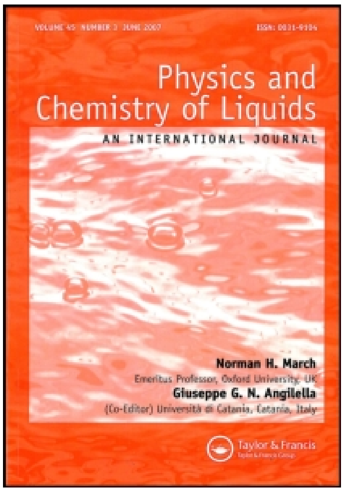

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Critical Behaviour of Monatomic and Symmetric Charged Liquids in Approximate Theories of Structure

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A **k** space analysis of the hypernetted chain (HNC) theory of a monatomic liquid is presented for d dimensions. Assuming the existence of a critical point, the total correlation function is shown to have long-range behaviour proportional to $r^{-2d/3}$ for short-range interactions.

The case of a symmetric charged liquid is then considered in HNC theory and in another approximate treatment of higher-order correlation functions. The number-number structure factor as $k \to 0$ can diverge in both approximate theories whereas the charge-charge structure factor exhibits Debye–Hückel behaviour.

The critical ratio $(pV/RT)_{n_c,T_c}$ is reduced from the superposition approximation value of 1/2 in the monatomic fluid, while in the charged fluid the 'correction' to 1/2 involves both number-number and charge-charge correlation functions.

1 INTRODUCTION

Whereas scaling and renormalization arguments have given a number of results which appear to be universal for short-range forces for liquid-vapour critical phenomena, interest has been moving back towards the predictions of the statistical mechanical hierarchy.[1-3] In this context, doubts have been expressed as to the universality of the critical exponent η in the long-range decay of the total correlation function $h(r) = g(r) - 1$ as $r^{-(1+\eta)}$ for three dimensions.[4]

Our purpose in the present paper is first to consider the critical exponent η in d dimensions from the hypernetted chain (HNC) theory of structure, and secondly to treat a symmetric charged liquid at the critical point. In this latter

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case, we have considered not only the HNC theory but also another approximate treatment of higher-order correlation functions. In addition to the treatment of the critical exponent η, we have studied the way in which the critical ratio $(pV/RT)_{n_c, T_c}$, n_c and T_c being the critical density and temperature respectively, depends on the approximations adopted in the three-particle terms.

2 HYPERNETTED CHAIN THEORY OF MONATOMIC FLUID

The hypernetted chain equation[4,5] reads

$$h(r) = -1 + \exp[-u(r) + h(r) - c(r)] \tag{2.1}$$

where $u(r)$ is the pair potential $\phi(r)$ written in units of $k_B T$ and $c(r)$ is the Ornstein–Zernike direct correlation function. Taking the gradient of Eq. (2.1), and using $h(r)$ as expressed there, one can write

$$\nabla c(r) = -[1 + h(r)]\nabla u(r) + h(r)\nabla[h(r) - c(r)]. \tag{2.2}$$

This Eq. (2.2) is now in a form suitable for Fourier transform, the result being

$$h(k) = \frac{p(k) + q(k)}{1 - p(k) - q(k)} \tag{2.3}$$

where

$$p(k) = -n \int d\mathbf{r}\, \frac{i\mathbf{k} \cdot \nabla u(r)}{k^2} [1 + h(r)] \exp(i\mathbf{k} \cdot \mathbf{r}) \tag{2.4}$$

and

$$q(k) = n \int d\mathbf{r}\, \frac{i\mathbf{k} \cdot \nabla}{k^2} [h(r) - c(r)] h(r) \exp(i\mathbf{k} \cdot \mathbf{r}), \tag{2.5}$$

n being the number density. In Eqs. (2.3)–(2.5), the integrals are d-dimensional.

