, and evaporation takes place in this case. For charged hard spheres the "attractiveness", being represented as a contribution to the pressure with the opposite sign to that of hard spheres, arises indirectly from the Coulomb tail of the pair potential, but it displays a particular statistical mechanical effect due to the phenomenon of short-range structure forming in the fluid and it leads to evaporation in the same way.

It is convenient to approach the evaporation properties from an assessment of the critical point location. As at the critical point distinction between liquid and vapour disappears, and the densities of both phases are exactly the same with isothermal compressibility tending to infinity, ordinary definition of zero values of the first and the second derivatives of pressure with respect to density can be used. This leads to the following system of equations for critical temperature and density (value of critical pressure is computed later using the equation of state):

$$\begin{cases} \dfrac{(1+2\zeta)^2-\zeta^3(4-\zeta)}{(1-\zeta)^4}-\dfrac{\lambda^3(1+\lambda)}{12\zeta(1+2\lambda)}=0 \\ \dfrac{2+5\zeta-\zeta^2}{(1-\zeta)^5}-\dfrac{\lambda^3(1+\lambda)^2[1-2\lambda^2]}{6\zeta^2(1+2\lambda)^3}=0 \end{cases}, \tag{11}$$

where $\zeta \equiv \eta_c$ and $\lambda \equiv \Gamma_c d$ are the critical values of packing fraction and the inverse screening length. Numerical compilations confirm that (11) has a unique solution in the physically reasonable range of parameters.

Estimation of evaporation temperature and density drop between both coexisting phases at pressure lower than the critical involves solving the three equation system:

$$\begin{cases} F_{\mathrm{chs}}(T_e,\eta_L)-F_{\mathrm{chs}}(T_e,\eta_G)=aP_0(\eta_G^{-1}-\eta_L^{-1}) \\ P_{\mathrm{chs}}(T_e,\eta_L)=P_0 \\ P_{\mathrm{chs}}(T_e,\eta_G)=P_0, \end{cases} \tag{12}$$

where the first is the equality of Gibbs free energies of both phases; the second and the third reflect mechanical equilibrium at a given pressure P_0. The above proposition must be resolved for designated $P_0 < P_c$ concerning T_e, η_L and η_G.

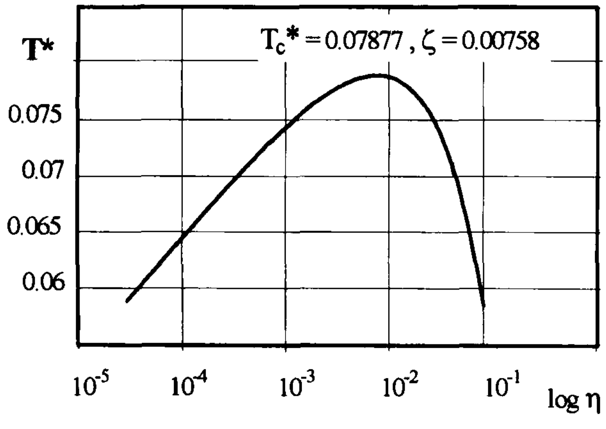

Figure 1 Liquid-vapour phase diagram calulated for MSA RPM.

We next discuss the critical behaviour. For this purpose the equation of state in the critical region can be stated as usual: $\Delta p = A\Delta t + B\Delta t\Delta\eta + C\Delta\eta^3 + \ldots$, here $\Delta_p = (P - P_c)/P_c, \Delta t = (T - T_c)/T_c, \Delta\eta = (\eta - \eta_c)/\eta_c$ and coefficients in the expansion of correspondent pressure deviations from the critical one in powers of relative changes of temperature and packing fraction are equal to

$$A = 1 + \frac{\lambda^3(1+\lambda)}{2\pi P_c^*(1+2\lambda)}, \quad B = \frac{\lambda^3(1+\lambda)(3+8\lambda+6\lambda^2)}{4\pi P_c^*(1+2\lambda)^3},$$

$$C = \frac{1}{\pi P_c^*}\left[12\zeta^3\frac{5+6\zeta-\zeta^2}{(1-\zeta)^6} + \frac{\lambda^3(1+\lambda)(1+12\lambda+16\lambda^2-12\lambda^3-20\lambda^4)}{48(1+2\lambda)^5}\right].$$

