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FLUCTUATIONS IN A DENSE ONE-COMPONENT PLASMA

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The complete set of fluctuation formulae for the density, the pressure and the energy density of a one-component plasma is derived. The momentum balance equation contains a source term proportional to the electric field generated by the density fluctuations. This term, which diverges for small wave number, is shown to have a profound influence on the fluctuation formulae.

1. Introduction

In a plasma the fluctuations in macroscopic quantities are strongly influenced by the long-range Coulomb forces, since non-uniformities in the charge distribution are effectively suppressed. As a consequence the mean-square values of these fluctuations differ considerably from those of a neutral fluid.

Since fluctuation formulae play an important role in the analysis of the static and dynamic properties of a macroscopic system, it is of interest to derive them from microscopic theory by means of the methods of statistical mechanics. It is the purpose of this paper to present such a derivation and to obtain a complete set of fluctuation formulae for the density, the pressure and the energy density. As a model we shall use the classical one-component plasma, which consists of charged particles in a neutralizing background.

The fluctuations in a one-component plasma have been considered before[1–3]. However, in these treatments several assumptions on the precise form of thermodynamic fluctuation theory for a system with long-range interactions and on the behaviour of the pair correlation function for large distances were introduced. In the present paper the fluctuation formulae will be derived from first principles.

2. Balance equations of particle number, momentum and energy

In the course of the derivation of the fluctuation formulae we shall need the

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microscopic balance equations for the one-component plasma. These will be considered in the present section.

The Fourier-transformed particle density is defined as

$$n(\boldsymbol{k}) = \sum_{\alpha} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}, \tag{2.1}$$

with α labelling the particles, with positions $\boldsymbol{r}_\alpha$ and momenta $\boldsymbol{p}_\alpha$. Likewise, for the momentum density and the kinetic energy density we have

$$\boldsymbol{g}(\boldsymbol{k}) = \sum_{\alpha} \boldsymbol{p}_\alpha \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}, \tag{2.2}$$

$$\varepsilon^{\mathrm{kin}}(\boldsymbol{k}) = \sum_{\alpha} \frac{p_\alpha^2}{2m} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}. \tag{2.3}$$

The definition of the microscopic potential energy density depends on the way in which the long-range Coulomb interaction energy of the particles is localized. A convenient choice is[2])

$$\varepsilon^{\mathrm{pot}}(\boldsymbol{r}) = \tfrac{1}{2}[\boldsymbol{E}(\boldsymbol{r})]^2 - \varepsilon^{\mathrm{pot,\,self}}(\boldsymbol{r}). \tag{2.4}$$

Here $\boldsymbol{E}(\boldsymbol{r})$ is the electric field at the position $\boldsymbol{r}$:

$$\begin{aligned}\boldsymbol{E}(\boldsymbol{r}) &= -\boldsymbol{\nabla}\left[\sum_{\alpha} \frac{e}{4\pi|\boldsymbol{r}-\boldsymbol{r}_\alpha|} - \int^{V} \mathrm{d}\boldsymbol{r}' \frac{ne}{4\pi|\boldsymbol{r}-\boldsymbol{r}'|}\right] \\ &= -\frac{\mathrm{i}}{V} \sum_{\boldsymbol{q}(\neq \boldsymbol{0})} \frac{e\boldsymbol{q}}{q^2} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} n(\boldsymbol{q}),\end{aligned} \tag{2.5}$$

with V the volume of the system and $n = N/V$ the density. Furthermore, $\varepsilon^{\mathrm{pot,\,self}}(\boldsymbol{r})$ is the infinite self-energy, which is incorporated in $\frac{1}{2}E^2$. Upon Fourier transformation (2.4) becomes

$$\varepsilon^{\mathrm{pot}}(\boldsymbol{k}) = -\frac{1}{2V} \sum_{\boldsymbol{q}(\neq \boldsymbol{0}, \neq \boldsymbol{k})} \frac{e^2 \boldsymbol{q}\cdot(\boldsymbol{k}-\boldsymbol{q})}{q^2(\boldsymbol{k}-\boldsymbol{q})^2} \sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta} - \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}. \tag{2.6}$$

For small $\boldsymbol{k}$ one may write

$$\varepsilon^{\mathrm{pot}}(\boldsymbol{k}) = \frac{1}{2V} \sum_{\boldsymbol{q}(\neq \boldsymbol{0}, \neq \boldsymbol{k})} \frac{e^2}{q^2} \sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta} - \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}. \tag{2.7}$$

The total energy density $\varepsilon(\boldsymbol{k})$ is given by the sum of (2.3) and (2.6) or (2.7). For $\boldsymbol{k} = \boldsymbol{0}$ one recovers the Hamiltonian of the one-component plasma.