2.1 Finite range, or exponentially decaying, potentials

To make progress, let us assume that $u(r)$ has a finite range, or an exponential decay. In these cases, $p(k)$ in Eq. (2.4) has a Taylor expansion about $k = 0$ in even powers of k. Thus, all non-analytic behaviour in $h(k)$ at small k at the critical point must come from $q(k)$ in Eq. (2.5). It is useful to rewrite Eq. (2.5) in terms of $h(k)$ and $c(k)$ as

$$q(k) = (2\pi)^{-d} n^{-1} \int d\mathbf{q} \frac{\mathbf{k} \cdot \mathbf{q}}{k^2} [h(q) - c(q)] h(|\mathbf{q} - \mathbf{k}|) \tag{2.6}$$

where

$$h(q) = n \int d\mathbf{r}\, h(r) \exp(i\mathbf{q} \cdot \mathbf{r}) \quad \text{etc.} \tag{2.7}$$

We shall assume, in studying the analytic structure of $q(k)$ at small k, that the integral in Eq. (2.6) is dominated by the small q behaviour[6] of the correlation functions. Assuming as a trial form of $h(q)$, the Ornstein–Zernike behaviour

$$h(q) \propto \frac{1}{q^2 + \lambda^2} \tag{2.8}$$

the contribution of $c(q)$ being unimportant at small q, the integration in Eq. (2.6) can be performed by inserting Eq. (2.8), yielding at the critical point where $\lambda \to 0$, a non-analytic term of the form k^{d-4} in $q(k)$. If $d > 6$, this form does not change the behavior of $h(k)$ in Eq. (2.3) and (2.8) at small k, provided some conditions are fulfilled. These amount to the vanishing of the denominator at $k = 0$ in Eq. (2.3):

i.e.
$$1 - p(0) - q(0)|_{n_c, T_c} = 0. \tag{2.9}$$

We turn to the more interesting, non-classical case of $d < 6$. Here we take as a trial function for $h(k)$ the power law $k^{\eta-2}$. This yields for small k

$$h(k) = \left. \frac{p(0) + q(0) + q_s k^{d-2(2-\eta)} + 0(k^2)}{1 - p(0) - q(0) - q_s k^{d-2(2-\eta)} + 0(k^2)} \right|_{n_c, T_c} \tag{2.10}$$

where $q(0)$ is the k-independent part of $q(k)$. The conclusion is that it is possible to have the behaviour proportional to $k^{\eta-2}$ if

$$d - 2(2 - \eta) > 0 \tag{2.11}$$

if Eq. (2.9) is satisfied with $q(0)$ now identified with $q(k = 0)$ and one obtains

$$\eta = 2 - \frac{d}{3} \tag{2.12}$$

For $d = 3$, evidently $\eta = 1$, and this is the same long-range behaviour of $h(r)$ as found using directly the superposition approximation.

The prediction that $\eta = 1$ in three dimensions from Eq. (2.12) is not compatible with the low values[7] of η, in the range $0.03 < \eta < 0.06$. In two dimensions, the correct result from the Ising model is $\eta = 1/4$, again in strong disagreement with the value of 4/3 predicted by Eq. (2.12). Also, the dimensionality distinguishing classical from non-classical behaviour is known to be $d = 4$, not $d = 6$ as predicted by the HNC theory.[4,8]

The value of pV/RT at the critical point can be obtained explicitly from Eq. (2.9), where $p(0)$ is directly related to the virial pressure. The result is

$$\left(\frac{pV}{RT}\right)_{n_c, T_c} = \frac{1}{2} - \frac{q(0)}{2} \tag{2.13}$$

where

$$q(0) = \frac{n}{d}\int \mathrm{d}r\, h(r) r \frac{\mathrm{d}}{\mathrm{d}r}[h(r) - c(r)]. \tag{2.14}$$

The value of 1/2 in Eq. (2.13) is characteristic of the superposition approximation[9]; the 'correction' $q(0)/2$ being the characteristic feature of the HNC theory.

