

EQUILIBRIUM PROPERTIES OF A MULTI-COMPONENT IONIC MIXTURE

II. FLUCTUATION FORMULAE

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The complete set of fluctuation formulae for the partial densities, the pressure and the energy density of a multi-component ionic mixture is derived from equilibrium statistical mechanics. Sum rules for the pair correlation functions are used to write the fluctuation formulae in terms of thermodynamical quantities.

1. Introduction

Fluctuation formulae are of fundamental importance for the analysis of the static and dynamical properties of macroscopic systems. In particular, knowledge of the behaviour of the large-scale fluctuations is essential in a derivation of the collective modes, which dominate the asymptotic behaviour of time correlation functions.

For fluids of neutral particles the fluctuation formulae are well known. The fluctuation properties of plasmas are qualitatively different, however, since in these systems non-uniformities in the charge distribution are effectively suppressed by the long-range Coulomb forces.

Recently a statistical derivation of the fluctuation formulae has been given for the special case of a one-component plasma, which consists of charged particles in a neutralizing background^{1,2}). The fluctuations in this model are somewhat degenerate, since charge and density fluctuations are not independent. As a consequence all fluctuation expressions containing the particle density tend to zero for vanishing wavenumber.

In an ionic mixture particles of several species, with different charges and masses, move in a neutralizing background. Although charge density fluctuations are suppressed in these mixtures as well, the partial densities of the various species may fluctuate on a macroscopic scale, so that the degeneracy that occurs in the one-component case is now removed.

In the following a systematic statistical derivation of the complete set of fluctuation formulae for general multi-component ionic mixtures will be presented. To that end we shall start from the microscopic expressions for the partial densities, the pressure and the energy density. The fluctuation expressions for these quantities will be written in terms of Ursell functions the properties of which have been studied in the first paper of this series³). The sum rules for the pair correlation functions as derived in ref. 3 will enable us to express the fluctuation formulae for ionic mixtures in terms of thermodynamic quantities.

2. Microscopic expressions for the partial densities, the pressure and the energy density

In the following we shall need the microscopic balance equations of particle number, momentum and energy. From these the microscopic expressions for the partial densities, the pressure tensor and the energy density are obtained directly. In our presentation we shall closely follow the treatment given in refs. 2 and 4 for the one-component plasma.

The Fourier transform of the particle density $n_\sigma(\mathbf{k})$ of the species with label σ is

$$n_\sigma(\mathbf{k}) = \sum_\alpha e^{-i\mathbf{k}\cdot\mathbf{r}_{\sigma\alpha}}, \quad (2.1)$$

with $\mathbf{r}_{\sigma\alpha}$ the position of the particle α of component σ . The continuity equation for n_σ reads

$$Ln_\sigma(\mathbf{k}) = -\frac{\mathbf{k}}{m_\sigma} \cdot \mathbf{g}_\sigma(\mathbf{k}), \quad (2.2)$$

with L the Liouville operator in phase space and m_σ the mass of the particles of species σ . The Fourier transform of the momentum density of component σ is given by

$$\mathbf{g}_\sigma(\mathbf{k}) = \sum_\alpha \mathbf{p}_{\sigma\alpha} e^{-i\mathbf{k}\cdot\mathbf{r}_{\sigma\alpha}}, \quad (2.3)$$

with $\mathbf{p}_{\sigma\alpha}$ the momentum of particle α .

The momentum balance equation can be written as

$$L \sum_\sigma \mathbf{g}_\sigma(\mathbf{k}) = -\mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) - q_v \frac{\mathbf{k}}{k^2} \sum_\sigma e_\sigma n_\sigma(\mathbf{k}). \quad (2.4)$$

The pressure tensor $\boldsymbol{\tau}(\mathbf{k})$ is the sum of a kinetic and a potential part,

$$\begin{aligned} \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) &= \mathbf{k} \cdot \sum_{\sigma\alpha} \frac{P_{\sigma\alpha} P_{\sigma\alpha}}{m_\sigma} e^{-i\mathbf{k} \cdot \mathbf{r}_{\sigma\alpha}} \\ &+ \frac{1}{V} \sum_{\mathbf{q} (\neq \mathbf{0}, \neq \mathbf{k})} \sum'_{\sigma_1\alpha_1, \sigma_2\alpha_2} e_{\sigma_1} e_{\sigma_2} \frac{\mathbf{q}}{q^2} e^{i\mathbf{q} \cdot (\mathbf{r}_{\sigma_1\alpha_1} - \mathbf{r}_{\sigma_2\alpha_2}) - i\mathbf{k} \cdot \mathbf{r}_{\sigma_1\alpha_1}}. \end{aligned} \quad (2.5)$$

