On the compressibility of a one-component plasma

M Baus†

Chimie-Physique II, Université Libre de Bruxelles, CP 231, B—1050 Bruxelles, Belgium

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Abstract. We consider a fluid of charged particles embedded in a neutralising background and, in contradistinction with ordinary fluids, define its isothermal compressibility from the k^4-term of the small-wavevector expansion ($k \to 0$) of the static structure factor $S(k)$. We then show that this compressibility can nevertheless also be written as a thermodynamic derivative but that contrary to what happens for ordinary fluids it is *not* a positive semidefinite quantity, in agreement with the recent numerical results obtained for charged fluids.

1. Introduction

Recently the study of ionic fluids has attracted a lot of interest. The presence in these systems of long-ranged Coulomb forces makes it necessary to reconsider some of the well known results for ordinary fluids. An impression of the present state of knowledge can be obtained from two recent and complementary reviews (March and Tosi 1976, Baus 1978).

In this work we will be concerned only with the simplest such ionic fluid generally known as the one-component plasma (OCP). The OCP is composed of one species of mobile point charges embedded in an inert neutralising background. The interaction potential between the mobile charges is assumed to be purely Coulombic although the presence of non-Coulombic short-ranged forces will not alter the characteristic features of the OCP. Here this system will be described classically and only its static properties will be considered.

The main purpose of this work then will be to proof the *equivalance* between two independent definitions of the isothermal compressibility of the OCP, one obtained from the static structure factor $S(k)$ and one obtained from the equation of state of the OCP. This well known problem for ordinary fluids has to be reconsidered for the case of the OCP mainly because $S(k)$ *vanishes* with k as a result of the long-ranged Coulomb interactions. In the literature this equivalence was assumed *a priori* and was shown to lead moreover to negative values of the compressibility in the case of a strongly-coupled OCP. Such negative values have been obtained both from approximate theories of the equation of state (Totsuji and Ichimaru 1974) and from computer simulations (Vieille-fosse and Hansen 1975). We will show that these negative values do not result from some improper identification of the compressibility but instead reflect the particular properties of the OCP. We will however say nothing about the question, which is still the object of a strong debate, of what precisely happens to the OCP at the point where its compressibility first becomes negative.

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In § 2 we outline the proof for ordinary fluids following hereby very closely the work of Schofield (1966). This allows us to introduce the basic definitions and to fix the notation. In § 3 we review the various definitions of the compressibility of the OCP. The equivalence proof for the OCP is given in § 4 while the corresponding equation of state is calculated in § 5. Our conclusions are summarised in the final section.

2. Compressibility of ordinary fluids

2.1. Basic definitions

All information of interest for the study of the static properties of fluid systems can be most conveniently derived from the static structure factor, $S(k)$, of the number density fluctuations, $n_k(t) = \sum_{j=1}^N \exp i\mathbf{k} \cdot \mathbf{x}_j(t)$ of the N particles located at time t at the positions $\{\mathbf{x}_j(t)\}$. More precisely we have[†]:

$$S(k) = (1/n)\langle n_{-k}(0)n_k(0)\rangle \tag{1}$$

where $\langle \ldots \rangle$ denotes a canonical equilibrium average, *divided* by the volume Ω and followed by the thermodynamic limit[‡] $(N \to \infty, \Omega \to \infty)$ at fixed density $n = N/\Omega$. It is also very convenient to introduce as an auxiliary function the Ornstein–Zernike direct correlation function $c(k)$ related to $S(k)$ by the well known relation:

$$S(k) = (1 - c(k))^{-1}. \tag{2}$$

Notice that our definitions of $S(k)$ and $c(k)$ are standard except that we have made them dimensionless by absorbing an appropriate density factor into the definition of $c(k)$ and $S(k)$. We now *define* the isothermal compressibility χ_T through the relation:

$$\lim_{k=0} S(k) = \chi_T/\chi_T^0 \tag{3}$$

where the ideal gas compressibility, $\chi_T^0 = \beta/n$, also makes the RHS of equation (3) dimensionless $(\beta = (k_B T)^{-1}$ is the inverse equilibrium temperature in energy units). Equation (3) is usually referred to as the compressibility sum rule because of the fact that $S(k)$ is also the zeroth-order frequency sum rule of the dynamic structure factor

$$S(k, \omega) \quad \text{i.e.} \quad S(k) = \int d\omega \, S(k, \omega).$$

Using equation (2) we can translate equation (3) into the equivalent definition:

$$\lim_{k=0} c(k) = 1 - (\chi_T^0/\chi_T). \tag{4}$$

We now would also like to give χ_T its thermodynamic meaning as a thermodynamic derivative:

$$\frac{\chi_T^0}{\chi_T} = \beta \frac{\partial p}{\partial n}\bigg|_T \tag{5}$$

