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Sum Rules for the One-Component Plasma with Additional Short-Range Forces

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It is proved that, in the one-component plasma, with interactions including a non-Coulombic short-range part, the density derivative of the correlation functions $\rho_n(r_1,..., r_n)$ can be simply expressed as an integral of $\rho_{n+1}(r_1,..., r_{n+1})$. This result is applied to prove the relation between the fourth moment of ρ_2 and the compressibility.

KEY WORDS: One-component plasma; BBGKY hierarchy; sum rules; screening.

1. INTRODUCTION

In the study of classical Coulomb systems, the use of the BBGKY hierarchy, with some additional assumption of clustering properties for the density correlation functions, turned out to be very fruitful. In this way, the rigorous proofs of the perfect screening conditions and of the Stillinger–Lovett sum rules have been established for charged particles with interactions including a short-range part.[1–4] Another sum rule links the fourth moment of the two-point correlation function to the compressibility. This rule can be easily obtained on the basis of appealing but not rigorous arguments.[5,6] By using the BBGKY hierarchy (with clustering assumptions), this rule has been proved[7–9] for particles interacting via purely Coulombic forces. It is therefore interesting to look at the case where a short-range potential is added to the Coulombic one.

So we are dealing with ions of one species, interacting via Coulombic forces and some short-range forces, imbedded in a uniform background

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which ensures the electrical neutrality. The statistics is that of the canonical ensemble, and the dimension of space is 2 or 3. The system and the various assumptions concerning the correlation function are introduced in Section 2. Then, in Section 3, we establish a new and simple equation which expresses the volume derivative of the n-point correlation function with the help of correlation functions of order $\leqslant n+1$,[2] without first taking the thermodynamic limit. The problems concerning this are discussed before applying the result to the proof of the aforementioned sum rule relative to the fourth moment of the two-point correlation function (Section 4). Some technical calculations are given in Appendix A. The perfect screening conditions needed in Sections 3 and 4 are recalled in Appendix B.

2. GENERAL FRAMEWORK

We consider a set of N point ions of mass m and charge e in a vessel of volume V. The numerical density is $\rho = N/V$. These ions are classical and interact via Coulomb forces [potential $v_c(r)$] and also via short-range two-body forces [potential $v_s(r)$]. The dimension of the space is $\nu = 2$ or 3. A uniform and rigid background ensures the electrical neutrality and the short-range force $F_s = -\nabla v_s(r)$ is assumed to be covariant under rotations and integrable on R^ν. Then the Hamiltonian is

$$H_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V_N(r_1, \dots, r_n) \tag{1}$$

$$V_N(r_1, \dots, r_n) = \frac{1}{2} \sum_{i \neq j} v(r_i, r_j)$$

where p_i and r_i are the momentum and the position of the particle i, and the effective potential $v(r_i, r_j)$ is given by

$$\begin{aligned} v(r_i, r_j) = {} & v_s(r_i - r_j) + v_c(r_i - r_j) \\ & - \frac{\rho}{N-1} \int_V dr\, [v_c(r - r_i) + v_c(r - r_j)] \\ & + \frac{\rho^2}{N(N-1)} \int_{V^2} dr\, dr'\, v_c(r - r') \end{aligned} \tag{2}$$

$$v_c(r) = \begin{cases} e^2/|r|, & \nu = 3 \\ -e^2 \ln(|r|/\sigma); & \nu = 2 \end{cases}$$

σ is an arbitrary constant fixing the zero energy level.

[2] A. Alastuey simultaneously obtains this result in a different way and directly in the thermodynamic limit (to be published).

In a finite-volume canonical ensemble of temperature $T=\beta^{-1}$ measured in energy units, the n-point correlation functions are defined by

$$\begin{gathered} \rho_n^V(r_1,\ldots, r_n) = \langle \hat{\rho}_n(r_1,\ldots, r_n)\rangle \\ \hat{\rho}_n(r_1,\ldots, r_n) = [\hat{\rho}_1(r_1)\cdots\hat{\rho}_1(r_n)]_{\mathrm{SL}}, \qquad \hat{\rho}_1(r) = \sum_{i=1}^{N} \delta(r-r_i) \end{gathered} \tag{3}$$

where the symbol $[\cdots]_{\mathrm{SL}}$ means that the self terms are left out and the symbol $\langle\cdots\rangle$ stands for the canonical average. From the definition (3) of the functions ρ_n^V, the sum rules follow:

$$\begin{gathered} \int_V dr_{n+1}\, \rho_{n+1}^V(r_1,\ldots, r_{n+1}) = (N-n)\, \rho_n^V(r_1,\ldots, r_n) \qquad (n\geqslant 1) \\ \int_V dr_1\, \rho_1^V(r_1) = N \end{gathered} \tag{4}$$

