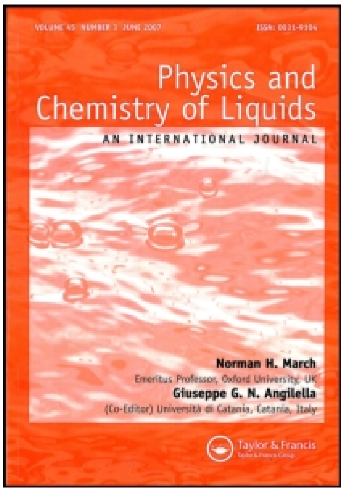

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LONG-WAVELENGTH ANALYSIS OF THE DIRECT CORRELATION FUNCTION FOR COULOMB LIQUIDS

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The long-wavelength structure of the cooperative part $\tilde{c}_c(k)$ of the direct correlation function $\tilde{c}(k) = \tilde{c}_p(k) + \tilde{c}_c(k)$ is inferred by comparing its known potential part $\tilde{c}_p(k)$ (Kumar *et al.*, *Phys. Chem. Liquids*, **11**, 271 (1982)) with a similarly structured part which quite naturally emerges from the Ornstein-Zernike relation plus the first Born-Green-Yvon equation for the one-component plasma.

KEY WORDS: One-component plasma, compressibility.

1 INTRODUCTION

Some time ago, Kumar *et al.*[1,2] proposed that, for reasons of consistency between virial and long-wavelength compressibility considerations, the Ornstein-Zernike direct correlation function $c(r)$ can be written as the sum of two contributions

$$c(r) = c_p(r) + c_c(r), \tag{1.1}$$

where the subscripts p and c refer respectively to the potential and cooperative contributions. The potential piece

$$\begin{aligned} c_p(r) &= -\beta\phi(r)\frac{1}{2dnr^{d-1}}\frac{\partial^2}{\partial n\,\partial r}(n^2r^dg(r)) \\ &= -\beta\phi(r) - \beta\phi(r)\frac{1}{2dn}\frac{\partial}{\partial n}n^2\nabla\cdot\mathbf{r}h(r);\ \beta = (k_BT)^{-1} \end{aligned} \tag{1.2}$$

for d-dimensional systems was defined to satisfy the asymptotic condition:

$$c(r) = -\beta\varphi(r);\quad \text{large } r \text{ limit.} \tag{1.3}$$

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In Eq. (1.2), $g(r) = \exp(-\beta U(r))$ is the pair correlation function defined in terms of the potential of mean force $U(r)$ while $h(r) = g(r) - 1$ is the total pair correlation function. Equation (1.2) is valid both for (a) neutral liquids with pair potentials $\phi(r)$ dropping off faster than $1/r^d$ and (b) the one-component plasma (OCP) with a charge-compensating background[3].

As to the cooperative contribution, thermodynamic consistency requires that

$$\tilde{c}_c(k = 0) = n \int d\mathbf{r}\; c_c(r) = 0. \tag{1.4}$$

Apart from the condition (1.4), an explicit structure for $\tilde{c}_c(k)$ has yet to be worked out.

For the class of density-independent pair potentials $\phi(r)$ which have Fourier transforms $\tilde{\phi}(k)$, it is tempting to explore the structures of $\tilde{c}_p(k)$ and $\tilde{c}_c(k)$ by comparing the Fourier-transformed Eq. (1.2) for $\tilde{c}_p(k)$ with that in an alternative representation of $\tilde{c}(k)$ defined through

$$\tilde{c}(k) = \tilde{b}_p(k) + \tilde{b}_c(k), \tag{1.5}$$

In this, also exact, representation of $\tilde{c}(k)$, $\tilde{b}_p(k)$ and $\tilde{b}_c(k)$ are defined through the equations:

$$\tilde{b}_p(k) = -\frac{\beta n \tilde{\phi}(k)}{1 - n\sum(k)}, \tag{1.6}$$

$$\tilde{b}_c(k) = \frac{-n\sum(k)}{1 - n\sum(k)}, \tag{1.7}$$

and

$$\sum(k) = \frac{1}{N}\sum_{\mathbf{q}} \frac{\mathbf{k}\cdot\mathbf{q}}{k^2}\, \beta n\, \tilde{\phi}(q)\{\tilde{h}(|\mathbf{k}-\mathbf{q}|) + n\tilde{t}(\mathbf{k}-\mathbf{q}, \mathbf{q})\}. \tag{1.8}$$