[†] Notice that with the present definition we have $S(k) = n8\pi^3\delta(k) + (1/n)\langle \delta n_{-k}\delta n_k\rangle$ where $\delta n_k = n_k(0) - N\delta_k^{K}$. For $k \neq 0$ this difference with the usual definition of $S(k)$ is immaterial and in the present context equation (1) is the most convenient.

[‡] For the OCP this limit does not exist for the grand-canonical ensemble. Here we have thus to depart slightly from the original work of Schofield (1966).

where p is the thermodynamic pressure entering the equation of state $p = p(n, T)$. In order to establish the equivalence between the two definitions of say equation (4) and equation (5) and identify hereby the microscopic expression of the thermodynamic pressure p, we use the microscopic theory of thermodynamic fluctuations in the original setting of Schofield (1968).

2.2. *Microscopic theory of thermodynamic fluctuations*

To any microscopic density $a(r, t)$ we associate its Fourier transform:

$$a_k(t) = \int dr\, a(r, t) \exp i\mathbf{k} \cdot \mathbf{r} \tag{6}$$

and from the set of microscopic variables $\{a_k(t)\}$ we select an orthogonal set of r conserved variables $\{x_k^j(t); j = 1, \ldots, r\}$. The fact that the $x_k^j(t)$ variables are conserved implies that there are r microscopic conservation laws of the form $\dot{x}_k^j(t) = i\mathbf{k} \cdot \mathbf{\mathcal{J}}_k^j(t)$, where $\dot{x}_k^j(t)$ is the time derivative of $x_k^j(t)$ and $\mathbf{\mathcal{J}}_k^j(t)$ the current conjugated to $x_k^j(t)$. If we define moreover the component of a variable $a_k(t)$ along the variable $b_k(t)$, i.e. the projection of $a_k(t)$ onto $b_k(t)$, by

$$\langle b_{-k}(t) a_k(t) \rangle / \langle b_{-k}(t) b_k(t) \rangle$$

then the set of conserved variables will be orthogonal if $\langle x_{-k}^i(t) x_k^j(t) \rangle$ vanishes for all $i \neq j$. With the aid of these definitions we can decompose each $a_k(t)$ into a conserved part, $a_k'(t)$, and a nonconserved part, $a_k''(t)$, by projecting $a_k(t)$ onto the various conserved variables according to:

$$a_k(t) = a_k'(t) + a_k''(t) \tag{7a}$$

$$a_k'(t) = \sum_{j=1}^{r} \frac{\langle x_{-k}^j(t) a_k(t) \rangle}{\langle x_{-k}^j(t) x_k^j(t) \rangle} x_k^j(t) \tag{7b}$$

where in equation (7b), r now denotes the total number of conserved variables, i.e. $r = 5$ for the one-component systems considered here. Let now a and $\{x^j\}$ denote the macroscopic variables corresponding respectively to $a_k(t)$ and $\{x_k^j(t)\}$. We have, for instance,

$$a = \langle \lim_{k=0} a_k(t) \rangle$$

where the $k \to 0$ limit has to be taken before the ensemble average implied by $\langle \ldots \rangle$ because of the translational invariance of the equilibrium ensemble. Now if the macroscopic variable, a, is only a function of the conserved variables $\{x^j\}$, i.e. if we expect that $a = a(\{x^j\})$, then a small change Δx^j in the various x^j values will produce a change Δa in the a variable given by:

$$\Delta a = \sum_{j=1}^{r} \frac{\partial a}{\partial x^j} \Delta x^j \tag{8}$$

where it is understood that the derivative $(\partial a / \partial x^j)$ is taken keeping all x^i with $i \neq j$ constant. In order to reproduce equation (8) from equation (7) we proceed as follows. We first take the macroscopic limit $(k \to 0)$ and then take the average of equation (7) with the difference of two equilibrium distributions differing only slightly from each other in the macroscopic parameters x^j. Equation (8) will then follow from equation (7)

provided we make the following identifications:

$$\frac{\partial a}{\partial x^i} = \lim_{k=0} \frac{\langle x^i_{-k} a_k \rangle}{\langle x^i_{-k} x^i_k \rangle} \tag{9a}$$

$$a = \langle \lim_{k=0} a_k \rangle \qquad x^i = \langle \lim_{k=0} x^i_k \rangle \tag{9b}$$