These functions ρ_n^V also satisfy the BBGKY hierarchy equations

$$\begin{aligned} \partial_i\rho_n^V(r_1,\ldots, r_n) = &-\beta\rho_n^V(r_1,\ldots, r_n) \sum_{j=1, j\neq i}^{n} \partial_i v(r_i, r_j) \\ &-\beta\int_V dr_{n+1}\, \partial_i v(r_i, r_{n+1})\, \rho_{n+1}^V(r_1,\ldots, r_{n+1}) \end{aligned} \tag{5}$$

By taking the gradient $\partial_i\equiv\partial/\partial r_i$ of $v(r_i, r_j)$, (2), we are led to

$$\begin{aligned} &\partial_i\rho_n^V(r_1,\ldots, r_n) \\ &\quad = -\beta\rho_n^V(r_1,\ldots, r_n) \sum_{j=1, j\neq i}^{n} \{\partial_i v_c(r_i-r_j) + \partial_i v_s(r_i-r_j)\} \\ &\qquad -\beta\int_V dr_{n+1}\, \partial_i v_s(r_i-r_{n+1})\, \rho_{n+1}^V(r_1,\ldots, r_{n+1}) \\ &\qquad -\beta\int_V dr_{n+1}\, \partial_i v_c(r_i-r_{n+1})\{\rho_{n+1}^V(r_1,\ldots, r_{n+1}) - \rho\rho_n^V(r_1,\ldots, r_n)\} \end{aligned} \tag{6}$$

The pressure P^V, defined as $-\partial F_N/\partial V$, where F_N is the free energy, is easily obtained by using a well-known scaling argument,

$$\beta P^V = \rho - \frac{\beta}{2vV} \int_{V^2} dr_1\, dr_2 (r_1 - r_2) \cdot \partial_1 v_s(r_1 - r_2)\, \rho_2^V(r_1, r_2)$$
$$- \frac{\beta}{2vV} \int_{V^2} dr_1\, dr_2 (r_1 - r_2) \cdot \partial_1 v_c(r_1 - r_2)$$
$$\times \{\rho_2^V(r_1, r_2) - \rho\rho_1^V(r_1) - \rho\rho_1^V(r_2) + \rho^2\} \tag{7}$$

In the thermodynamic limit (TL), the n-point correlation functions will be denoted $\rho_n(r_1,..., r_n)$ (in a general way a quantity f^V becomes f in the TL), and the associated truncated (Ursell) functions $\rho_n^T(r_1,..., r_n)$ are assumed (i) to be invariant under space rotations and translations, (ii) to be symmetrical in any permutation of the particles, and (iii) to tend to zero faster than some power of the distance when a particle is removed to infinity (clustering hypothesis); this point will be specified more fully in the following. In the TL the BBGKY hierarchy becomes[1]

$$\partial_i \rho_n(r_1,..., r_n)$$
$$= -\beta\rho_n(r_1,..., r_n) \sum_{j=1, j\neq i}^{n} \{\partial_i v_c(r_i - r_j) + \partial_i v_s(r_i - r_j)\}$$
$$-\beta \int_{R^v} dr_{n+1}\, \partial_i v_s(r_i - r_{n+1})\, \rho_{n+1}(r_1,..., r_{n+1})$$
$$-\beta \int_{R^v} dr_{n+1}\, \partial_i v_c(r_i - r_{n+1}) \{\rho_{n+1}(r_1,..., r_{n+1}) - \rho\rho_n(r_1,..., r_n)\} \tag{8}$$

and the pressure (6) in this limit is

$$\beta P = \rho - \frac{\beta}{2v} \int_{R^v} dr\, r \cdot \nabla v_s(r)\, \rho_2(r) - \frac{\beta}{2v} \int_{R^v} dr\, r \cdot \nabla v_c(r)\, \rho_2^T(r) \tag{9}$$

3. VOLUME DERIVATIVE OF ρ_n^V

In this part we shall show that the derivative of ρ_n^V with respect to the volume V can be exactly and simply expressed with the help of $\rho_m^V(m \leqslant n+1)$ functions. This result is obtained by writing the volume derivative of ρ_n^V, which follows from the definition of ρ_n^V, and by using the hierarchy equations (5). We perform the derivative of ρ_n^V,

$$\rho_n^V(r_1,..., r_n) = \frac{\int_V dr_1' \cdots \int_V dr_N'\, e^{-\beta V_N} [\hat\rho(r_1) \cdots \hat\rho(r_n)]_{\text{SL}}}{\int_V dr_1' \cdots \int_V dr_N'\, e^{-\beta V_N}} \tag{10}$$