Equations (1.6)–(1.8) result from the combination of the Ornstein-Zernike relation

$$\tilde{c}(k) = 1 - \frac{1}{S(k)} = \frac{n\tilde{h}(k)}{1 + n\tilde{h}(k)} \tag{1.9}$$

and the first Born-Green-Yvon (BGY) equation linking the total pair and triplet correlation functions $\tilde{h}$ and $\tilde{t}$. In this paper, we carry out the investigation of the link between the b's and the c's above, at long wavelengths for the simplest of all Coulomb liquids; the strongly correlated OCP.

By definition, Eq. (1.5) satisfies the compressibility rule

$$\tilde{c}(k \to 0) = -\beta n \tilde{\phi}(k \to 0) + 1 - \beta\left(\frac{\partial p}{\partial n}\right)_T \tag{1.10}$$

derived from

$$S(k \to 0) = \frac{k_B T}{\left(\dfrac{\partial p}{\partial n}\right)_T + n\tilde{\phi}(k)}. \tag{1.11}$$

While the explicit structure of $\tilde{c}_p(k)$ in terms of $\tilde{h}(k)$ is already known (from Eq. (1.2)), the structure of $\tilde{b}_p(k)$ is not. Thus, a comparison between the two is possible only if one has additional information about the triplet correlation function $\tilde{t}$, eg., approximating $\tilde{t}$ in terms of $\tilde{h}$ clusters. This is the rationale for the long-wavelength decoupling approximation (4.1) below, which is expected to reproduce Eq. (1.10) to a high degree of accuracy.

The plan of the paper is as follows. In Section 2 we transform Eq. (1.2) for $c_p(r)$ into k-space formulae for the two-dimensional (2d) OCP with ln r pair potential and for the 3d OCP. The former is an ideal reference OCP whose thermodynamic properties have been studied by a number of investigators[3–6]. In Section 3, we then calculate $c_p(k \to 0)$ and in section 4 we analyze the long-wavelength behaviour of $\tilde{b}_p(k)$ and $\tilde{b}_c(k)$. In Section 5, the results of the previous two sections are compared and conclusions are drawn.

2 k-SPACE FORMULATION OF $c_p(r)$

The aim below is to calculate the Fourier transform

$$\tilde{c}_p(k) = n \int d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r})c_p(r) \tag{2.1}$$

for the 2d OCP with ln r pair potential and also for the 3d OCP. Let us start with the 2d OCP.

The Fourier transform of its pair potential $\phi(r) = -\bar{e}^2 \ln r$ is $\tilde{\phi}(k) = 2\pi\bar{e}^2/k^2$; where $\bar{e}$ is the charge per unit length. The coupling strength for this system is characterized by the plasma parameter

$$\Gamma = \bar{\beta}\bar{e}^2 \tag{2.2}$$

where $\bar{\beta}^{-1}$ is the thermal energy per unit length. The steps leading to the Fourier transformation of Eq. (1.2) with $d = 2$ are as follows;

$$\begin{aligned}
\tilde{c}_p(k) &= -\bar{\beta}n\tilde{\phi}(k) - \frac{\bar{\beta}}{4}\frac{\partial}{\partial n} n^2 \int d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r})\phi(r)\nabla\cdot\mathbf{r}h(r) \\
&= -\bar{\beta}n\tilde{\phi}(k) - \frac{\Gamma}{4}\frac{\partial}{\partial n} n^2 \int d\mathbf{r}\, \mathbf{r}h(r)\cdot\nabla(\exp(-i\mathbf{k}\cdot\mathbf{r}) \ln r) \\
&= -\bar{\beta}\tilde{\phi}(k) - \frac{\Gamma}{4}\frac{\partial}{\partial n} n^2\left\{\tilde{h}(k) - \int d\mathbf{r}\, h(r)(i\mathbf{k}\cdot\mathbf{r}) \ln r \exp(-i\mathbf{k}\cdot\mathbf{r})\right\}.
\end{aligned} \tag{2.3}$$