The continuity equation, which expresses the conservation of the number of particles, may be written as

$$\mathrm{i}Ln(\boldsymbol{k}) = -\mathrm{i}\boldsymbol{k}\cdot\frac{\boldsymbol{g}(\boldsymbol{k})}{m}. \tag{2.8}$$

Here L is the Liouville operator in phase space, which for an arbitrary function F determines its time derivative as $\dot{F} = \mathrm{i}LF$.

The momentum balance equation follows by evaluating the time derivative of $\boldsymbol{g}(\boldsymbol{k})$:

$$\mathrm{i}L\boldsymbol{g}(\boldsymbol{k}) = -\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}^{\mathrm{kin}}(\boldsymbol{k}) + \sum_{\alpha}\dot{\boldsymbol{p}}_\alpha\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}, \tag{2.9}$$

with $\boldsymbol{\tau}^{\mathrm{kin}}(\boldsymbol{k})$ the kinetic pressure tensor,

$$\boldsymbol{\tau}^{\mathrm{kin}}(\boldsymbol{k}) = \sum_{\alpha}\frac{\boldsymbol{p}_\alpha\boldsymbol{p}_\alpha}{m}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}. \tag{2.10}$$

Furthermore $\dot{\boldsymbol{p}}_\alpha$ follows from the equation of motion

$$\dot{\boldsymbol{p}}_\alpha = e\boldsymbol{E}'(\boldsymbol{r}_\alpha), \tag{2.11}$$

with $\boldsymbol{E}'(\boldsymbol{r}_\alpha)$ the electric field (at the position $\boldsymbol{r}_\alpha$) due to all particles $\beta \neq \alpha$ in the system. With the help of (2.5) one gets

$$\dot{\boldsymbol{p}}_\alpha = -\frac{\mathrm{i}}{V}\sum_{\boldsymbol{q}(\neq\boldsymbol{0})}\frac{e^2\boldsymbol{q}}{q^2}\sum_{\beta(\neq\alpha)}\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta}}. \tag{2.12}$$

Substituting this expression into (2.9), writing separately the contribution $\boldsymbol{q} = \boldsymbol{k}$ and symmetrizing the remaining terms with respect to the interchanges $\alpha \leftrightarrow \beta$, $\boldsymbol{q} \leftrightarrow \boldsymbol{k} - \boldsymbol{q}$ we obtain

$$\begin{aligned}\mathrm{i}L\boldsymbol{g}(\boldsymbol{k}) = {} & -\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}^{\mathrm{kin}}(\boldsymbol{k}) - \mathrm{i}\frac{ne^2\boldsymbol{k}}{k^2}n(\boldsymbol{k}) \\ & -\frac{\mathrm{i}}{2V}\sum_{\boldsymbol{q}(\neq\boldsymbol{0},\neq\boldsymbol{k})}\left[\frac{e^2\boldsymbol{q}}{q^2} + \frac{e^2(\boldsymbol{k}-\boldsymbol{q})}{(\boldsymbol{k}-\boldsymbol{q})^2}\right]\sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}}\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta}-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}.\end{aligned} \tag{2.13}$$

For small $\boldsymbol{k}$ the third term may be expanded, with the result

$$\mathrm{i}Lg(\boldsymbol{k}) = -\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\tau}(\boldsymbol{k}) - \mathrm{i}\frac{ne^2\boldsymbol{k}}{k^2}\,n(\boldsymbol{k})\,. \tag{2.14}$$

Here $\boldsymbol{\tau} = \boldsymbol{\tau}^{\mathrm{kin}} + \boldsymbol{\tau}^{\mathrm{pot}}$ contains the potential pressure

$$\boldsymbol{\tau}^{\mathrm{pot}}(\boldsymbol{k}) = \frac{1}{2V}\sum_{\boldsymbol{q}(\neq \boldsymbol{0},\neq \boldsymbol{k})}\frac{e^2}{q^2}\left(\boldsymbol{U} - \frac{2\boldsymbol{q}\boldsymbol{q}}{q^2}\right)\sum_{\substack{\alpha,\beta\\ \alpha\neq\beta}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta} - \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}\,. \tag{2.15}$$

with $\boldsymbol{U}$ the unit tensor. This expression differs from that given in ref. 2 by the exclusion of the term $\boldsymbol{q} = \boldsymbol{k}$ in the sum. Correspondingly, the balance equation (2.14) contains a term proportional to the electric field generated by the density fluctuation $n(\boldsymbol{k})$ (cf. ref. 3). This term will play an important role in the derivation of the fluctuation formulae.