by using the well-known scaling for the integration variables $r_i' = x_i V^{1/\nu}$,[3]

$$
\begin{aligned}
V\frac{\partial}{\partial V}\rho_n^V(r_1,..., r_n)
&= -\frac{1}{\nu}\sum_{i=1}^{n} \partial_i \cdot [r_i \rho_n^V(r_1,..., r_n)] \quad \text{(A)}\\
&-\frac{\beta}{\nu}\int_{V^2} dr_{n+1}\, dr_{n+2}\, r_{n+1}\cdot \partial_{n+1} v(r_{n+1}, r_{n+2})\\
&\times [\langle \hat{\rho}_2(r_{n+1}, r_{n+2})\, \hat{\rho}_n(r_1,..., r_n)\rangle\\
&-\rho_2^V(r_{n+1}, r_{n+2})\, \rho_n^V(r_1,..., r_n)] \quad \text{(B)}\\
&+\frac{\beta\rho}{\nu}\int_{V^2} dr_{n+1}\, dr_{n+2}\, r_{n+1}\cdot \partial_{n+1} v_c(r_{n+1} - r_{n+2})\\
&\times [\langle (\hat{\rho}_1(r_{n+2}) - \rho)\, \hat{\rho}_n(r_1,..., r_n)\rangle\\
&-[\rho_1^V(r_{n+2}) - \rho]\, \rho_n^V(r_1,..., r_n)] \quad \text{(C)}
\end{aligned}
\tag{11}
$$

The transformation of (11) to (13) is given in Appendix A. Here we just sketch the calculation. The canonical average $\langle \cdots \rangle$ in terms (B) and (C) are expressed with the functions $\rho_m^V (m \leqslant n+2)$. First ρ_{n+2}^V is eliminated by using the hierarchy (5) and, once more with the help of the hierarchy (5) and of the sum rules (4), the total (A) + (B) is reduced to an integral on the boundary of the vessel S,

$$
(\text{A}) + (\text{B}) = \frac{1}{\nu}\oint_S ds \cdot r[\rho_{n+1}^V(r_1,..., r_n, r) - \rho_1^V(r)\, \rho_n^V(r_1,..., r_n)] \tag{12}
$$

The term (C) does not make difficulties. Finally, the volume derivative of ρ_n^V is

$$
\begin{aligned}
V\frac{\partial}{\partial V}\rho_n^V(r_1,..., r_n) &= \frac{1}{\nu}\oint_S ds \cdot r\rho_{n+1}^{VT}(r_1,..., r_n \mid r)\\
&+ \beta\rho\rho_n^V(r_1,..., r_n)\frac{1}{\nu}\int_V dr(r\cdot\nabla)\, \Phi_n^V(r_1,..., r_n \mid r)
\end{aligned}
\tag{13}
$$

[3] N is kept fixed here and ρ, which appears in V_N in (2), is set equal to N/V.

where Φ_n^V and $\rho_{n+1}^{VT}(r_1,..., r_n | r)$ are defined by

$$\Phi_n^V(r_1,..., r_n | r) = \int_V dr' \, v_c(r-r') \, D_n^V(r_1,..., r_n | r')$$

$$D_n^V(r_1,..., r_n | r) = \sum_{i=1}^{n} \delta(r-r_i) + \frac{\rho_{n+1}^V(r_1,..., r_n, r)}{\rho_n^V(r_1,..., r_n)} - \rho_1^V(r) \tag{14}$$

$$\rho_{n+1}^{VT}(r_1,..., r_n | r) = \rho_{n+1}^V(r_1,..., r_n, r) - \rho_1^V(r) \, \rho_n^V(r_1,..., r_n)$$

At this stage we make some comments on this result. Equation (13) is exact for a finite system in the sense that it follows directly and without any approximations from the definitions (3) of the ρ_n^V. The term with Φ_n^V comes from the compression (or expansion) of the background during the variation of V via the explicit dependence of the effective potential $v(r_i, r_j)$ on V. Here Φ_n^V is the potential of the charge distribution which is situated near the points $r_1,..., r_n$ and such that the total charge is zero [from (4)],

$$\int_V dr \, D_n^V(r_1,..., r_n | r) = 0 \tag{15}$$

Nevertheless, we point out that D_n^V is not the charge density around n fixed ions, because the background gives a contribution $-\rho$ instead of $-\rho_1^V(r)$. Here the presence of $\rho_1^V(r)$ ensures that no contribution to Φ_n^V comes from the neighborhood of the boundary where the two quantities are different. This point is important in the TL.