The classical type of equation of state in the critical region provides the means to find "macroscopic" critical indices β, γ and δ at once, with values 0.5, 1 and 3, respectively. Though the expansion coefficients differ from those predicted by van der Waals theory, critical behaviour of both models is identical. It is important to note that the coefficients (16) are independent of diameter, charge and dielectric constant and their numerical values are $A = 13.474$, $B = 13.228$ and $C = 0.271$ ($\zeta = 0.00758$, $\lambda = 0.5054$). Curiously, the coefficient C has a rather small value and may be some modification of the theory would lead to its vanishing completely in order to yield a non-classical equation of state. Such formulation suggests that the next term in the expansion will be at least of fifth order in $\Delta\eta$, so exponent δ possibly may have the magnitude of 5, and thus may be close to the magnetic material spherical model.

This prediction of the critical parameters is in complete agreement with the calculations of Telo da Gama *et al.*,[17] in spite of different initial approximation for the direct correlation functions. Figure 1 represents the phase diagram of liquid-vapour in the $T^* - \eta$ plane on logarithmic scale. Figure 2 shows the coexistence curve confining at T_c^*, P_c^* in the P–T plane. The location of the critical point is

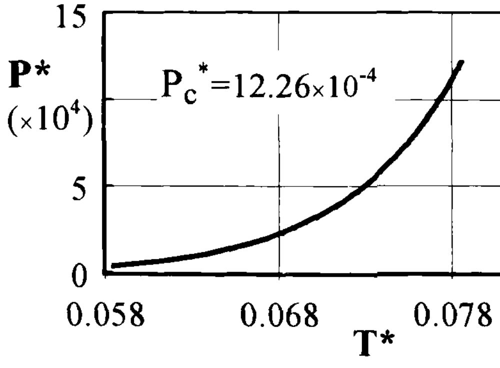

Figure 2 Evaporation pressure dependence upon temperature along the liquid-vapour coexistence curve.

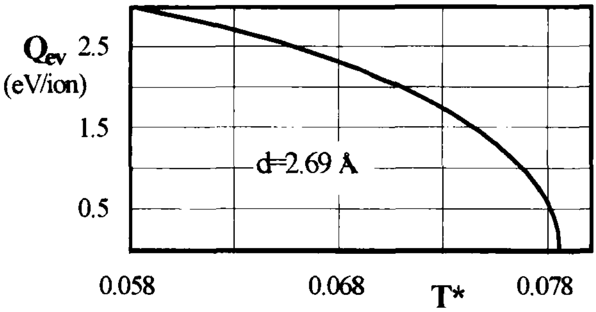

Figure 3 Vapour to liquid enthalpy change along curve of first order phase transitions for example with $d = 2.69$ Å(KF). It is well seen that square root behaviour nearby critical point corresponding to classical order parameter exponent.

associated with the critical density $\rho_c d^3 = 0.01448$, temperature $T_c^* = d\varepsilon kT_c/e^2 = 0.07877$ and pressure $P_c^* = P_c d^3/kT_c = 12.26 \times 10^{-4}$.

To draw an example roughly corresponding to KF ($d = 2.69$Å) liquid to vapour enthalpy change along the coexistence curve below critical point is shown in Figure 3.

Heat capacities at constant pressure, isobaric bulk modulus and isothermal compressibility diverge in the critical region with exponent γ. Figure 3 shows such irregularity for heat capacity at constant pressure. Heat capacity at constant volume differs slightly from the van der Waals one only by the drop magnitude of the former that is obviously equal to zero at the critical point. For the latter, as is accepted[21], over-critical vapour phase is the ideal gas by itself, and this change is equal to $9/2k$. Nevertheless, the critical exponent $\alpha = 0$ for both models.