The balance equation for the kinetic energy follows from (2.3) as

$$\mathrm{i}L\varepsilon^{\mathrm{kin}}(\boldsymbol{k}) = -\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{j}_\varepsilon^{\mathrm{kin}}(\boldsymbol{k}) - \frac{\mathrm{i}}{V}\sum_{\boldsymbol{q}(\neq\boldsymbol{0})}\frac{e^2}{q^2}\sum_{\substack{\alpha,\beta\\ \alpha\neq\beta}}\frac{\boldsymbol{q}\cdot\boldsymbol{p}_\alpha}{m}\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta} - \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}\,, \tag{2.16}$$

with the kinetic energy current

$$\boldsymbol{j}_\varepsilon^{\mathrm{kin}}(\boldsymbol{k}) = \sum_\alpha \frac{\boldsymbol{p}_\alpha}{m}\frac{p_\alpha^2}{2m}\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}\,, \tag{2.17}$$

which describes the convection of the kinetic energy. The balance equation of the potential energy is obtained by differentiation of (2.6) with respect to time

$$\mathrm{i}L\varepsilon^{\mathrm{pot}}(\boldsymbol{k}) = \frac{\mathrm{i}}{V}\sum_{\boldsymbol{q}(\neq\boldsymbol{0},\neq\boldsymbol{k})}\frac{e^2\boldsymbol{q}\cdot(\boldsymbol{k}-\boldsymbol{q})}{q^2(\boldsymbol{k}-\boldsymbol{q})^2}\sum_{\substack{\alpha,\beta\\ \alpha\neq\beta}}\frac{(\boldsymbol{k}-\boldsymbol{q})\cdot\boldsymbol{p}_\alpha}{m}\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta} - \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha} \tag{2.18}$$

By expansion, or equivalently from (2.7), one gets for small $\boldsymbol{k}$

$$\mathrm{i}L\varepsilon^{\mathrm{pot}}(\boldsymbol{k}) = -\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{j}_\varepsilon^{\mathrm{pot}}(\boldsymbol{k}) + \frac{\mathrm{i}}{V}\sum_{\boldsymbol{q}(\neq\boldsymbol{0},\neq\boldsymbol{k})}\frac{e^2}{q^2}\sum_{\substack{\alpha,\beta\\ \alpha\neq\beta}}\frac{\boldsymbol{q}\cdot\boldsymbol{p}_\alpha}{m}\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta} - \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha}\,, \tag{2.19}$$

with the potential energy current

$$j_\varepsilon^{\text{pot}}(\boldsymbol{k}) = \frac{1}{V} \sum_{\boldsymbol{q}(\neq \boldsymbol{0}, \neq \boldsymbol{k})} \frac{e^2}{q^2} \left(\boldsymbol{U} - \frac{\boldsymbol{q}\boldsymbol{q}}{q^2} \right) \cdot \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \frac{\boldsymbol{p}_\alpha}{m} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta} - \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\alpha} . \tag{2.20}$$

The term with $\boldsymbol{q} = \boldsymbol{k}$ in (2.16) may be neglected in the thermodynamic limit. As a consequence one finds from (2.16) and (2.19)

$$\mathrm{i}L\varepsilon(\boldsymbol{k}) = -\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{j}_\varepsilon(\boldsymbol{k}) , \tag{2.21}$$

with $\boldsymbol{j}_\varepsilon(\boldsymbol{k})$ the sum of (2.17) and (2.20).

3. Thermodynamic relations

The equilibrium properties of the one-component plasma follow with the use of the canonical ensemble. In particular, the internal energy and the static pressure are obtained from the canonical partition function and its derivatives[4]). An alternative way to determine these quantities starts from the microscopic expressions of the previous section. Putting $\boldsymbol{k} = \boldsymbol{0}$ in (2.3) and (2.7) and taking the canonical average we get in the thermodynamic limit

$$\begin{aligned} \frac{1}{V} \langle \varepsilon(\boldsymbol{k} = \boldsymbol{0}) \rangle &= \frac{3}{2} n k_\mathrm{B} T + \frac{1}{2V^2} \sum_{\boldsymbol{q}(\neq \boldsymbol{0})} \frac{e^2}{q^2} \left\langle \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta}} \right\rangle \\ &= \frac{3}{2} n k_\mathrm{B} T + \frac{1}{2} n^2 \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \frac{e^2}{q^2} h(q) \equiv n u , \end{aligned} \tag{3.1}$$

with u the internal energy per particle. Here we used the definition for the Fourier transform of the pair correlation function

$$\frac{1}{V} \left\langle \sum_{\substack{\alpha, \beta \\ \alpha \neq \beta}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\alpha\beta}} \right\rangle = n^2 h(q) . \tag{3.2}$$