Now we look at the more difficult question of the TL of Eq. (13). We shall not give a real proof of that TL. Information on such delicate problems may be found in ref. 14. We take the n points fixed in the bulk and indefinitely increase the volume V in such a way that the boundary moves away from the n points. The surface term in (13) vanishes in this limit because of the clustering assumption on the correlation functions [in fact, it is enough that $\rho_{n+1}^T(r_1,..., r_n | r)$ decreases faster than $r^{-\nu}$]. The behavior of Φ_n^V is linked to that of ρ_{n+1}^{VT}.[1] This point and the perfect screening condition (PSC) which follow are considered in Appendix B. We assume that the clustering is enough to make $\Phi_n(r_1,..., r_n | r)$ decrease more than $r^{-\nu}$, which is equivalent to saying that the lowest nonvanishing multipole moment of $D_n(r_1,..., r_n | r)$ is at least of order 3. It follows that

$$\frac{\partial}{\partial \rho} \ln \rho_n(r_1,..., r_n)$$

$$= -\frac{\beta}{\nu} \int_{R^\nu} dr (r \cdot \nabla) \int_{R^\nu} dr' \, v_c(r-r') \, D_n(r_1,..., r_n | r') \tag{16}$$

and we write

$$\frac{\partial}{\partial \rho} \ln \rho_n(r_1,..., r_n) = -\frac{\beta}{V} \lim_{R_0 \to \infty} \int_{R^\nu} dr' \, D_n(r_1,..., r_n \mid r') \times \int_{r \leqslant R_0} dr (r \cdot \nabla) \, v_c(r - r') \tag{17}$$

The last integral is easily calculated,

$$\frac{1}{V} \int_{r \leqslant R_0} dr (r \cdot \nabla) \, v_c(r - r') = -\tfrac{1}{2} e^2 (R_0^2 - r'^2) V_\nu \tag{18}$$

$$V_3 = 4\pi/3, \qquad V_2 = \pi$$

Taking into account the perfect screening condition

$$\int_{R^\nu} D_n(r_1,..., r_n \mid r) = 0 \tag{19}$$

which is the TL of (15) or which follows from the clustering assumption for the ρ_n, (B4), we get the final result

$$\frac{\partial}{\partial \rho} \ln \rho_n(r_1,..., r_n) = -\frac{\beta e^2}{2} V_\nu \int_{R^\nu} dr \, r^2 D_n(r_1,..., r_n \mid r) \tag{20}$$

This one is also easily written [see (B4)]

$$\frac{\partial}{\partial \rho} \rho_n(r_1,..., r_n) = -\frac{\beta e^2}{2} V_\nu \int_{R^\nu} dr \times \left\{ r^2 - \frac{1}{n} \sum_{i=1}^{n} r_i^2 \right\} \{\rho_{n+1}(r_1,..., r_n, r) - \rho \rho_n(r_1,..., r_n)\} \tag{21}$$

Equation (20) or (21) does not depend on the origin of the coordinate system, because of (B4).

Before we look at the consequences of this result, we recall that the rhs of (20) or (21) comes from the compression of the background during the variation of V. The question now is what happens in the limit of vanishing charges? Of course $\partial \rho_n / \partial \rho$ is not zero for a non-Coulombic fluid. As in this case Φ_n^V is zero in (13), the volume derivative of ρ_n is given by the first surface integral, which has to be nonzero. The answer to this problem is that the clustering assumption is not valid for terms of order N^{-1}.[10] If we take into account this corrective term for non-Coulombic fluid, we do not obtain with (13) any new equation, but only the wall theorem[11] for the compressibility. So we have implicitly that the clustering properties are valid for the ρ_n up to term N^{-1} in our case.

A simple consequence of (21) is the second moment sum rule of Stillinger and Lovett (SL). Equation (21) for $n=1$ leads to

$$1 = -\frac{\beta e^2}{2} V_v \int_{R^v} dr\, r^2 \rho_2^T(r) \tag{22}$$

which was first rigorously proved in ref. 4.

4. COMPRESSIBILITY SUM RULE

We shall now prove the compressibility sum rule. The result follows from Eq. (20), from the PSC ($l=0$, 1, and 2) for ρ_2 and ρ_3, and from the hierarchy (8) for $n=2$. Of course, these three ingredients are not independent. From (9), we deduce the compressibility

$$\beta \left.\frac{\partial P}{\partial \rho}\right|_T = 1 - \frac{\beta}{2v} \int_{R^v} dr (r \cdot \nabla)\, v_s(r) \frac{\partial \rho_2(r)}{\partial \rho} - \frac{\beta}{2v} \int_{R^v} dr (r \cdot \nabla)\, v_c(r) \frac{\partial \rho_2^T(r)}{\partial \rho} \tag{23}$$