In early work of Levesque,[10] the HNC equation was solved numerically for a square well interaction as well as for a Lennard-Jones potential. The predictions corresponding to Eq. (2.13) were respectively 0.42 ± 0.03 and 0.38 ± 0.04. These values show that the 'correction' $q(0)/2$ to the superposition value is ~ 0.1. It is worth remarking that the recent measurements of pV/RT at the critical point of liquid Hg (N. E. Cusack: private communication) give a value of about 0.38. This is the highest value we can find of all systems so far studied experimentally.

Finally, for short-range potentials, it is of some interest to discuss the coefficient D in the asymptotic form

$$h(r) \sim \frac{D}{r^{d-2+\eta}} = \frac{D}{r^{2d/3}}. \tag{2.15}$$

Using Eq. (2.10) one finds a relation between $h(k)$ at small k and the non-analytic term $q_s k^{d-2(2-\eta)}$, the result being

$$D^3 = \frac{d}{3}\Gamma\left(1 + \frac{d}{3}\right)\Gamma\left(\frac{2d}{3}\right)\frac{\sin\{\pi d/6\}}{n^2 \pi^{d+1}} \tag{2.16}$$

which reduces to the result of Green[4] for the case $d = 3$. This yields a positive value of D for all $d < 6$, in contrast to the superposition approximation which gives negative D. Fisher[11] has argued that D should be positive.

2.2 Long-range inverse power potentials

We consider now a pair potential $\phi(r) \sim \text{const}/r^{d+\sigma}$ where the constant should be negative to simulate attractive forces at long range. The potential enters only $p(k)$ in Eq. (2.4) and $p(k)$ can contribute a non-analytic term of the type k^σ as the leading contribution. For $\sigma > 2$, this does not affect the analysis presented in Section 2.1. When $\sigma < 2$, this term affects the argument and a new borderline dimensionality $d = 3\sigma$ between two different behaviours results. For $d > 3\sigma$, one simply obtains

$$\eta = 2 - \sigma \tag{2.17}$$

while for $d < 3\sigma$ one finds the result (2.12).

3 HYPERNETTED CHAIN THEORY OF SYMMETRIC CHARGED FLUID

Below we shall extend the foregoing considerations to a binary fluid of charged particles interacting via a Coulomb potential with Fourier transform proportional to k^{-2} in d-dimensions, supplemented by a short-range repulsive potential ($1 \leq d$). The motivation is to examine the effects of the Coulomb interactions on the critical behaviour of such a fluid. We do this on the simplest model of a binary charged fluid, namely a 'symmetric' system of positive and negative ions which are identical except for the sign of their charges.

The most direct description of particle density fluctuations in this symmetric model, which allows direct contact to be made with the results for a monatomic liquid presented in the preceding section, is through the total number density fluctuations and the charge density fluctuations.[12] These are defined by

$$N(\mathbf{r}) = n_1(\mathbf{r}) + n_2(\mathbf{r}) \tag{3.1}$$

and

$$Q(\mathbf{r}) = n_1(\mathbf{r}) - n_2(\mathbf{r}) \tag{3.2}$$

respectively, in terms of the densities $n_1(\mathbf{r})$ and $n_2(\mathbf{r})$ of positive and negative ions. The interaction potentials, in units of $k_B T$, are

$$u_{11}(r) = u_{22}(r) = u(r) + u_c(r) \tag{3.3}$$

and

$$u_{12}(r) = u(r) - u_c(r) \tag{3.4}$$

where $u(r)$ is the short-range repulsion and $u_c(r)$ the Coulomb potential. In terms of these potentials and of the total and direct correlation functions for the density variables (3.1) and (3.2), the equations of the HNC theory can be written as

$$c_{NN}(r) = -u(r) + h_{NN}(r) - \tfrac{1}{2}\{\ln[1 + h_{NN}(r) + h_{QQ}(r)] + \ln[1 + h_{NN}(r) - h_{QQ}(r)]\} \quad (3.5)$$

and

$$c_{QQ}(r) = -u_c(r) + h_{QQ}(r) - \tfrac{1}{2}\{\ln[1 + h_{NN}(r) + h_{QQ}(r)] - \ln[1 + h_{NN}(r) - h_{QQ}(r)]\}. \quad (3.6)$$

We have taken into account, in writing these equations from the immediate extension of Eq. (2.1) to the binary fluid, the fact that the cross-correlation functions $g_{NQ}(r)$ and $c_{NQ}(r)$ are identically zero in the present symmetric model.