Here e_σ is the charge of the particles of species σ . The prime at the summation symbol stands for the restriction $\sigma_i\alpha_i \neq \sigma_j\alpha_j$ ($i \neq j$). In writing the potential part of the pressure tensor periodic boundary conditions in a box with volume V have been assumed. The exclusion of the terms with $\mathbf{q} = \mathbf{0}$ and $\mathbf{q} = \mathbf{k}$ is a consequence of the presence of the neutralizing background; its charge density is $q_v = Q/V = \sum_\sigma e_\sigma N_\sigma/V$, with N_σ the particle number of species σ .

The energy density $\varepsilon(\mathbf{k})$ in Fourier space is the sum of a kinetic part and a potential part. The definition of the latter depends on the way in which the long-range Coulomb interaction energy is localized. Choosing^{2,4)}

$$\varepsilon^{\text{pot}}(\mathbf{r}) = \frac{1}{2} [\mathbf{E}(\mathbf{r})]^2 - \varepsilon^{\text{pot, self}}(\mathbf{r}), \quad (2.6)$$

with \mathbf{E} the electric field at the position \mathbf{r} and $\varepsilon^{\text{pot, self}}$ the infinite self-energy incorporated in $\frac{1}{2} E^2$, we get the following expression for the total energy density:

$$\begin{aligned} \varepsilon(\mathbf{k}) &= \sum_{\sigma\alpha} \frac{P_{\sigma\alpha}^2}{2m_\sigma} e^{-i\mathbf{k} \cdot \mathbf{r}_{\sigma\alpha}} \\ &- \frac{1}{2V} \sum_{\mathbf{q} (\neq \mathbf{0}, \neq \mathbf{k})} \sum'_{\sigma_1\alpha_1, \sigma_2\alpha_2} e_{\sigma_1} e_{\sigma_2} \frac{\mathbf{q} \cdot (\mathbf{k} - \mathbf{q})}{q^2 |\mathbf{k} - \mathbf{q}|^2} e^{i\mathbf{q} \cdot (\mathbf{r}_{\sigma_1\alpha_1} - \mathbf{r}_{\sigma_2\alpha_2}) - i\mathbf{k} \cdot \mathbf{r}_{\sigma_1\alpha_1}}. \end{aligned} \quad (2.7)$$

The energy density fulfils an energy balance equation of the form

$$L\varepsilon(\mathbf{k}) = -\mathbf{k} \cdot \mathbf{j}_\varepsilon(\mathbf{k}), \quad (2.8)$$

with an energy-current density $\mathbf{j}_\varepsilon(\mathbf{k})$, the explicit form of which will not be needed in the following.

The purpose of this paper is to derive expressions for the equilibrium ensemble average of products of two microscopic quantities chosen from the set $n_\sigma(\mathbf{k})$, $\mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k})$ and $\varepsilon(\mathbf{k})$. To obtain these fluctuation formulae we will use some results following from the BBGKY-hierarchy for the Ursell functions. These will be the subject of the next section.

3. Results from the hierarchy

In the first paper of this series³⁾ we have studied the Ursell functions $h_{\sigma_1 \dots \sigma_k}^{(k)}$ of a multi-component ionic mixture. These functions are defined by making the usual cluster expansion of the k -particle correlation functions $g_{\sigma_1 \dots \sigma_k}^{(k)}$ that are given by

$$n_{\sigma_1} \dots n_{\sigma_k} g_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) = \left\langle \sum'_{\alpha_1, \dots, \alpha_k} \delta(\mathbf{r}_1 - \mathbf{r}_{\sigma_1 \alpha_1}) \dots \delta(\mathbf{r}_k - \mathbf{r}_{\sigma_k \alpha_k}) \right\rangle, \quad (3.1)$$

$$k = 2, 3, \dots$$

Here the brackets denote an average with an equilibrium ensemble that is chosen such that the particle numbers N_σ of the species σ vary, while the total charge $Q = \sum_\sigma N_\sigma e_\sigma$ is kept constant³⁾. The averaged particle densities are $n_\sigma = \langle N_\sigma \rangle / V$.