The density derivative of ρ_2 is given by (20),

$$\frac{\partial}{\partial \rho} \rho_2(r) = -\frac{\beta e^2 V_v}{2} \int_{R^v} dr'\, r'^2 \{\rho_3^S(r, r') + \rho_2(r)\, \delta(r'-r)\} \tag{24}$$

where we have introduced the function ρ_3^S

$$\rho_3^S(r, r') = \rho_3(r, r') - \rho\rho_2(r) = \rho_3^T(r, r') + \rho\rho_2^T(r') + \rho\rho_2^T(r'-r) \tag{25}$$

with r and r', respectively, equal to $r_2 - r_1$ and $r_3 - r_1$. Contrary to $\rho_3(r, r')$, $\rho_3^S(r, r')$ is not invariant in the exchange of r and r'. By taking into account the second moment sum rule of SL, (22), and the PSC ($l=0$) for ρ_2^T, we obtain the density derivative of ρ_2^T

$$\frac{\partial}{\partial \rho} \rho_2^T(r) = -\frac{\beta e^2 V_v}{2} \int_{R^v} dr'\, r'^2 \{\rho_3^T(r, r') + \rho_2^T(r)\, \delta(r'-r)\} \tag{26}$$

This result was first shown for the one-component plasma (without v_s) in a much more complicated way which involves the four-point correlation function.[(7),4] Introducing the notation

$$
\begin{aligned}
\mathscr{L}^T[f(r, r')] &= \int_{R^{2\nu}} dr\, dr'\, f(r, r')\{\rho_3^T(r, r') + \rho_2^T(r)\,\delta(r'-r)\} \\
L^T[f(r, r')] &= \int_{R^{2\nu}} dr\, dr'\, f(r, r')\,\rho_3^T(r, r') \\
\mathscr{L}^S[f(r, r')] &= \int_{R^{2\nu}} dr\, dr'\, f(r, r')\{\rho_3^S(r, r') + \rho_2(r)\,\delta(r'-r)\} \\
L^S[f(r, r')] &= \int_{R^{2\nu}} dr\, dr'\, f(r, r')\,\rho_3^S(r, r')
\end{aligned}
\tag{27}
$$

we write the compressibility in the form

$$
\beta \left.\frac{\partial P}{\partial \rho}\right|_T = 1 + \frac{\beta^2 e^2 V_\nu}{4\nu}\,[\mathscr{L}^S[r\cdot\nabla v_s(r) r'^2] + \mathscr{L}^T[r\cdot\nabla v_c(r) r'^2]] \tag{28}
$$

Now, by using the symmetry of ρ_3 and the PSC ($l = 0$, 1, and 2) for ρ_3, we shall transform (28) into a three-point integral which can be reduced to a two-point integral with the help of the hierarchy. ρ_3^T and ρ_3^S are invariant under the transformations $r \to -r$ and $r' \to r' - r$. It follows, for any function $f(|r|)$ such that the integrals converge, that

$$
L^{T,S}\left[\frac{f(|r|)}{r^2}(r'^2 - r\cdot r')(r^2 - 2r\cdot r')\right] = 0 \tag{29}
$$

We introduce unit vectors $\hat{r}$, $\hat{r}'$ and express $(\hat{r}\cdot\hat{r}')^2$ in terms of the functions $g_n(\hat{r}\cdot\hat{r}')$ which occur in the PSC (B5),

$$
(\hat{r}\cdot\hat{r}')^2 = \frac{\nu-1}{\nu}\,g_2(\hat{r}\cdot\hat{r}') + \frac{1}{\nu}\,g_0(\hat{r}\cdot\hat{r}'), \qquad (\hat{r}\cdot\hat{r}') = g_1(\hat{r}\cdot\hat{r}') \tag{30}
$$

Then, by using the PSC ($l = 1, 2$) for ρ_3^T and ρ_3^S, we are led to

$$
\mathscr{L}^{T,S}[f(|r|) r'^2] = \frac{2\nu}{\nu+2}\,\mathscr{L}^{T,S}\left[f(|r|)\frac{r'^3}{r}\,g_1(\hat{r}\cdot\hat{r}')\right] \tag{31}
$$

[4] The sign before $v_2(x)$ in Eq. (48) of ref. 7 has to be read minus.