Turning next to the 3d OCP, the Fourier transform of its pair potential $\phi(r) = (Ze)^2/r$ is $\tilde{\phi}(k) = 4\pi(Ze)^2/k^2$. The coupling strength is now characterized by $\Gamma = \beta(Ze)^2/a$, where $a = (3/4\pi n)^{1/3}$ is the ion sphere radius. Setting $d = 3$ in Eq. (1.2) and repeating the steps above, we arrive at

$$\tilde{c}_p(k) = -\beta n\tilde{\phi}(k) - \frac{\beta}{6}\frac{\partial}{\partial n} n^2\left\{\frac{1}{V}\sum_{\mathbf{q}} \tilde{\phi}(q)\tilde{h}(|\mathbf{k}-\mathbf{q}|) + \int d\mathbf{r}(i\mathbf{k}\cdot\mathbf{r})\phi(r)h(r)\exp(-i\mathbf{k}\cdot\mathbf{r})\right\}. \tag{2.4}$$

3 LONG-WAVELENGTH BEHAVIOUR OF $\tilde{c}_p(k)$

Let us now turn to treat the long wavelength behaviour of $\tilde{c}_p(k)$, starting again with the 2d OCP.

3.1 *2d OCP*

At small k, Eq. (2.2) readily yields the result

$$\tilde{c}_p(k \to 0) = -\bar{\beta} n\tilde{\phi}(k \to 0) + \frac{\Gamma}{4} - \frac{\Gamma k^2}{8}\frac{\partial}{\partial n} n^2\left\{\tilde{h}''(0) - \int d\mathbf{r}\, r^2 h(r)\ln r\right\}. \tag{3.1}$$

From the exact equation of state[7,8] specific to this reference OCP:

$$p = nk_BT\left(1 - \frac{\Gamma}{4}\right), \tag{3.2}$$

the isothermal compressibility is calculated to be given by

$$\left(\frac{\partial p}{\partial n}\right)_T = k_BT\left(1 - \frac{\Gamma}{4}\right), \tag{3.3}$$

since $\Gamma = \bar{\beta}\bar{e}^2$ is density independent. Equation (3.1) can therefore be written as

$$\tilde{c}_p(k \to 0) = -\bar{\beta} n\tilde{\phi}(k \to 0) + 1 - \bar{\beta}\left(\frac{\partial p}{\partial n}\right)_T + O(k^2). \tag{3.4}$$

In view of the condition (1.4), the expression (3.4) satisfies the compressibility rule (1.10) and is therefore exact through $O(k^0)$.

3.2 *3d OCP*

Turning next to the 3d OCP, the $k \to 0$ limit of Eq. (2.4) is similarly found to be

$$\tilde{c}_p(k \to 0) = -\beta n\tilde{\phi}(k \to 0) - \frac{\beta}{6}\frac{\partial}{\partial n} n^2 \frac{1}{V}\sum_{\mathbf{q}} \tilde{\phi}(q)\tilde{h}(q) + O(k^2). \tag{3.5}$$

With the equation of state given by[9]

$$\begin{aligned} p &= nk_BT\left\{1 + \frac{\beta n}{6}\int d\mathbf{r}\ \phi(r)h(r)\right\} \\ &= nk_BT\left\{1 + \frac{\beta n}{6V}\sum_{\mathbf{q}} \tilde{\phi}(q)\tilde{h}(q)\right\} \end{aligned} \tag{3.6}$$

whence

$$\beta\left(\frac{\partial p}{\partial n}\right)_T = 1 + \frac{\partial}{\partial n}\frac{\beta n^2}{6V}\sum_{\mathbf{q}} \tilde{\phi}(q)\tilde{h}(q), \tag{3.7}$$

Eq. (3.5) takes the form

$$\tilde{c}_p(k \to 0) = -\beta n\tilde{\phi}(k \to 0) + 1 - \beta\left(\frac{\partial p}{\partial n}\right)_T + O(k^2) \tag{3.8}$$

which is again in precise accord with the compressibility rule (1.10).