Likewise one derives from (2.10) and (2.15)

$$\frac{1}{V} \langle \boldsymbol{\tau}(\boldsymbol{k} = \boldsymbol{0}) \rangle = n k_\mathrm{B} T \boldsymbol{U} + \frac{1}{6} n^2 \boldsymbol{U} \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \frac{e^2}{q^2} h(q) \equiv P \boldsymbol{U} , \tag{3.3}$$

with P the thermodynamic pressure. As is well known the internal energy and the pressure are not independent for a one-component plasma

$$P = \tfrac{1}{2} n k_B T + \tfrac{1}{3} n u . \qquad (3.4)$$

As a consequence one finds by differentiation with respect to temperature and density

$$\left(\frac{\partial P}{\partial T}\right)_n = \tfrac{1}{3} n c_V + \tfrac{1}{2} n k_B , \qquad (3.5)$$

$$\frac{c_V}{k_B} = -\frac{9}{n k_B T \kappa_T} + \frac{2n}{k_B T} \int \frac{dq}{(2\pi)^3} \frac{e^2}{q^2} h(q) + \frac{21}{2} , \qquad (3.6)$$

with c_V the specific heat at constant volume and κ_T the isothermal compressibility. These relations will be used in the next section.

4. Fluctuations of density, pressure and energy

The fluctuation formulae for a one-component plasma differ from those of a neutral gas owing to the long-range nature of the Coulomb interaction. To derive the fluctuation formulae in a systematic way and to show their mutual dependence we start from the momentum balance equation (2.14). After multiplication by $V^{-1}[n(\boldsymbol{k})]^*$ and taking the average we get

$$\frac{1}{V}\langle [n(\boldsymbol{k})]^* L \boldsymbol{g}(\boldsymbol{k})\rangle = -\frac{1}{V}\langle [n(\boldsymbol{k})]^* \boldsymbol{k}\cdot \boldsymbol{\tau}(\boldsymbol{k})\rangle - k_B T \frac{k_D^2}{k^2} \boldsymbol{k} \frac{1}{V}\langle [n(\boldsymbol{k})]^* n(\boldsymbol{k})\rangle , \qquad (4.1)$$

with the Debye wave number $k_D = (ne^2/k_B T)^{1/2}$. With the use of the hermiticity of L and the continuity equation (2.8) the left-hand side becomes

$$-\frac{1}{mV}\langle [\boldsymbol{k}\cdot \boldsymbol{g}(\boldsymbol{k})]^* \boldsymbol{g}(\boldsymbol{k})\rangle = -\frac{1}{mV}\left\langle \sum_\alpha \boldsymbol{k}\cdot \boldsymbol{p}_\alpha \boldsymbol{p}_\alpha \right\rangle = -n k_B T \boldsymbol{k} . \qquad (4.2)$$

The factor with the density fluctuations at the right-hand side of (4.1) reads

$$\frac{1}{V}\langle [n(\boldsymbol{k})]^* n(\boldsymbol{k})\rangle = n[1 + n h(\boldsymbol{k})] , \qquad (4.3)$$

where the definition (3.2) of the pair correlation function has been used. Substitution of (4.2) and (4.3) into (4.1) gives

$$\frac{1}{V}\langle [n(\boldsymbol{k})]^* \boldsymbol{k} \cdot \boldsymbol{\tau}(\boldsymbol{k})\rangle = nk_{\mathrm{B}}T\boldsymbol{k}\left\{1 - \frac{k_{\mathrm{D}}^2}{k^2}[1 + nh(k)]\right\}. \tag{4.4}$$

Since the left-hand side is finite for small $\boldsymbol{k}$ it follows that one has

$$1 + nh(k) = \mathcal{O}(k^2), \tag{4.5}$$

for small $\boldsymbol{k}$. The contribution of the kinetic pressure to the left-hand side of (4.4) is easily evaluated; it is proportional to (4.3). Hence an alternative form for (4.4) is

$$\frac{1}{V}\langle [n(\boldsymbol{k})]^* \boldsymbol{k} \cdot \boldsymbol{\tau}^{\mathrm{pot}}(\boldsymbol{k})\rangle = nk_{\mathrm{B}}T\boldsymbol{k}\left\{-nh(k) - \frac{k_{\mathrm{D}}^2}{k^2}[1 + nh(k)]\right\}. \tag{4.6}$$

Let us return now to the momentum balance equation (2.14) and multiply it by $V^{-1}[\boldsymbol{\tau}^{\mathrm{pot}}(\boldsymbol{k})]^*$. Taking the average we get

$$\frac{1}{V}\langle [\tau_{ij}^{\mathrm{pot}}(\boldsymbol{k})]^* L g_m(\boldsymbol{k})\rangle = -\frac{1}{V}\langle [\tau_{ij}^{\mathrm{pot}}(\boldsymbol{k})]^* [\boldsymbol{k} \cdot \boldsymbol{\tau}(\boldsymbol{k})]_m\rangle$$
$$- k_{\mathrm{B}}T\frac{k_{\mathrm{D}}^2}{k^2}\frac{1}{V}\langle [\tau_{ij}^{\mathrm{pot}}(\boldsymbol{k})]^* n(\boldsymbol{k})\rangle k_m . \tag{4.7}$$