The compressibility, given by (28), becomes

$$\beta \frac{\partial P}{\partial \rho}\bigg|_T = 1 + \frac{\beta^2 e^2 V_\nu}{\nu+2} [\mathscr{L}^S[\hat{r}\cdot\nabla v_s(r)\, r'^3 g_1(\hat{r}\cdot\hat{r}')] + \mathscr{L}^T[\hat{r}\cdot\nabla v_c(r)\, r'^3 g_1(\hat{r}\cdot\hat{r}')]] \tag{32}$$

By integrating the hierarchy equation (8) for $n=2$ with some function $g(|r|)$, it is easily shown that

$$\mathscr{L}^S[\hat{r}\cdot\nabla v_s(r)\, g(|r'|)\, g_1(\hat{r}\cdot\hat{r}')] + \mathscr{L}^T[\hat{r}\cdot\nabla v_c(r)\, g(|r'|)\, g_1(\hat{r}\cdot\hat{r}')] = \frac{1}{\beta}\int_{R^\nu} dr\, \rho_2^T(r) r^{-\nu+1} \frac{d}{dr}\{r^{\nu-1} g(|r|)\} + \rho^2 \int_{R^\nu} dr\, r^{-\nu+1} \times \frac{d}{dr}\{r^{\nu-1} g(|r|)\}\, \Phi_1(0|r) \tag{33}$$

where Φ_1 satisfies

$$\Phi_1(0|r) = \int_{R^\nu} dr'\, v_c(r-r')\{\delta(r') + \rho^{-1}\rho_2^T(r')\} = \rho^{-1}\int_{R^\nu} dr'\{v_c(r-r') - v_c(r)\}\, \rho_2^T(r') \tag{34}$$

For $g(|r|) = r^3$, this relation allows us to express the compressibility (32) only in terms of two-point integrals

$$\beta \frac{\partial P}{\partial \rho}\bigg|_T = 1 + \frac{\beta^2 e^2 V_\nu}{2}\left[\frac{1}{\beta}\int_{R^\nu} dr\, r^2 \rho_2^T(r) + \rho^2 \int_{R^\nu} dr\, r^2 \Phi_1(0|r)\right] \tag{35}$$

Finally, taking account of the SL sum rule (22), we are led to

$$\beta \frac{\partial P}{\partial \rho}\bigg|_T = \frac{\beta^2 e^2 V_\nu}{2} \rho^2 \int_{R^\nu} dr\, r^2 \Phi_1(0|r) = -\frac{\beta^2 e^4 V_\nu^2 \rho}{8} \frac{\nu}{\nu+2}\int_{R^\nu} dr\, r^4 \rho_2^T(r) \tag{36}$$

which implies that $\Phi_1(0|r)$ and $\rho_2^T(r)$ are, respectively, more decreasing than $r^{-(\nu+2)}$ and $r^{-(\nu+4)}$.

5. CONCLUSION

The volume derivatives of the functions ρ_n^V appear very useful in Coulombic fluids, unlike in neutral fluids. It has been admitted that the clustering properties were valid for the ρ_n up to the term N^{-1}. This point remains open and is linked to the fact that the long-range nature of the Coulomb potential imposes local neutrality (PSC), which makes the system incompressible.[1] The compressibility (36) is not related to the density fluctuation, but to the variation of the free energy when the whole system (with its background) is compressed.

APPENDIX A

Here we give some details on the transformation of Eq. (11) to (13). First we write (B) with the help of the function ρ_m^V $(m \leqslant n+2)$ by using

$$\begin{aligned}
&\hat{\rho}_2(r_{n+1}, r_{n+2})\, \hat{\rho}_n(r_1,..., r_n) \\
&\quad = \hat{\rho}_{n+2}(r_1,..., r_{n+2}) + \sum_{i=1}^{n} \delta(r_i - r_{n+2})\, \hat{\rho}_{n+1}(r_1,..., r_i,..., r_n, r_{n+1}) \\
&\qquad + \sum_{i=1}^{n} \delta(r_i - r_{n+1})\, \hat{\rho}_{n+1}(r_1,..., r_i,..., r_n, r_{n+2}) \\
&\qquad + \sum_{i \neq j \in [1,...,n]} \delta(r_i - r_{n+1})\, \delta(r_j - r_{n+2})\, \hat{\rho}_n(r_1,..., r_i,..., r_j,..., r_n)
\end{aligned}$$