We consider first Eq. (3.6) and ask about the possibility that the asymptotic behaviour of $c_{QQ}(r)$ is affected by the asymptotic behaviour of $h_{NN}(r)$ and $h_{QQ}(r)$. Taking the gradient of Eq. (3.6), we can write for large r

$$\nabla c_{QQ}(r) \sim -\nabla u_c(r) + \nabla[h_{NN}(r)h_{QQ}(r)] \quad (3.7)$$

with Fourier transform

$$c_{QQ}(k) \sim -u_c(k) + (2\pi)^{-d}n^{-1}\int d\mathbf{q}\,\frac{\mathbf{k}\cdot\mathbf{q}}{k^2}\,h_{QQ}(q)h_{NN}(|\mathbf{q}-\mathbf{k}|). \quad (3.8)$$

Assuming $h_{NN}(r) \sim r^{-(d-2+\eta_N)}$ and $h_{QQ}(r) \sim r^{-(d-2+\eta_Q)}$, with the restrictions $\eta_N > (2-d)$ from the condition that $h_{NN}(r)$ shall tend to zero at large r and $\eta_Q > 4-d$ from the condition that the Coulomb energy be finite, it is easily shown that in a consistent solution of Eq. (3.8) the last term on the right-hand side can contribute only terms of the form k^s with $s > 0$.

Therefore the Debye-Hückel asymptotic behaviour

$$c_{QQ}(k) \sim -u_c(k) \quad (3.9)$$

must necessarily be preserved. The leading correction to this result can only be a constant, coming from the regular terms in Eq. (3.6).

To illustrate the derivation of this result, let us consider the case $d \leq 2$, where the analysis is extremely simple. From examining the behaviour of the integral in Eq. (3.8) at small k and assuming that this is determined by the integrand at small q, one has from $h_{QQ}(q) \sim q^{\eta_Q-2}$ and $h_{NN}(q) \sim q^{\eta_N-2}$ that this integral can contribute a leading term of the type k^s with $s = d-4+\eta_N+\eta_Q$. The inequalities that we have already given for η_N and η_Q yield $s > (2-d)$. Therefore $s > 0$ for $d \leq 2$ so that the Debye-Hückel term $-u_c(k)$ in Eq. (3.8) remains dominant in the small k limit and there are no divergent corrections to it. For $d > 2$, on the other hand, if one assumes that s can be negative, one finds a contradiction when one determines $h_{QQ}(k)$ from $c_{QQ}(k)$ and uses the result to recalculate the integral in Eq. (3.3). Therefore, s can only be positive and the result (3.9) holds as stated there.

We can now turn to Eq. (3.5) and carry out its analysis in parallel with that given in Section 2 for the monatomic fluid, since $h_{QQ}(r)$ contributes only regular terms. All the results for the monatomic fluid are recovered, except that the definitions (2.4) and (2.5) for $p(k)$ and $q(k)$ are replaced by

$$p(k) = -n \int \mathrm{d}\mathbf{r}\, i \frac{\mathbf{k} \cdot \nabla u(r)}{k^2} \{[1 + h_{NN}(r)]^2 - h_{QQ}^2(r)\} \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (3.10)$$

and

$$q(k) = n \int \mathrm{d}\mathbf{r}\, i \left\{ \frac{\mathbf{k} \cdot \nabla}{k^2} [h_{NN}(r) - c_{NN}(r)][2h_{NN}(r) + h_{NN}^2(r) - h_{QQ}^2(r)] \right.$$
$$\left. - h_{NN}(r) \frac{\mathbf{k} \cdot \nabla h_{NN}(r)}{k^2} + h_{QQ}(r) \frac{\mathbf{k} \cdot \nabla h_{QQ}(r)}{k^2} \right\}. \quad (3.11)$$