Because of the stationary character of the equilibrium ensemble and the fact that only equal-time correlations will be considered here we have dropped the time variable in equation (9) and will do this henceforth. The underlying assumption used in obtaining equation (9) is that the nonconserved part, a''_k, of a_k does not contribute to the change in the macroscopic variable a produced by the changes in the conserved variables. To a lesser extent we have also assumed that the limits of the products appearing in the RHS of equation (7b) are given by the products of the limits involved†.

2.3. The microscopic pressure fluctuations

Let us write the microscopic conservations for the number density and total momentum density as:

$$\dot{n}_k = i\boldsymbol{k} \cdot \boldsymbol{j}_k \tag{10a}$$

$$\dot{\boldsymbol{j}}_k = i\boldsymbol{k} \cdot \boldsymbol{\sigma}_k \tag{10b}$$

where $\boldsymbol{j}_k$ and $\boldsymbol{\sigma}_k$ are the variables corresponding to the current density and stress tensor. The explicit microscopic expression of $\boldsymbol{j}_k$ and $\boldsymbol{\sigma}_k$ will not be needed here but they can be found, for instance, in Schofield (1966). We now *define* the microscopic fluctuation of the mechanical pressure, p_k, by:

$$p_k = m\hat{\boldsymbol{k}} \cdot \boldsymbol{\sigma}_k \cdot \hat{\boldsymbol{k}} \tag{11}$$

where $\hat{\boldsymbol{k}} = \boldsymbol{k}/|\boldsymbol{k}|$ is the unit vector along $\boldsymbol{k}$ and m the mass of the particles. Notice that in the present equilibrium context it is justified to call any variable a_k a fluctuation because its equilibrium average $\langle a_k \rangle$ vanishes for $k \neq 0$ although $\langle \lim_{k=0} a_k \rangle$ will in general be different from zero.

Before closing this section let us recall an important sum rule involving p_k. As already observed above, the stationary property of the equilibrium distribution implies that all equal-time correlation functions $\langle a_{-k}(t)b_k(t) \rangle$ are in fact time-independent, i.e. $\langle a_{-k}(t)b_k(t) \rangle = \langle a_{-k}(0)b_k(0) \rangle$. As noted by Schofield (1966) this property can be used to obtain sum rules. Indeed, taking the time derivative at $t = 0$ of $\langle a_{-k}(t)b_k(t) \rangle$ we obtain because of the stationarity property that $\langle \dot{a}_{-k}b_k \rangle + \langle a_{-k}\dot{b}_k \rangle = 0$ and specialising to the particular case $a_k = n_k$ and $b_k = \dot{n}_k$ we obtain the well known second-order frequency sum rule of the dynamic structure factor, $\int d\omega \, \omega^2 \rho(\boldsymbol{k}, \omega) \equiv -\langle n_{-k}\ddot{n}_k \rangle$ in the form:

$$\langle \dot{n}_{-k}\dot{n}_k \rangle + \langle n_{-k}\ddot{n}_k \rangle = 0. \tag{12}$$

From equation (10) we have moreover:

$$\langle n_{-k}\ddot{n}_k \rangle = -\langle n_{-k}\boldsymbol{k} \cdot \boldsymbol{\sigma}_k \cdot \boldsymbol{k} \rangle \tag{13}$$

while by virtue of the fact that in a classical system the velocity and position averages

† This is to say, we assume that all these limits do in fact exist.

factorise we also have the simple result:

$$\langle \dot{n}_{-k} \dot{n}_k \rangle = nk^2 v_0^2 \tag{14}$$

where $v_0 = (m\beta)^{-1/2}$ is the thermal velocity. Substituting the result of equations (13) and (14) into equation (12) and using the definition of equation (11) we rewrite the sum rule, equation (12), as:

$$p^0 = \langle n_{-k} p_k \rangle \tag{15}$$

where $p^0 = n/\beta$ is the ideal gas pressure.