It follows that

$$\begin{aligned}
(\mathrm{B}) = & \left.\begin{aligned} & -\frac{\beta}{V} \int_{V^2} dr_{n+1}\, dr_{n+2}\, r_{n+1} \cdot \partial_{n+1} v(r_{n+1}, r_{n+2}) \\
& \times \rho_{n+2}^V(r_1,..., r_{n+2}) \\
& -\frac{\beta}{V} \sum_{i=1}^{n} \int_V dr_{n+1}\, r_{n+1} \cdot \partial_{n+1} v(r_{n+1}, r_i) \\
& \times \rho_{n+1}^V(r_1,..., r_i,..., r_{n+1}) \end{aligned} \right\} (\mathrm{B}\alpha) \\
& \left.\begin{aligned} & -\frac{\beta}{V} \sum_{i=1}^{n} \int_V dr_{n+1}\, r_i \cdot \partial_i v(r_i, r_{n+1}) \\
& \times \rho_{n+1}^V(r_1,..., r_i,..., r_{n+1}) \\
& -\frac{\beta}{V} \sum_{i \neq j \in [1,...,n]} r_i \cdot \partial_i v(r_i, r_j) \\
& \times \rho_n^V(r_1,..., r_i,..., r_j,..., r_n) \end{aligned} \right\} (\mathrm{B}\beta)
\end{aligned}$$

$$\left.\begin{aligned}&+\frac{\beta}{v}\int_{V^2} dr_{n+1}\, dr_{n+2}\, r_{n+1}\cdot\partial_{n+1}v(r_{n+1}, r_{n+2})\\&\times\rho_2^V(r_{n+1}, r_{n+2})\,\rho_n^V(r_1,..., r_n)\end{aligned}\right\}\ (\mathrm{B}\gamma)$$

$(\mathrm{B}\alpha)$ is written in the form

$$(\mathrm{B}\alpha) = -\frac{\beta}{v}\int_V dr_{n+1}\, r_{n+1}\cdot\left[\sum_{i=1}^{n}\partial_{n+1}v(r_{n+1}, r_i)\,\rho_{n+1}^V(r_1,..., r_{n+1})\right.$$
$$\left.+\int_V dr_{n+2}\,\partial_{n+1}v(r_{n+1}, r_{n+2})\,\rho_{n+2}^V(r_1,..., r_{n+2})\right]$$

The term in brackets is the rhs of the hierarchy (5) for $\partial_{n+1}\rho_{n+1}^V$-$(r_1,..., r_{n+1})$.

Thus we are led for $(\mathrm{B}\alpha)$ to

$$(\mathrm{B}\alpha) = \frac{1}{v}\int_V dr_{n+1}\, r_{n+1}\cdot\partial_{n+1}\rho_{n+1}^V(r_1,..., r_{n+1})$$

In the same way

$$(\mathrm{B}\beta) = -\frac{\beta}{v}\sum_{i=1}^{n} r_i\cdot\left[\sum_{\substack{j=1\\ j\neq i}}^{n}\partial_i v(r_i, r_j)\,\rho_n^V(r_1,..., r_n)\right.$$
$$\left.+\int_V dr_{n+1}\,\partial_i v(r_i, r_{n+1})\,\rho_{n+1}^V(r_1,..., r_{n+1})\right]$$

is transformed to

$$(\mathrm{B}\beta) = \frac{1}{v}\sum_{i=1}^{n} r_i\cdot\partial_i\rho_n^V(r_1,..., r_n)$$

by using the hierarchy (5) for $\partial_i\rho_n^V(r_1,..., r_n)$ and $(\mathrm{B}\gamma)$ is equal to

$$(\mathrm{B}\gamma) = -\frac{1}{v}\rho_n^V(r_1,..., r_n)\int_V dr_{n+1}\, r_{n+1}\cdot\partial_{n+1}\rho_1^V(r_{n+1})$$

with the help of the hierarchy (5) for $\partial_{n+1}\rho_1^V(r_{n+1})$.

The total (B) is obtained

$$(\mathrm{B}) = \frac{1}{v}\int_V dr_{n+1}\, r_{n+1}\cdot\partial_{n+1}\{\rho_{n+1}^V(r_1,..., r_{n+1}) - \rho_1^V(r_{n+1})\,\rho_n^V(r_1,..., r_n)\}$$
$$+\frac{1}{v}\sum_{i=1}^{n} r_i\cdot\partial_i\rho_n^V(r_1,..., r_n)$$

and for $(\mathrm{A})+(\mathrm{B})$ we get

$$(\mathrm{A})+(\mathrm{B}) = -n\rho_n^V(r_1,..., r_n) + \frac{1}{v}\int_V dr\, r\cdot\partial\{\rho_{n+1}^V(r_1,..., r_n, r) - \rho_1^V(r)\,\rho_n^V(r_1,..., r_n)\}$$

$$= \frac{1}{v}\oint_S ds\cdot r\{\rho_{n+1}^V(r_1,..., r_n, r) - \rho_1^V(r)\,\rho_n^V(r_1,..., r_n)\}$$

$$-n\rho_n^V(r_1,..., r_n) - \int_V dr\,\{\rho_{n+1}^V(r_1,..., r_n, r) - \rho_1^V(r)\,\rho_n^V(r_1,..., r_n)\}$$

which gives (12) by taking into account the sum rules (4) for the ρ_n^V.