Macroscopic scaling assumptions alone provide no possibility to find "microscopic" exponents specifying radial distribution function and structure factor behaviour. For its estimation it is necessary to review the order parameter spatial fluctuations[20]. By taking into account only the long-wave fluctuations contributing the main part of the "singular" term in the free energy functional, as expected in

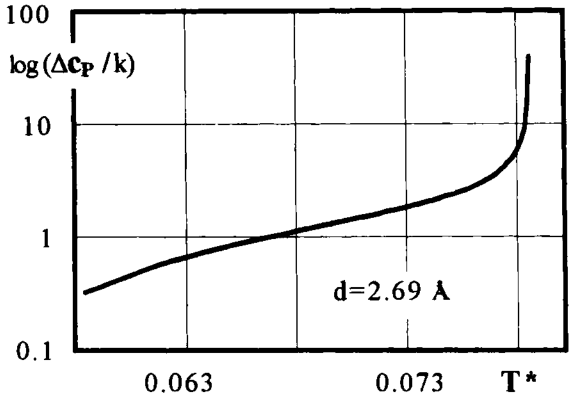

Figure 4 Vapour to liquid change of heat capacity at constant pressure along curve of first order phase transitions for example with $d=2.69$ Å(KF). Scale on y-axis is logarithmic.

Ginzburg–Landau theory, the distribution of these fluctuations can be found. Then, the correlation function at large distances has the typical Ornstein–Zernike form: $g(R)\approx R^{-1}\exp(-R/R_c)$, where radius of correlations $R_c\approx(2\Gamma_c)^{-1}(-2B\Delta t)^{-1/2}$, so the exponent ν has the value of 0.5. One might compare it with the detailed depiction of the decay GMSA correlation functions presented in Ref. 8.

4 TEMPERATURE AND PRESSURE DEPENDENCES OF THE THERMODYNAMIC PROPERTIES

A look at the thermodynamic properties' behaviour in a wide temperature and pressure range is of specific interest, because it allows one to examine the problems of building up a quantitative theory of fluid salt systems. Recently, a number of studies have been performed on the successful exploration of MSA charged hard spheres in aqueous electrolyte solutions up to very high concentrations[14], for which thermodynamic self-consistency connected with equation of state becomes important as well. Thus, it also has to be cleared up what one could expect from the theory in the density regions that cannot be attained in aqueous solution, but directly relating to ionic melts.

The results of estimation for entropy and isothermal compressibility are presented in Figures 5 and 6 for temperatures up to 6000 K and five different pressures from 1 to 450 atm (up to $\approx 10P_c$). The computations have been accomplished by means of numerical procedure of solving the equation of state concerning packing fraction. Newton method with initial quantities of relative density computing at the previous step on temperature was used. The magnitude of the step was 10 K, packing fraction value starting the procedure for the liquid phase has been set up equal to 0.45 and for the vapour one has been determined from solving of the evaporation topic.

Thermodynamic characteristics supplied on these figures demonstrate representative depiction of fluid systems as a whole. Some peculiarities are outlined by signifi-

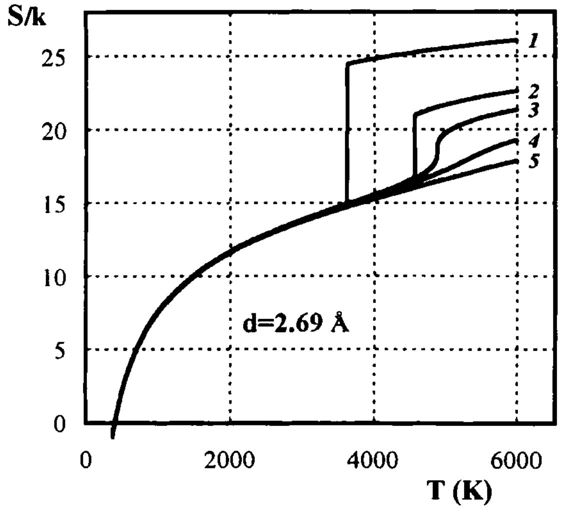

Figure 5 Entropy dependence on temperature for five different pressures. Digits near the curves related to the values of pressure equal to 1, 18, 43, 150 and 450 atm.