4 LONG WAVELENGTH ANALYSIS OF $\tilde{b}_p(k)$ AND $\tilde{b}_c(k)$

While the exact long-wavelength behaviour of the direct correlation function is known (cf Eq. (1.10)) it is still necessary to evaluate $\tilde{b}_p(k \to 0)$ and $\tilde{b}_c(k \to 0)$ separately if one is to make contact with the analysis of the previous section. To carry out the evaluation, we shall appeal to the decomposition approximation for the total triplet correlation function

$$\tilde{t}(\mathbf{k}-\mathbf{q}, \mathbf{q}) = \tilde{h}(|\mathbf{k}-\mathbf{q}|)\tilde{h}(q) + \tilde{h}(|\mathbf{k}-\mathbf{q}|)\tilde{h}(k) + \tilde{h}(q)\tilde{h}(k) + n\tilde{h}(|\mathbf{k}-\mathbf{q}|)\tilde{h}(q)\tilde{h}(k) \tag{4.1}$$

for arbitrary coupling strength Γ.[10] Substitution into Eq. (1.8) and the first BGY eqn gives

$$\sum(k) = \frac{1}{N}\sum_{\mathbf{q}} \frac{\mathbf{k}\cdot\mathbf{q}}{k^2}\beta n\tilde{\phi}(q)S(k)S(q)\tilde{h}(|\mathbf{k}-\mathbf{q}|) \tag{4.2}$$

and

$$S(k)=\frac{1}{1+\beta n\tilde{\phi}(k)-\dfrac{1}{V_d}\sum_{\mathbf{q}}\dfrac{\mathbf{k}\cdot\mathbf{q}}{k^2}\beta n\tilde{\phi}(q)S(q)\tilde{h}(|\mathbf{k}-\mathbf{q}|)}\tag{4.3}$$

where V_d denotes the d-dimensional 'volume'.

4.1 2*d OCP*

The evaluation of Eq. (4.3) for the 2d OCP is carried out via the following steps:

$$\begin{aligned}\lim_{k\to 0}\frac{1}{A}\sum_{\mathbf{q}}\frac{\mathbf{k}\cdot\mathbf{q}}{q^2}S(q)\tilde{h}(|\mathbf{k}-\mathbf{q}|)&=-\frac{1}{A}\sum_{\mathbf{q}}\frac{k^2\cos^2\phi}{q}S(q)\tilde{h}'(q)\\&=\frac{-k^2}{2A}\sum_{\mathbf{q}}\frac{1}{q}S(q)\tilde{h}'(q)\\&=\frac{-k^2}{2A}\sum_{\mathbf{q}}\frac{1}{q}\frac{\partial}{\partial q}\left[\tilde{h}(q)+\frac{1}{2}n\tilde{h}^2(q)\right]\\&=\frac{k^2}{4\pi}\tilde{h}(0)\left[1+\frac{1}{2}n\tilde{h}(0)\right]=-\frac{k^2}{8\pi n}.\end{aligned}\tag{4.4}$$

In reaching the final step in Eq. (4.4), we have exploited the fact that $\tilde{h}(0)=-1/n$ for an OCP. From Eq. (4.4), it follows that

$$S(k\to 0)=\frac{1}{\beta n\tilde{\phi}(k)+1-\dfrac{\Gamma}{4}}.\tag{4.5}$$

Substituting Eq. (4.5) into (4.2), one arrives at

$$-n\sum(k\to 0)=\frac{k^2}{8\pi n}\left\{1-\frac{1}{\beta n\tilde{\phi}(k)}\left(1-\frac{\Gamma}{4}\right)\right\},\tag{4.6}$$

whence from Eqs. (1.6) and (1.7):

$$\tilde{b}_p(k\to 0)=-\beta n\tilde{\phi}(k)+\frac{\Gamma}{4}-\frac{k^2}{8\pi n}\tag{4.7}$$

and

$$\tilde{b}_c(k \to 0) = \frac{k^2}{8\pi n}. \tag{4.8}$$

Addition of Eqs. (4.7) and (4.8) per Eq. (1.5) gives Eq. (1.10).