At the left-hand side we again employ the hermiticity of L. Subsequently we insert the time derivative of (2.15). Carrying out the average over the momenta and using (3.2) we obtain

$$\frac{n^2 k_{\mathrm{B}}T}{2V}\sum_{\boldsymbol{q}(\neq \boldsymbol{0}, \neq \boldsymbol{k})}\frac{e^2}{q^2}\left(\delta_{ij} - \frac{2q_i q_j}{q^2}\right)[(q_m - k_m)h(q) - q_m h(|\boldsymbol{q} - \boldsymbol{k}|)] . \tag{4.8}$$

As before, in the thermodynamic limit the discrete sum may be replaced by an integral. When the pair correlation function is expanded in powers of $\boldsymbol{k}$ and use is made of the isotropy of the integration one finds up to first order in $\boldsymbol{k}$

$$\frac{1}{2}n^2 k_{\mathrm{B}}T\int\frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3}\frac{e^2}{q^2}\left[-\frac{1}{3}\delta_{ij}k_m h(q) + \frac{1}{15}(3\delta_{ij}k_m - 2\delta_{im}k_j - 2\delta_{jm}k_i)q\frac{\mathrm{d}h}{\mathrm{d}q}\right]. \tag{4.9}$$

Upon partial integration of the terms that contain $\mathrm{d}h/\mathrm{d}q$ this expression becomes

$$-\frac{1}{15} n^2 k_B T(4\delta_{ij} k_m - \delta_{im} k_j - \delta_{jm} k_i) \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \frac{e^2}{q^2} h(q) . \qquad (4.10)$$

For small $\boldsymbol{k}$ we have derived now from (4.7) the identity

$$\frac{1}{V} \langle [\tau_{ij}^{\text{pot}}(\boldsymbol{k})]^* [\boldsymbol{k} \cdot \boldsymbol{\tau}(\boldsymbol{k})]_m \rangle = -k_B T \frac{k_D^2}{k^2} \frac{1}{V} \langle [\tau_{ij}^{\text{pot}}(\boldsymbol{k})]^* n(\boldsymbol{k}) \rangle k_m$$

$$+ \frac{1}{15} n^2 k_B T(4\delta_{ij} k_m - \delta_{im} k_j - \delta_{jm} k_i) \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \frac{e^2}{q^2} h(q) . \qquad (4.11)$$

Since both the left-hand side and the last term at the right-hand side are proportional to $\boldsymbol{k}$, we conclude

$$\frac{1}{V} \langle [\boldsymbol{\tau}^{\text{pot}}(\boldsymbol{k})]^* n(\boldsymbol{k}) \rangle = \mathcal{O}(k^2) . \qquad (4.12)$$

With the use of (4.6) we get

$$1 + nh(k) = \frac{k^2}{k_D^2} + \mathcal{O}(k^4) . \qquad (4.13)$$

Mulitplying (4.11) by k_i and substituting (4.6) at the right-hand side we get

$$\frac{1}{V} \langle [\boldsymbol{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\boldsymbol{k})]^* \boldsymbol{k} \cdot \boldsymbol{\tau}(\boldsymbol{k}) \rangle = -n(k_B T)^2 \frac{k_D^2}{k^2} \left\{ -nh(k) - \frac{k_D^2}{k^2} [1 + nh(k)] \right\} \boldsymbol{KK}$$

$$+ \frac{1}{5} n^2 k_B T \left(\boldsymbol{kk} - \frac{1}{3} k^2 \boldsymbol{U} \right) \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \frac{e^2}{q^2} h(q) , \qquad (4.14)$$

in second order in $\boldsymbol{k}$. In the limit $\boldsymbol{k} \to \boldsymbol{0}$ the expression $V^{-1} \langle [\tau_{ij}^{\text{pot}}]^* \tau_{mn} \rangle$ is, on account of its symmetry in the indices (i, j), (n, m) and the isotropy of the system, a linear combination of the invariant tensors $\delta_{ij} \delta_{mn}$ and $\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm}$. Hence we obtain from (4.14)

$$\frac{1}{V} \langle [\tau_{ij}^{\text{pot}}(\boldsymbol{k})]^* \tau_{mn}(\boldsymbol{k}) \rangle = -n(k_B T)^2 \frac{k_D^2}{k^2} \left\{ -nh(k) - \frac{k_D^2}{k^2} [1 + nh(k)] \right\} \delta_{ij} \delta_{mn}$$