In particular, one finds again

$$\eta_N = 2 - \frac{d}{3} \qquad (d < 6) \quad (3.12)$$

(cf. Eq. (2.12)) and

$$h_{NN}(r) \sim \frac{D}{r^{2d/3}} \qquad (d < 6) \quad (3.13)$$

with $D > 0$ (cf. Eq. (2.15)). The criticality condition is again of the form of Eq. (2.9), with $p(0)$ and $q(0)$ determined by Eqs. (3.10) and (3.11). Relating $p(0)$ to the expression of the virial pressure,

$$\frac{pV}{RT} = 1 - \frac{n}{2d} \int \mathrm{d}\mathbf{r}\, r \left\{ [1 + h_{NN}(r)] \frac{\mathrm{d}u(r)}{\mathrm{d}r} + h_{QQ}(r) \frac{\mathrm{d}u_c(r)}{\mathrm{d}r} \right\} \quad (3.14)$$

and using Eqs. (3.5), (3.6) and (3.11) we find

$$(pV/RT)_{n_c, T_c} = \frac{1}{2} - \frac{n}{2d} \int \mathrm{d}\mathbf{r}\, r \left\{ h_{NN}(r) \frac{\mathrm{d}}{\mathrm{d}r} [h_{NN}(r) - c_{NN}(r)] + \right.$$
$$\left. + h_{QQ}(r) \frac{\mathrm{d}}{\mathrm{d}r} [h_{QQ}(r) - c_{QQ}(r)] \right\}. \quad (3.15)$$

We note that the predictions (3.12) and (3.13) for the number-number correlation function are identical with the corresponding predictions for the monatomic fluid. In the formula (3.15), both $h_{NN}(r)$, which exhibits long-range behaviour as in Eq. (3.13), and $h_{QQ}(r)$ which does not have critical behaviour, appear but it is not clear to us, in the absence of detailed numerical information, that one can neglect the charge-charge terms compared with the number-number contributions. One can show that all the above results are valid, provided $1 \leq d \leq 3$, for a Coulomb potential proportional to $1/r$.

4 MODIFIED SUPERPOSITION APPROXIMATION FOR THE SYMMETRIC CHARGED FLUID

We have at various points in Section 2 compared the results of the HNC theory for the monatomic fluid with the well-known results of the superposition approximation. The question thus arises of what would be the result of applying this latter approximation to the symmetric charged fluid. Unfortunately, even far from criticality, the consistent use of the superposition approximation in the hierarchical equations for *both* $h_{NN}(r)$ and $h_{QQ}(r)$ leads to a violation of the Debye–Hückel behaviour (3.9). This approximation must therefore be modified in the hierarchical equation for $h_{QQ}(r)$ (cf. the discussion given by Abramo and Tosi[13] for the one-component classical plasma).

Replacing therefore the superposition approximation in the equation for $h_{QQ}(r)$ by a combination of the STLS approximation[13] and of the convolution approximation, so as to preserve away from criticality both the Debye–Hückel limiting behaviour and the correct behaviour of triplet functions for small interparticle separations, the equation for $h_{QQ}(r)$ is written as

$$\begin{aligned}-\nabla h_{QQ}(r) = {} & h_{QQ}(r)\nabla u(r) + [1 + h_{NN}(r)]\nabla u_c(r) \\ & + n \int d\mathbf{r}'\, \nabla u(r') h_{QQ}(r') h_{QQ}(|\mathbf{r} - \mathbf{r}'|) \\ & + n \int d\mathbf{r}'\, \nabla u_c(r')[h_{QQ}(|\mathbf{r} - \mathbf{r}'|) + h_{NN}(r') h_{QQ}(|\mathbf{r} - \mathbf{r}'|) \\ & + h_{NN}(r) h_{QQ}(|\mathbf{r} - \mathbf{r}'|) \\ & + n \int d\mathbf{r}''\, h_{NN}(r'') h_{QQ}(|\mathbf{r} - \mathbf{r}''|) h_{QQ}(\mathbf{r}' - \mathbf{r}'')] \end{aligned} \tag{4.1}$$