2.4. The equation of state

We now return to the original problem and combine equations (1) and (2) with equation (15) to obtain:

$$1 - c(k) = \beta \frac{\langle n_{-k} p_k \rangle}{\langle n_{-k} n_k \rangle} \tag{16}$$

so that equation (4) becomes now:

$$\frac{\chi_T^0}{\chi_T} = \beta \lim_{k=0} \frac{\langle n_{-k} p_k \rangle}{\langle n_{-k} n_k \rangle} \tag{17}$$

and hence the inverse compressibility is also the $k \to 0$ limit of the projection of the pressure fluctuation p_k onto the density fluctuation n_k. According to equation (9) the RHS of equation (17) can finally also be written as a thermodynamic derivative which becomes identical with equation (5), i.e. the desired result, provided we identify the thermodynamic presure p as:

$$p = \langle \lim_{k=0} p_k \rangle \tag{18}$$

where p_k was defined by equation (11) (notice also the trivial result $n = \langle \lim_{k=0} n_k \rangle$). Hence the isothermal compressibility defined by equation (4) is consistent with the thermodynamic definition of equation (5) provided the derivative $\partial p/\partial n|_T$ is computed from the equation of state given by equation (18). Notice finally that because of rotational invariance we also have:

$$\langle \lim_{k=0} \hat{k} \cdot \sigma_k \cdot \hat{k} \rangle = \tfrac{1}{3} \langle \lim_{k=0} \sigma \hbar_k \rangle \tag{19}$$

so that equation (18) is in fact the virial equation of state. This then constitutes the proof of the equivalence of the two definitions of the compressibility for ordinary simple fluids. As shown by Schofield (1966) the expressions introduced above can also be rewritten in terms of the reduced equilibrium distribution functions. For later reference we quote here the result obtained for equation (18):

$$p = p^0 - \frac{n^2}{6} \int dr g(r) r \cdot \nabla v(r) \tag{20}$$

where $p^0 = n/\beta$, $v(r)$ is the interaction potential and $g(r)$ the equilibrium pair distribution related to $S(k)$ by

$$S(k) = n 8\pi^3 \delta(k) + 1 + n \int dr (g(r) - 1) \exp i k \cdot r. \tag{21}$$

We close this section by observing that from equation (15) and the fact that $\langle n_{-k}n_k\rangle \equiv \langle|n_k|^2\rangle$ it follows from equation (17) that χ_T is a positive semidefinite quantity.

3. Compressibility of the OCP

Whereas the previous section merely served as an introduction we now come to our main topic. For the OCP equations (1) and (2) are still valid but already for equation (3) things change because for the OCP, $S(k)$ *vanishes* with k. The basic observation here is that in the OCP the charge- and number-density fluctuations are proportional to each other so that $S(k)$ also describes the charge-density fluctuations bringing naturally the long-ranged Coulomb forces into play. This is most easily seen by recalling that the direct correlation function $c(k)$ which is still defined by equation (2), is expected to have the following small k behaviour:

$$c(k) = -n\beta V_k \qquad \text{for } k \to 0 \tag{22}$$

where V_k is the Fourier transform of the potential. Indeed, for large interparticle separations (or small k) one expects $c(k)$ to take on its weak-coupling value because distant particles can only be weakly coupled. Now the weak-coupling value of $c(k)$ is precisely $-n\beta V_k$ and hence we have equation (22). If, however, at least part of the potential is Coulombic[†], say

$$V_k = V_k^c + V_k^{nc} \qquad \text{with } V_k^c = 4\pi e^2/k^2$$

e being the charge of the mobile particles, then $c(k)$ is seen from equation (22) to *diverge* as $-k_D^2/k^2$, for small k, whereas from equation (2) $S(k)$ is seen to vanish as k^2/k_D^2 for small k (here $k_D^2 = 4\pi e^2 n\beta$ is the square of the Debye wavevector). As we have argued elsewhere (Baus 1975) one can expect however that once we have extracted this singular contribution

$$c^S(k) = -k_D^2/k^2 \qquad \text{from } c(k) = c^S(k) + c^R(k)$$

the remainder, $c^R(k)$, will be a regular function of k for small k, i.e.:

$$c(k) = -\frac{k_D^2}{k^2} + c^R(0) + \mathcal{O}(k^2) \tag{23}$$

or equivalently, using equation (2):

$$S(k) = (k^2/k_D^2) + (k^4/k_D^4)(C^R(0) - 1) + \mathcal{O}(k^6). \tag{24}$$

These results, equations (23) and (24), differ profoundly from equations (3) and (4) and reflect the manner in which the Coulomb forces affect the macroscopic behaviour $(k \to 0)$. Using equation (21) the content of equation (24) can also be translated into real-space position sum rules for $g(r)$:

$$n \int \mathrm{d}\mathbf{r}\, (g(r) - 1) = -1 \tag{25a}$$

$$n \int \mathrm{d}r \frac{(i\hat{\mathbf{k}} \cdot \mathbf{r})^2}{2!} (g(r) - 1) = k_D^{-2} \tag{25b}$$