$$+ \frac{1}{15} n^2 k_B T(4\delta_{ij} \delta_{mn} - \delta_{im} \delta_{jn} - \delta_{in} \delta_{jm}) \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \frac{e^2}{q^2} h(q) , \qquad (4.15)$$

for vanishing $\boldsymbol{k}$. Since one has according to (4.12)

$$\frac{1}{V}\langle[\tau_{ij}^{\mathrm{pot}}(\boldsymbol{k})]^{*}\tau_{mn}^{\mathrm{kin}}(\boldsymbol{k})\rangle = k_{\mathrm{B}}T\delta_{mn}\frac{1}{V}\langle[\tau_{ij}^{\mathrm{pot}}(\boldsymbol{k})]^{*}n(\boldsymbol{k})\rangle = \mathcal{O}(k^{2}), \tag{4.16}$$

the pressure tensor $\tau_{mn}(\boldsymbol{k})$ at the left-hand side of (4.15) may be replaced by $\tau_{mn}^{\mathrm{pot}}(\boldsymbol{k})$, at least in the limit $\boldsymbol{k}\to\boldsymbol{0}$. We now employ the relation

$$\varepsilon^{\mathrm{pot}}(\boldsymbol{k}) = \mathrm{Tr}\,\boldsymbol{\tau}^{\mathrm{pot}}(\boldsymbol{k}), \tag{4.17}$$

which follows from (2.7) and (2.15). Contraction of the indices i, j and m, n in (4.15) then yields

$$\frac{1}{V}\langle[\varepsilon^{\mathrm{pot}}(\boldsymbol{k})]^{*}\varepsilon^{\mathrm{pot}}(\boldsymbol{k})\rangle = -9n(k_{\mathrm{B}}T)^{2}\frac{k_{\mathrm{D}}^{2}}{k^{2}}\left\{-nh(k) - \frac{k_{\mathrm{D}}^{2}}{k^{2}}[1 + nh(k)]\right\} + 2n^{2}k_{\mathrm{B}}T\int\frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^{3}}\frac{e^{2}}{q^{2}}h(q), \tag{4.18}$$

for $\boldsymbol{k}\to 0$. This result should be compared with the well-known expression for the energy fluctuations of a system in the canonical ensemble:

$$\frac{1}{V}\langle\varepsilon(\boldsymbol{k})^{*}\varepsilon(\boldsymbol{k})\rangle = nk_{\mathrm{B}}T^{2}c_{V}. \tag{4.19}$$

for $\boldsymbol{k}\to\boldsymbol{0}$. In a way analogous to (4.16) we may prove $V^{-1}\langle[\varepsilon^{\mathrm{pot}}(\boldsymbol{k})]^{*}\varepsilon^{\mathrm{kin}}(\boldsymbol{k})\rangle = \mathcal{O}(k^{2})$. Furthermore, a simple averaging over the momenta yields, with the use of (4.5),

$$\frac{1}{V}\langle[\varepsilon^{\mathrm{kin}}(\boldsymbol{k})]^{*}\varepsilon^{\mathrm{kin}}(\boldsymbol{k})\rangle = \frac{3}{2}n(k_{\mathrm{B}}T)^{2}, \tag{4.20}$$

for $\boldsymbol{k}\to\boldsymbol{0}$, so that (4.19) leads to

$$\frac{1}{V}\langle[\varepsilon^{\mathrm{pot}}(\boldsymbol{k})]^{*}\varepsilon^{\mathrm{pot}}(\boldsymbol{k})\rangle = nk_{\mathrm{B}}T^{2}\left(c_{V} - \frac{3}{2}k_{\mathrm{B}}\right). \tag{4.21}$$

An alternative form for this expression is found by employing (3.6)

$$\frac{1}{V}\langle[\varepsilon^{\mathrm{pot}}(\boldsymbol{k})]^{*}\varepsilon^{\mathrm{pot}}(\boldsymbol{k})\rangle = -9n(k_{\mathrm{B}}T)^{2}\left(\frac{1}{nk_{\mathrm{B}}T\kappa_{T}} - 1\right) + 2n^{2}k_{\mathrm{B}}T\int\frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^{3}}\frac{e^{2}}{q^{2}}h(q). \tag{4.22}$$

Comparing (4.18) and (4.22) we have derived now the leading terms of the structure factor for small $\boldsymbol{k}$,

$$1 + nh(k) = \frac{k^2}{k_{\rm D}^2} - \frac{1}{nk_{\rm B}T\kappa_T}\frac{k^4}{k_{\rm D}^4} + \cdots$$
$$= \frac{1}{k_{\rm D}^2/k^2 + 1/nk_{\rm B}T\kappa_T + \cdots}\,. \tag{4.23}$$

It should be remarked that this result has been obtained without making assumptions on the behaviour of the direct correlation function for small $\boldsymbol{k}$ or on thermodynamic fluctuation theory for a one-component plasma, as has been done in refs. 1 and 3. An important role in the present derivation was played by the microscopic momentum balance equation (2.14), which contains the characteristic Coulomb divergence for small $\boldsymbol{k}$.