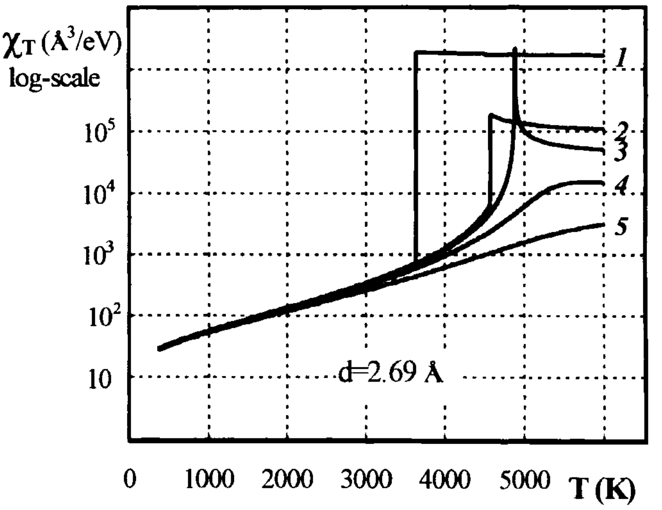

Figure 6 Isothermal compressibility dependence on temperature for five different pressures. Notations for digits are the same as on Figure 4. Specified singularity (with $\gamma = 1$) at P near P_c is well seen.

cant magnitude of the Coulomb interaction acting in the fluid. The model predicts some lower values on density. For example, at normal pressure near-melting packing fractions (≈ 0.45) correspond to temperatures of about 500 K. From our viewpoint it relates to the absence of interactions due to ion-dipole forces acting between the ions proportional to $-R^{-4}$, and also with dielectric properties of such fluids. These forces must contribute to the equation of state the term describing some compression, and probably it should lead to a near-quantitative explanation of the alkali halide fluids' behaviour. At the same time, the introducing of ions' permittivities and sizes' mismatch should breaks the corresponded states law.

As is confirmed, a model of this type (with isotropic radial distribution function) cannot give any phase transition into the crystal phase, though it is capable to show a boundary of liquid phase absolute instability. Indeed, Figure 5 illustrates an argument based on the known paradox found by Kauzman (see for example[22]). At low temperatures the heat capacity sharply increases as the temperature goes to zero, that is entropy reduces across zero point (magnitude of ideal crystal) to negative values. Therefore, such system must either crystallise or freeze the configuration with topological properties of liquid, i.e., it has to be turned into glass by itself. The above behaviour could be possibly related to specified failings of MSA charged hard spheres remarked on in[8,17] regarding the determination of pair distribution functions, although it is not obvious, since the Kauzman paradox has the universal character for any undercooled liquid.

5 CONCLUSION

Inasmuch, because critical behaviour of this model corresponds to classical theories of van der Walls–Landau type, it might be concluded that the main basis of such picture resides in the existence of infinite radius of pairwise interaction. Situation in this sense looks like the issue for fluid of hard spheres plus attraction of exponential form, and for this event in one-dimensional case Kac, Uhlenbeck and Hemmer (see, for example[21]) have found the exact statistical integral and showed the total identity to the van der Waals theory combined with Maxwell construction. Most likely, an effective pair potential determined in Debye–Hückel theory of electrolyte for charged hard spheres is close to the exponential form at least for long distances. As a consequence, it guides to the realisation of the above scenario about classical peculiarity of the equation of state for charged hard spheres in the critical region.

Concerning the quantitative side of the results presented, the following may be noted. Taking into account Coulomb interaction makes possible to reduce the difference between theory and experiment compared with the simple hard sphere model. For example, in hard sphere systems predicted density values characterising a liquid close to melting temperature at normal pressure can be achieved only at temperatures near 0.1 K. Thus, the charging process yields an increase of these temperatures up to a few hundred degrees, at the same time melting temperatures of salt systems like alkali halides are much higher. Hence, for obtaining quantitative accordance of thermodynamic properties' predicted by the theory with experiment it is necessary to consider the succeeding terms in the expansion of the electrostatic energy of the ions in powers of the inverse length affected by ionic polarizability in a dielectric formalism.