APPENDIX B

Here we recall the link between the asymptotic behavior of the functions ρ_n^T and Φ_n and we give the perfect screening conditions (PSC) which are needed in Sections 3 and 4. From the hierarchy equation (6), it is easily shown that the function $\rho_{n+1}^{VT}(r_1,..., r_n | r)$, (14), satisfies

$$\begin{aligned}
&\nabla\rho_{n+1}^{VT}(r_1,..., r_n | r)\\
&\quad = -\beta\int_V dr'\,\nabla v_s(r-r')\\
&\quad\times\Big[\rho_{n+2}^V(r_1,..., r_n, r, r') - \rho_2^V(r, r')\,\rho_n^V(r_1,..., r_n)\\
&\quad + \rho_{n+1}^V(r_1,..., r_n, r)\sum_{i=1}^n \delta(r'-r_i)\Big]\\
&\quad -\beta\int_V dr'\,\nabla v_c(r-r')\\
&\quad\times\Big[\rho_{n+2}^{VT}(r_1,..., r_n | r, r') + \rho_{n+1}^{VT}(r_1,..., r_n | r)\\
&\quad\times\Big\{\sum_{i=1}^n \delta(r'-r_i) + \rho_1^V(r') - \rho\Big\}\Big]\\
&\quad -\beta\rho_1^V(r)\,\rho_n^V(r_1,..., r_n)\,\nabla\Phi_n^V(r_1,..., r_n | r)
\end{aligned}\tag{B1}$$

where the truncated function

$$\begin{aligned}
&\rho_{n+2}^{VT}(r_1,..., r_n | r, r')\\
&\quad = \rho_{n+2}^V(r_1,..., r_n, r, r') - \rho_1^V(r)\,\rho_{n+1}^V(r_1,..., r_n, r')\\
&\quad - \rho_1^V(r')\,\rho_{n+1}^V(r_1,..., r_n, r)\\
&\quad - \rho_2^V(r, r')\,\rho_n^V(r_1,..., r_n) + 2\rho_1^V(r')\,\rho_1^V(r)\,\rho_n^V(r_1,..., r_n)
\end{aligned}\tag{B2}$$

will, in the TL, exhibit clustering properties for the two variables r and r'. We shall not go into details of the TL of (B1).[1] We just mention that the clustering property for $\Phi_n(r_1,..., r_n | r)$ follows from the clustering properties of $\rho^T_{n+1}(r_1,..., r_n | r)$ and $\rho^T_{n+2}(r_1,..., r_n | r, r')$ and from the short-range behavior of v_s. We shall assume that the clustering of these functions and v_s are such that

$$\lim_{|r| \to \infty} r^\nu \Phi_n(r_1,..., r_n | r) = 0 \tag{B3}$$

$r_1,..., r_n$ fixed and finite.

It follows from the definition of Φ_n, (14), that

$$\int dr'\, r'^l g_l(\hat{r} \cdot \hat{r}')\, D_n(r_1,..., r_n | r') = 0, \qquad l = 0, 1, 2 \tag{B4}$$

where

$$\begin{aligned} g_l(\hat{r} \cdot \hat{r}') &= P_l(\hat{r} \cdot \hat{r}') \qquad (\nu = 3) \\ &= \cos(l\phi) \qquad (\nu = 2) \\ \cos\phi &= (\hat{r} \cdot \hat{r}') \end{aligned} \tag{B5}$$

The P_l are the Legendre polynomials. We deduce from (B4) the following PSC:

$$\begin{aligned} l = 0: \qquad & \int dr'\, \rho^T_2(r') = -\rho \\ & \int dr'\, \rho^T_3(r, r') = -2\rho^T_2(r) \\ & \int dr'\, \rho^S_3(r, r') = -2\rho_2(r) \\ l = 1: \qquad & \int dr'\, r' g_1(\hat{r} \cdot \hat{r}')\, \rho^T_3(r, r') = -r\rho^T_2(r) \\ & \int dr'\, r' g_1(\hat{r} \cdot \hat{r}')\, \rho^S_3(r, r') = -r\rho_2(r) \\ l = 2: \qquad & \int dr'\, r'^2 g_2(\hat{r} \cdot \hat{r}')\, \rho^T_3(r, r') = -r^2\rho^T_2(r) \\ & \int dr'\, r'^2 g_2(\hat{r} \cdot \hat{r}')\, \rho^S_3(r, r') = -r^2\rho_2(r) \end{aligned} \tag{B6}$$

ρ^S_3 is defined by (25).

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