The complete set of formulae for the averages of the fluctuations of the density, the pressure and the energy density follows straightforwardly from the above results. The pressure fluctuations for $\boldsymbol{k} \to \boldsymbol{0}$ are found by insertion of (4.23) into (4.15)

$$\frac{1}{V}\langle [\tau_{ij}^{\rm pot}(\boldsymbol{k})]^* \tau_{mn}(\boldsymbol{k})\rangle = -n(k_{\rm B}T)^2\left(\frac{1}{nk_{\rm B}T\kappa_T} - 1\right)\delta_{ij}\delta_{mn}$$
$$+ \frac{1}{15}n^2k_{\rm B}T(4\delta_{ij}\delta_{mn} - \delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})\int \frac{{\rm d}\boldsymbol{q}}{(2\pi)^3}\frac{e^2}{q^2}h(q)\,. \tag{4.24}$$

A similar formula, with the complete pressure instead of the potential pressure, is easily obtained. In fact, the mixed contributions, with both the kinetic and the potential pressure, are of order k^2 according to (4.16). Adding the purely kinetic contribution we get

$$\frac{1}{V}\langle [\tau_{ij}(\boldsymbol{k})]^* \tau_{mn}(\boldsymbol{k})\rangle = n(k_{\rm B}T)^2(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm})$$
$$- n(k_{\rm B}T)^2\left(\frac{1}{nk_{\rm B}T\kappa_T} - 1\right)\delta_{ij}\delta_{mn}$$
$$+ \frac{1}{15}n^2k_{\rm B}T(4\delta_{ij}\delta_{mn} - \delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})\int \frac{{\rm d}\boldsymbol{q}}{(2\pi)^3}\frac{e^2}{q^2}h(q)\,, \tag{4.25}$$

for $\boldsymbol{k} \to \boldsymbol{0}$. Furthermore, multiplying (4.24) by k_m and substituting the result into (4.11) we get

$$\frac{1}{V}\langle[\boldsymbol{\tau}^{\text{pot}}(\boldsymbol{k})]^*n(\boldsymbol{k})\rangle = nk_{\text{B}}T\left(\frac{1}{nk_{\text{B}}T\kappa_T}-1\right)\frac{k^2}{k_{\text{D}}^2}\boldsymbol{U}, \tag{4.26}$$

for small $\boldsymbol{k}$. Since the corresponding kinetic contribution is proportional to (4.3) the complete density-pressure fluctuation formula is

$$\frac{1}{V}\langle[\boldsymbol{\tau}(\boldsymbol{k})]^*n(\boldsymbol{k})\rangle = \frac{k^2}{\kappa_T k_{\text{D}}^2}\boldsymbol{U}, \tag{4.27}$$

for small $\boldsymbol{k}$.

Finally we consider the energy flucuations. Employing (4.17) we derive from (4.24) for $\boldsymbol{k}\to\boldsymbol{0}$

$$\frac{1}{V}\langle[\varepsilon^{\text{pot}}(\boldsymbol{k})]^*\boldsymbol{\tau}(\boldsymbol{k})\rangle = -3n(k_{\text{B}}T)^2\left(\frac{1}{nk_{\text{B}}T\kappa_T}-1\right)\boldsymbol{U}+\frac{2}{3}n^2k_{\text{B}}T\boldsymbol{U}\int\frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3}\frac{e^2}{q^2}h(q)$$

$$= \left[k_{\text{B}}T^2\left(\frac{\partial P}{\partial T}\right)_n - n(k_{\text{B}}T)^2\right]\boldsymbol{U}, \tag{4.28}$$

where we used (3.5) and (3.6) to obtain the last result. Adding the corresponding kinetic contribution we get

$$\frac{1}{V}\langle[\varepsilon(\boldsymbol{k})]^*\boldsymbol{\tau}(\boldsymbol{k})\rangle = k_{\text{B}}T^2\left(\frac{\partial P}{\partial T}\right)_n\boldsymbol{U}, \tag{4.29}$$

for $\boldsymbol{k}\to\boldsymbol{0}$. Likewise by taking the trace of (4.26) one obtains

$$\frac{1}{V}\langle[\varepsilon^{\text{pot}}(\boldsymbol{k})]^*n(\boldsymbol{k})\rangle = 3nk_{\text{B}}T\left(\frac{1}{nk_{\text{B}}T\kappa_T}-1\right)\frac{k^2}{k_{\text{D}}^2}, \tag{4.30}$$

for small $\boldsymbol{k}$, and hence, by adding the kinetic terms to this expression,

$$\frac{1}{V}\langle[\varepsilon(\boldsymbol{k})]^*n(\boldsymbol{k})\rangle = 3nk_{\text{B}}T\left(\frac{1}{nk_{\text{B}}T\kappa_T}-\frac{1}{2}\right)\frac{k^2}{k_{\text{D}}^2}, \tag{4.31}$$

for small $\boldsymbol{k}$.