In our opinion there are two possibilities for improvements on the results presented here . First, to start from a more sophisticated pair potential form and to solve in the spirit of the initial work of Blum[12], or secondly, to use the MSA charged hard spheres system as a reference for perturbative calculations.

It is important to stress another important problem. The above analysis refers to the case of vacuum static dielectric constant. The approach to the problem would be more correct by introducing a step function of dielectric constant depending on distance. That is the first corresponding to internal dielectric permittivity of the ion, and the second related directly to the fluid structure forming phenomenon, for example in terms of Onsager equation[23]. May be this is the way to achieve the Ising universality class for certain ionic systems, at least in the case of liquid-liquid phase coexistence?

References

1. P. N. Vorontsov-Vel'yaminov and V. P. Chasovskikh, *High Temp. Phys.* (USSR) **13**, 1071 (1975) (in Russian).
2. V. P. Chasovskikh and P. N. Vorontsov-Vel'yaminov, *High Temp. Phys.* (USSR) **14**, 174 (1976) (in Russian).
3. G. Stell, V. C. Wu and B. Larsen, *Phys. Rev. Lett.*, **37**, 1369 (1976).
4. I. R. Yukhnovsky and M. F. Golovko, *Statistical Theory of Classical Equilibrium Systems* (Naukova Dumka, Kiev, 1980), Chap. 3, pp. 110–199 (in Russian).
5. G. Orcoulas and A. Z. Panagiotopoulos, *J. Chem. Phys.*, **101**, 1453 (1993).
6. J. P. Valleau, *J. Chem. Phys.*, **95**, 584 (1991).
7. M. E. Fischer, *J. Stat. Phys.*, **75**, 1 (1994).
8. R. J. Leote de Carvalho and R. Evans, *Molec. Phys.*, **83**, 619 (1994).
9. E. Gonzalezl-Tovar and C. W. Outhwaite, *Molec. Phys.*, **83**, 1273 (1994).
10. E. Waisman and J. L. Lebowitz, *J. Chem. Phys.*, **56**, 3086 (1972).
11. E. Waisman and J. L. Lebowitz, *J. Chem. Phys.*, **56**, 3093 (1972).
12. L. Blum, *Molec. Phys.*, **30**, 1529 (1975).
13. L. Blum and J.S. Høye, *J. Phys. Chem.*, **81**, 1311 (1977).
14. W. Sheng, N. Kalogerakis and P. R. Bishnoi, *J. Phys Chem.*, **97**, 5403 (1993).
15. A. H. Abramo, C. Caccamo, G. Pizzimenti, M. Parinello and M. Tosi, *J. Chem. Phys.*, **68**, 2889 (1978).
16. J. Boronat and M. Silbert, *Phys. Chem. Liquids*, **27**, 123 (1994).
17. M. M. Telo da Gama, R. Evans and T. J. Sluckin, *Molec. Phys.*, **41**, 1335 (1980).
18. G. A. Mansoori, N. F. Carnahan, K. E. Starling and T. W. Leland, *J. Chem. Phys.*, **54**, 1523 (1971).
19. K. Hiroike, *Molec. Phys.*, **33**, 1195 (1977).
20. L. D. Landau and E. M. Lifshitz, *Statisticheskaya Fizika* (Nauka, Moscow, 1976), Chap.14, pp. 486–560 (in Russian).
21. R. Balescu, *Equilibrium and Non-Equilibrium Statistical Mechanics* (MIR, Moscow, 1978), Part. 1, Chap. 9, pp. 322–354 (in Russian).
22. S. M. Stishov, *Uspekhi Fizicheskikh Nauk*, **159**, 93 (1988) (in Russian).
23. F. Stillinger, *Fused Salts*, ed. by B. R. Sundheim (MIR, Moscow, 1966), Chap. 2, pp. 76–184 (in Russian).