This is to be combined with the equation for $h_{NN}(r)$, which in the superposition approximation reads

$$\begin{aligned}-\nabla h_{NN}(r) = {} & [1 + h_{NN}(r)]\nabla u(r) + h_{QQ}(r)\nabla u_c(r) \\ & + n\int d\mathbf{r}'\, \nabla u(r')[g_{NN}(r)g_{NN}(r')g_{NN}(|\mathbf{r} - \mathbf{r}'|) \\ & + g_{QQ}(r)g_{QQ}(r')g_{QQ}(|\mathbf{r} - \mathbf{r}'|)] \\ & + n\int d\mathbf{r}'\, \nabla u_c(r')[g_{QQ}(r)g_{QQ}(|\mathbf{r} - \mathbf{r}'|)g_{NN}(r') \\ & + g_{NN}(r)g_{NN}(|\mathbf{r} - \mathbf{r}'|)g_{QQ}(r')]. \end{aligned} \tag{4.2}$$

From Eq. (4.1) in Fourier transform it is easily shown that

$$c_{QQ}(k) = -u_C(k) + p_Q(k) + q_Q(k) \tag{4.3}$$

where

$$p_Q(k) = -n\int d\mathbf{r}\, i\frac{\mathbf{k}\cdot\nabla u(r)}{k^2} h_{QQ}(r)\exp(i\mathbf{k}\cdot\mathbf{r}) \tag{4.4}$$

and

$$q_Q(k) = (2\pi)^{-d}n^{-1}\int d\mathbf{q}\,\frac{\mathbf{k}\cdot\mathbf{q}}{k^2}u_c(q)[1 + h_{QQ}(q)]h_{NN}(|\mathbf{q} - \mathbf{k}|). \tag{4.5}$$

By analyzing Eq. (4.3) at the critical point by essentially the same procedure used in Section 3 for the analysis of Eq. (3.6), it is easily shown that the only consistent solution is that which preserves the Debye–Hückel behaviour (3.9) at criticality.

Therefore, the analysis of Eq. (4.2) at the critical point can proceed essentially as for the analogous equation for the monatomic fluid (cf. Fishman[6]). The results which obtain for the monatomic fluid at criticality are thereby recovered, and in particular one recovers the appropriate value of the critical ratio

$$\left(\frac{pV}{RT}\right)_{n_c, T_c} = \frac{1}{2} \tag{4.6}$$

Unfortunately, we know of no experiments for simple charged fluids with which to compare the prediction (4.6). However, some theoretical estimates of pV/RT at the critical point have been discussed by Gillan[14] in connection with his work on significant structure theory. The largest value he records is for CsCl, the above ratio being 0.31. However, if we take more favourable examples of approximately symmetric alkali halides, namely NaF and RbCl, the ratios are 0.20 and 0.27 respectively.

5 SUMMARY

The main conclusion of our work is that, in the two approximate theories of symmetric charged fluids that we have studied, the charge-charge correlation function $c_{QQ}(r)$ exhibits Debye–Hückel behaviour even at the critical point. Therefore, the critical properties predicted have strong resemblance to those of monatomic fluids. The theories used for $h_{NN}(r)$ give asymptotic behaviour of the form $r^{-2d/3}$, which is known to be at variance with predicted critical correlation function behaviour. Nevertheless, in spite of these obvious limitations of the approximate structural theories we have employed, reasonable values of pV/RT at the critical point seem to be given by the HNC theory for a monatomic fluid.

Therefore, within the admittedly simplified symmetric model we have studied, the limitations of the theory for neutral fluids remain the prime obstacle to further progress and we feel that our work settles the main features of the charge-charge correlations.

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