As a check an alternative method may be employed to obtain information on the energy fluctuations. When the energy balance equation (2.21) is multiplied by $V^{-1}[\boldsymbol{g}(\boldsymbol{k})]^*$ and both sides are averaged with the canonical ensemble, one finds, upon using the hermiticity of L and the momentum balance equation (2.14), a relation between $\langle\varepsilon^*\tau\rangle$ and $\langle\varepsilon^* n\rangle$, which is indeed satisfied by the expressions in (4.29) and (4.31).

In (4.25), (4.27) and (4.29) we have obtained the fluctuation formulae for the total microscopic pressure tensor $\boldsymbol{\tau}(\boldsymbol{k})$. In particular, (4.25) gives the high-frequency elastic moduli of the one-component plasma; for a neutral fluid these moduli have been discussed earlier[5,6]). From the results given here the fluctuation formulae for the diagonal part $p(\boldsymbol{k}) = \frac{1}{3}\mathrm{Tr}\,\boldsymbol{\tau}(\boldsymbol{k})$ of the pressure tensor follow immediately. It should be noted that $p(\boldsymbol{k})$ differs from the 'thermodynamic part' $P(\boldsymbol{k})$ of the pressure fluctuation[6]). Whereas $p(\boldsymbol{k})$ is an independent quantity, the part $P(\boldsymbol{k})$ of the pressure fluctuation is a linear combination of the fluctuations in the density and in the energy. In fact, it follows by writing[6])

$$p(\boldsymbol{k}) = P(\boldsymbol{k}) + p'(\boldsymbol{k}), \tag{4.32}$$

with

$$\langle[\varepsilon(\boldsymbol{k})]^* p'(\boldsymbol{k})\rangle = \langle[n(\boldsymbol{k})]^* p'(\boldsymbol{k})\rangle = 0\,. \tag{4.33}$$

For a plasma one finds by using the fluctuation formulae derived above

$$P(\boldsymbol{k}) = \frac{1}{3}\left(1 + \frac{3k_\mathrm{B}}{2c_V}\right)\varepsilon(\boldsymbol{k}) - \frac{1}{2}k_\mathrm{B}T\left(1 + \frac{3k_\mathrm{B}}{2c_V} - \frac{3}{nc_V T\kappa_T}\right)n(\boldsymbol{k})\,, \tag{4.34}$$

for small wave vector. As a consequence one easily obtains

$$\frac{1}{V}\langle[P(\boldsymbol{k})]^* P(\boldsymbol{k})\rangle = \frac{1}{V}\langle[p(\boldsymbol{k})]^* p(\boldsymbol{k})\rangle - \frac{n(k_\mathrm{B}T)^2}{6c_V}\left(c_V - \frac{3}{2}k_\mathrm{B}\right), \tag{4.35}$$

for small $\boldsymbol{k}$, and from (4.32) with (4.33)

$$\frac{1}{V}\langle[P(\boldsymbol{k})]^* n(\boldsymbol{k})\rangle = \frac{1}{V}\langle[p(\boldsymbol{k})]^* n(\boldsymbol{k})\rangle\,, \tag{4.36}$$

$$\frac{1}{V}\langle[P(\boldsymbol{k})]^* \varepsilon(\boldsymbol{k})\rangle = \frac{1}{V}\langle[p(\boldsymbol{k})]^* \varepsilon(\boldsymbol{k})\rangle\,. \tag{4.37}$$

The complete set of formulae for the long wavelength fluctuations of the density, the pressure and the energy density has now been derived. As the results (4.3) (with (4.23)), (4.19), (4.25), (4.27), (4.29) and (4.31) show, only the averages of the products of the fluctuations in the pressure and in the energy density remain finite in the limit $\boldsymbol{k} \to \boldsymbol{0}$. The averages of products that contain the density fluctuations as a factor are all proportional to k^2, so that they vanish in the long-wavelength limit. The reason is that long-wavelength density fluctuations are suppressed in a one-component plasma as a consequence of the long-range character of the Coulomb interaction and the proportionality of density and charge fluctuations.

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