[†] As we will not be aiming at full generality it might be useful to point out here that most of the results derived below remain valid when a short ranged potential is added to the Coulomb potential.

$$n \int \, \mathrm{d}r \frac{(\mathrm{i}\hat{k} \cdot r)^4}{4!} (g(r) - 1) = k_D^{-4} (C^R(0) - 1) \tag{25c}$$

in which case equations $(25a, b)$ are usually referred to as the two Stillinger–Lovett moment conditions. Still another and perhaps more physical way of stating the same basic property expressed in equation (23) can be obtained by formulating it in terms of the static dielectric constant $\epsilon(k)$ defined by:

$$S(k) = (k^2/k_D^2)[1 - (1/\epsilon(k))]. \tag{26}$$

The condition formulated in equation (23) can now be re-expressed by requiring that the system exhibits perfect screening in the limit of small k, i.e. that $\epsilon(k)$ behaves like $\epsilon(k) = 1 + k_S^2/k^2$ for small k implying that the effective potential $V_k^{\mathrm{eff}} = V_k^c/\epsilon(k)$ exhibits perfect screening, $V_k^{\mathrm{eff}} = 4\pi e^2/(k^2 + k_S^2)$ for small k, with k_S as inverse screening length. This perfect screening condition is equivalent to the above condition provided the screening wavevector k_S is related to $c^R(0)$ of equation (23) through the relation:

$$(k_D^2/k_S^2) = 1 - c^R(0) \tag{27}$$

Finally, a straightforward application of macroscopic thermodynamic theory has led Vieillefosse and Hansen (1975) to the expression:

$$S(k) = \left(\frac{k_D^2}{k^2} + \frac{\chi_T^0}{\chi_T}\right)^{-1} \qquad \text{for } k \to 0 \tag{28}$$

where $\chi_T^0 = \beta/n$, while χ_T was defined by them as the isothermal compressibility of the OCP. For this definition of χ_T to be consistent with the above equation (23) we need to satisfy:

$$\lim_{k=0} [c(k) + (k_D^2/k^2)] \equiv c^R(0) = 1 - (\chi_T^0/\chi_T) \tag{29}$$

where we have used equation (2). This condition nicely fits the standard definition, equation (4), once the singular part $C^S(k) = -k_D^2/k^2$ has been extracted from $C(k)$. The *main question* now is whether the compressibility of the OCP defined by one of the above equivalent relations, for instance equation (29), also deserves its name, i.e. whether it can also be written as a thermodynamic derivative, for instance equation (5), and if yes with what definition of the thermodynamic pressure. That this question is not solely a matter of principle can be seen from the fact that if χ_T^{-1} is identified as $n(\partial p/\partial n)|_T$ (see equation (5)) and the pressure derivative computed from the following equation of state[†]:

$$p = p^0 + (n^2/6) \int \, \mathrm{d}r \, V(r)(g(r) - 1) \tag{30}$$

for a pure Coulomb potential $V(r) = e^2/2$, then the numerical results of both approximate theories (Totsuji and Ichimaru 1974) and of molecular dynamics studies (Vieillefosse and Hansen 1975) indicate that $(\partial p/\partial n)|_T$ takes on negative values when the system's coupling constant $\Gamma = e^2\beta[4(\pi/3)n]^{1/3}$ exceeds a critical value $\Gamma_c \sim 3$. Such an unusual behaviour for a compressibility immediately raises the question whether the

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[†] It is of interest to observe that this equation can also be obtained from the volume derivative of the free energy by the usual scaling procedure provided the background is explicitly taken into account before the thermodynamic limit is taken.

system exhibits a phase transition at $\Gamma = \Gamma_c$ or whether the compressibility has been improperly identified. Leaving aside the question of the phase transition (which has as yet not been observed)† we will show in the next section that the OCP compressibility defined by equation (29) can indeed be identified with equation (5) if equation (30) is used to define the pressure.