4.2 *3d OCP*

For the 3d OCP, repetition of the above procedures results in

$$\tilde{b}_p(k \to 0) = -\beta n\tilde{\phi}(k \to 0) + \left\{1 - \beta\left(\frac{\partial p}{\partial n}\right)_T + I\right\}\left\{1 - \frac{1}{\beta n\tilde{\phi}(k \to 0)}\right\}, \tag{4.9}$$

and

$$\tilde{b}_c(k \to 0) = \frac{1}{\beta n\tilde{\phi}(k \to 0)}\left\{1 - \beta\left(\frac{\partial p}{\partial n}\right)_T + I\right\}, \tag{4.10}$$

where

$$I = \frac{\beta n^2}{6V}\sum_q \tilde{\phi}(q)\left\{\frac{\partial \tilde{h}(q, n)}{\partial n} - \tilde{h}^2(q, n)\right\}. \tag{4.11}$$

Eqs. (4.9) and (4.10) add to give the direct correlation function

$$\tilde{c}(k \to 0) = -\beta n\tilde{\phi}(k \to 0) + 1 - \beta\left(\frac{\partial p}{\partial n}\right)_T + I. \tag{4.12}$$

While the expression (4.12) is structurally correct, it fails to quantitatively satisfy the compressibility requirement (1.10). The discrepancy between the two results must surely originate from the choice of the decomposition approximation (4.1) which, strictly speaking, is best for weak coupling situations. Indeed, it can be seen that for $\Gamma < 1$, substitution of the 'Debye-Huckel' pair correlation function

$$\tilde{h}^{DH}(q, n) = \frac{-\beta\tilde{\phi}(q)}{1 + \beta n\tilde{\phi}(q)} \tag{4.13}$$

into Eq. (4.11) leads to $I = 0$. As an aside, we may note that the defect in the model decoupling approximation notwithstanding, in the case of the 2d OCP, it is the specific equation of state (3.2) which precludes the possibility of occurrence of such a discrepancy. In any case, it seems a reasonable assumption that the appearance of I is, in fact, superficial, and that it can accordingly be omitted from Eqs. (4.9), (4.10) and (4.12).

5 CONCLUSIONS

Equations (4.7) and (4.9), with I set equal to zero as discussed immediately above, are identical to Eqs. (3.4) and (3.8) respectively through $O(k^0)$; all satisfying the compressibility rule (1.10).

The principal accomplishment of the present work is that, at long wavelengths, the potential part of the direct correlation function has been identified with a similarly structured term which emerges in a natural way from the combination of the Ornstein-Zernike relation with the Born-Green-Yvon equation for the OCP liquid. As a consequence of this identification, the long-wavelength structure of $\tilde{c}_c(k)$ for the d-dimensional OCP liquid is inferred: the conclusion being that

$$\tilde{c}_c(k \to 0) = \frac{1}{\beta n \tilde{\phi}(k \to 0)} \left\{ 1 - \beta \left(\frac{\partial p}{\partial n} \right)_T \right\}. \tag{5.1}$$

Equation (5.1) is certainly thermodynamically consistent.

We have not attempted to analyze $\tilde{b}_p(k)$ and $\tilde{b}_c(k)$ in Eq. (1.5) at short wavelengths. The assumed decoupling approximation (4.1) would surely have to be transcended in such a study. One demonstration that it is seriously flawed in the large-k domain is that Eq. (4.1) would lead to a decay as k^{-2} for $\tilde{b}_c(k)$ at large k. Because of this slow rate of decay, one would be lead to an unphysical divergence in $b_c(r)$ at small r. Further study of the three-body correlations is evidently an important direction for progress away from the long-wavelength limit.

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