4. The OCP compressibility as a thermodynamic derivative

We will now proceed just as in § 2 but starting this time from the definition given in equation (29) which we write as:

$$\frac{\chi_T^0}{\chi_T} = \lim_{k=0} \left(1 - c(k) - \frac{k_D^2}{k^2} \right) \tag{31}$$

or equivalently using equations (1.2) and equations (15) and (16):

$$\frac{\chi_T^0}{\chi_T} = \lim_{k=0} \left(\beta \frac{\langle n_{-k} p_k \rangle}{\langle n_{-k} n_k \rangle} - \frac{k_D^2}{k^2} \right). \tag{32}$$

Notice the difference between equation (32) and equation (17). At this point it is already clear that the OCP compressibility is not a positive semidefinite quantity‡ because the RHS of equations (32) is the *difference* of two positive and singular quantities (recall from equation (15) that $\langle n_{-k} p_k \rangle$ is always positive). Moreover the existence of the limit in the RHS of equation (32) is consistent with our previous relations since equation (15) and equations (1, 24) imply that both terms of the difference in the RHS of equation (32) exhibit the same small k singularity. We now proceed by extracting this singular behaviour. To do so we compute the pressure fluctuation p_k from equations (10) and (11) for the case of pure coulomb interactions ($V_k = 4\pi e^2/k^2$). Starting from

$$n_k = \sum_{j=1}^{N} \exp i\mathbf{k} \cdot \mathbf{x}_j$$

one obtains

$$\dot{n}_k = \sum_{j=1}^{N} i\mathbf{k} \cdot \mathbf{v}_j \exp i\mathbf{k} \cdot \mathbf{x}_j \equiv i\mathbf{k} \cdot \mathbf{j}_k \qquad \text{where } \mathbf{v}_j = \dot{\mathbf{x}}_j$$

and moreover

$$\ddot{n}_k = \sum_{j=1}^{N} \{(i\mathbf{k} \cdot \mathbf{v}_j)^2 + i\mathbf{k} \cdot \dot{\mathbf{v}}_j\} \exp i\mathbf{k} \cdot \mathbf{x}_j \equiv -\mathbf{k} \cdot \boldsymbol{\sigma}_k \cdot \mathbf{k} \equiv -(k^2/m)p_k$$

where the definitions of equations (10) and (11) have been used. As usual, we can split $p_k = p_k^K + p_k^P$ into a kinetic part:

$$p_k^K = m \sum_{j=1}^{N} (\hat{\mathbf{k}} \cdot \mathbf{v}_j)^2 \exp i\mathbf{k} \cdot \mathbf{x}_j \tag{33}$$

† Notice that because of the small k Coulomb-divergence displayed for instance in equation (28), the divergence of χ_T at $\Gamma = \Gamma_c$ does not lead to a divergence in $S(k)$. In this sense the OCP remains thermodynamically stable at $\Gamma = \Gamma_c$. This however may not be a sufficient condition to preclude the presence of more refined types of phase transitions.
‡ The same conclusion can also be obtained from the rigorous results of Lieb and Narnhofer (1975) indicating that the canonical free energy of the OCP lacks the appropriate convexity property.

and a potential part:

$$p_k^P = \sum_{j=1}^{N} -i \frac{k}{k^2} \cdot F_j \exp ik \cdot x_j \tag{34}$$

where $F_j = m\dot{v}_j$ is the force acting on particle j which for pure Coulomb interactions can be represented by the following Fourier series:

$$F_j = (4\pi e^2/\Omega) \sum_l{}' \sum_i{}' \, i \frac{l}{l^2} \exp il \cdot (x_i \cdot x_j). \tag{35}$$

In equation (35) the dash on the particle summation indicates that the self-interactions have to be excluded ($i \neq j$) while the dash on the l sum refers to the restriction $l \neq 0$ which takes into account the contribution of the neutralising background to the spatially homogeneous part of the electric potential. We now substitute equation (35) into equation (34) and further split p_k^P as $p_k^P = p_k' + p_k''$ by separating out the contribution to equation (34) from the $l = k$ term in the RHS of equation (35). The first term p_k' represents then a one-body contribution originating from the microscopic electric potential fluctuation ϕ_k related to n_k by Poisson's equation, $\phi_k = (4\pi e/k^2)n_k$:

$$p_k' = n \sum_{j=1}^{N} \frac{4\pi e^2}{k^2} \exp ik \cdot x_j \equiv \frac{4\pi e^2 n}{k^2} n_k \equiv en\phi_k \tag{36}$$

while the remaining term p_k'' represents an intrinsically two-body contribution:

$$p_k'' = (4\pi e^2/\Omega) \sum_l{}'' \sum_{i,j}{}' \, (k \cdot l/k^2 l^2) \exp[i(k-l) \cdot x_j + il \cdot x_i] \tag{37}$$

where the double dash on the l sum indicates that now both the values $l = 0$ and $l = k$ are to be excluded from the sum. Substituting now $p_k = p_k^K + p_k' + p_k''$ as obtained from equations (33, 36, 37) back into equation (32) we see that the contribution of the microscopic electric potential fluctuation ϕ_k to the mechanical pressure fluctuation p_k, namely p_k' defined in equation (3.6), exactly compensates the singular second term in the RHS of equation (32) leaving us with:

$$\frac{\chi_T^0}{\chi_T} = \beta \lim_{k=0} \frac{\langle n_{-k} p_k^T \rangle}{\langle n_{-k} n_k \rangle} \tag{38}$$

where the remainder $p_k^T = p_k^K + p_k''$ will be called, for reasons which will soon become clear, the thermal part of p_k. With the aid of equation (9) we now obtain from equation (38):

$$\frac{\chi_T^0}{\chi_T} = \beta \frac{\partial p}{\partial n}\bigg|_T \tag{39}$$

with however a thermodynamic pressure p defined by:

$$p = \langle \lim_{k=0} p_k^T \rangle \tag{40}$$

instead of the usual result of equation (18). Hence we have shown that the OCP compressibility χ_T defined by one of the equivalent definitions given in § 3, for instance equation (29), can also be expressed as a thermodynamic derivative provided equation (40) is adopted as the definition of the thermodynamic pressure p. We reach therefore the conclusion that in the case of the OCP the thermodynamic pressure p is not related to

the fluctuation of the full mechanical stress tensor σ_k through equation (11) but only to its thermal part $(p_k^T = p_k^K + p_k'')$ on the exclusion of its electric part (p_k'). Notice the similarity between our microscopic result and the macroscopic treatment of Vieillefosse and Hansen (1975) who have added, *a posteriori*, the contribution of the macroscopic electric field to the macroscopic stress tensor.

5. The equation of state of the OCP

We now compute the RHS of equation (40) explicitly with the aid of equations (33), (37). After some simple algebra we obtain:

$$p = p^0 + \left\langle \lim_{k=0} (4\pi e^2/\Omega) \sum_l'' \sum_{i,j}' (\boldsymbol{k} \cdot \boldsymbol{l}/k^2 l^2)(1 + i\boldsymbol{k} \cdot \boldsymbol{x}_i + \mathcal{O}(k^2)) \exp i\boldsymbol{l} \cdot (\boldsymbol{x}_i - \boldsymbol{x}_j) \right\rangle \tag{41}$$

and will now analyse separately each of the three contributions to the second term in the RHS of equation (41). The first contribution will, because of the rotational invariance of the equilibrium distribution, lead in the thermodynamic limit to an odd l integral and hence vanish. The third contribution is $\mathcal{O}(k)$ so that we are left over with only the second contribution which we symmetrise and rewrite as:

$$\langle \ldots i\boldsymbol{k} \cdot \boldsymbol{x}_j \exp i\boldsymbol{l} \cdot (\boldsymbol{x}_i - \boldsymbol{x}_j) \rangle = \tfrac{1}{2} \langle \ldots i\boldsymbol{k} \cdot (\boldsymbol{x}_j - \boldsymbol{x}_i) \exp i\boldsymbol{l} \cdot (\boldsymbol{x}_i - \boldsymbol{x}_j) \rangle$$

$$= \tfrac{1}{2} \langle \ldots - \boldsymbol{k} \cdot (\partial/\partial \boldsymbol{l}) \exp i\boldsymbol{l} \cdot (\boldsymbol{x} x_i - \boldsymbol{x}_j) \rangle. \tag{42}$$

We can write moreover:

$$\langle \ldots (\boldsymbol{k} \cdot \boldsymbol{l}/k^2 l^2)[-\boldsymbol{k} \cdot (\partial/\partial \boldsymbol{l})] \exp i\boldsymbol{l} \cdot (\boldsymbol{x}_i - \boldsymbol{x}_j) \rangle$$

$$= \langle \ldots \{-\boldsymbol{k} \cdot (\partial/\partial \boldsymbol{l})[(\boldsymbol{k} \cdot \boldsymbol{l}/k^2 l^2) \exp i\boldsymbol{l} \cdot (\boldsymbol{x}_i - \boldsymbol{x}_j)]$$

$$+ (1/l^2)(1 - 2(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{l}})^2) \exp i\boldsymbol{l} \cdot (\boldsymbol{x}_i - \boldsymbol{x}_j)\} \rangle \tag{43}$$

where the first term in the RHS of equation (43) leads to a surface term which will vanish in the thermodynamic limit leaving us finally with the result $(V_k = 4\pi e^2/k^2)$:

$$p = p^0 + \tfrac{1}{2} \left\langle \frac{1}{\Omega} \sum_l'' \sum_{i,j}' V_l (1 - 2(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{l}})^2) \exp i\boldsymbol{l} \cdot (\boldsymbol{x}_i - \boldsymbol{x}_j) \right\rangle \tag{44}$$

or converting the l sum into an integral, which should be understood as a principal value, we obtain:

$$p = p^0 + (n/2) \int (\mathrm{d}\boldsymbol{l}/8\pi^3) V_l (1 - 2(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{l}})^2)(S(l) - 1). \tag{45}$$

Taking into account the rotational invariance of $S(l)$, the angular factor can be taken out from the integral in equation (45) leaving us finally with the result:

$$p = p^0 + (n/6) \int (\mathrm{d}\boldsymbol{l}/8\pi^3) V_l (S(l) - 1) \tag{46}$$

which when converted to position-space leads on account of equation (21) and the principal value restriction precisely to the expected result, equation (30).

6. Conclusions

The isothermal compressibility χ_T of a one-component plasma (embedded in an inert neutralising background) can be defined from one of the equivalent relations (see equations (24), (25c), (27), (29)):

$$\frac{\chi_T^0}{\chi_T} = \lim_{k=0} \frac{k_D^4}{k^4} \left(\frac{k^2}{k_D^2} - S(k) \right) \tag{47a}$$

$$= nk_D^4 \int dr \frac{(\hat{\boldsymbol{k}} \cdot \boldsymbol{r})^4}{4!} (1 - g(r)) \tag{47b}$$

$$= k_D^2 \lim_{k=0} [k^2 \epsilon(k)]^{-1} \tag{47c}$$

$$= \lim_{k=0} \left(1 - c(k) - \frac{k_D^2}{k^2} \right) \tag{47d}$$

which all differ from the relations, equations (3, 4), valid for an ordinary (uncharged) fluid. We have shown that notwithstanding this difference the OCP compressibility can also be written as a thermodynamic derivative (see equations (38) and (39)):

$$\frac{\chi_T^0}{\chi_T} = \beta \lim_{k=0} \frac{\langle n_{-k} p_k^T \rangle}{\langle n_{-k} n_k \rangle} = \beta \frac{\partial p}{\partial n} \Big|_T \tag{48}$$

where however the thermodynamic pressure p has now to be defined from the thermal part (p_k^T) of the mechanical stress tensor fluctuation $(p_k = p_k^T + p_k')$ disregarding the contribution (p_k') of the fluctuating electric potential. In other words, the 'virial' equation of state corresponding to equation (48) is no longer given by equation (18, 20) but by:

$$p = \langle \lim_{k=0} p_k^T \rangle = p^0 + (n/6) \int (dl/8\pi^3) V_l(S(l) - 1).$$

Moreover, the compressibility is now given (see equation (48)) as the ratio of two vanishing correlation functions. Indeed, $\langle n_{-k} n_k \rangle$ vanishes by virtue of equation (24) while $\langle n_{-k} p_k^T \rangle$ vanishes with k on the basis of the observation that the sum rule, equation (15), is exhausted for small k by the p_k' contribution to p_k as is easily seen from equation (36). Finally, whereas $\langle n_{-k} n_k \rangle$ is positive semidefinite, $\langle n_{-k} p_k^T \rangle$ is not, and hence the OCP compressibility is not a positive semidefinite quantity. The negative values obtained in the literature for χ_T from equations (48) and (49) can thus not be ascribed to some artefact but result directly from the particular properties of the OCP and mainly from the singular behaviour of $c(k)$ displayed in equation (23).

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