The Ursell functions are assumed to possess the exponential clustering property^{3,5)}. As a consequence, their Fourier transforms, which are defined as

$$h_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{q}_2, \dots, \mathbf{q}_k) = \int d\mathbf{r}_{12} \dots d\mathbf{r}_{1k} e^{i\mathbf{q}_2 \cdot \mathbf{r}_{12} + \dots + i\mathbf{q}_k \cdot \mathbf{r}_{1k}} h_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k), \quad (3.2)$$

with $r_{ij} = r_i - r_j$, are regular functions of the variables $\mathbf{q}_2, \dots, \mathbf{q}_k$. From (3.1), (3.2) and the cluster expansion it follows that we may write

$$n_{\sigma_1} \dots n_{\sigma_k} h_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{q}_2, \dots, \mathbf{q}_k) = \frac{1}{V} \left\langle \sum'_{\alpha_1, \dots, \alpha_k} e^{i\mathbf{q}_2 \cdot (\mathbf{r}_{\sigma_1 \alpha_1} - \mathbf{r}_{\sigma_2 \alpha_2}) + \dots + i\mathbf{q}_k \cdot (\mathbf{r}_{\sigma_1 \alpha_1} - \mathbf{r}_{\sigma_k \alpha_k})} \right\rangle, \quad (3.3)$$

for $\mathbf{q}_j \neq \mathbf{0}$ ($j = 2, \dots, k$) and $\sum_{j=2}^k \mathbf{q}_j \neq \mathbf{0}$. The Ursell functions have the symmetry properties

$$\begin{aligned} h_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{q}_2, \dots, \mathbf{q}_k) &= h_{\sigma_1 \sigma_{p_2} \dots \sigma_{p_k}}^{(k)}(\mathbf{q}_{p_2}, \dots, \mathbf{q}_{p_k}) \\ &= h_{\sigma_k \sigma_{k-1} \dots \sigma_1}^{(k)}\left(\mathbf{q}_2, \dots, \mathbf{q}_{k-1}, -\sum_{j=2}^k \mathbf{q}_j\right), \end{aligned} \quad (3.4)$$

with $\{p_2, \dots, p_k\}$ a permutation of $\{2, \dots, k\}$. The simplest Ursell function is the two-particle function $h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q})$, which, on account of its regularity near $\mathbf{q} = \mathbf{0}$, may be expanded as

$$h_{\sigma_1\sigma_2}^{(2)}(\mathbf{q}) = a_{\sigma_1\sigma_2}^{(0)} + a_{\sigma_1\sigma_2}^{(1)}q^2 + a_{\sigma_1\sigma_2}^{(2)}q^4 + \dots, \quad (3.5)$$

with coefficients $a_{\sigma_1\sigma_2}^{(n)}$ that are symmetric in σ_1 and σ_2 .

The Ursell functions in position space satisfy sum rules that have been considered extensively in ref. 3. Part of these sum rules, which have a purely electrostatic origin, may be derived directly from the BBGKY hierarchy, without invoking the precise form of the ensemble average. On the other hand, the detailed structure of the ensemble average is important in the derivation of the so-called 'thermodynamic' sum rules in which the thermodynamic properties of the system show up.

It is obvious that the sum rules for the position-space Ursell functions may be translated directly to relations for the coefficients in the expansions of their Fourier transforms (3.2) for small wave vectors. However, to establish the relations that correspond to the 'electrostatic' sum rules, we prefer to start afresh from the BBGKY hierarchy in Fourier language, since such an independent derivation will provide us with several auxiliary relations that are needed in the remainder of the paper.

The BBGKY hierarchy equation for the three-particle Ursell function in Fourier language is

$$\begin{aligned} \beta e_{\sigma_1} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{k}, \mathbf{q}) &= \beta e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{k} - \mathbf{q}) \\ &+ \beta e_{\sigma_1} \frac{\mathbf{k}}{k^2} \left[e_{\sigma_2} + \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} h_{\sigma_2\sigma_3}^{(2)}(\mathbf{k}) \right] + \mathbf{k} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{k}). \end{aligned} \quad (3.6)$$

By considering the thermodynamic limit we could replace discrete summations over wave vectors by integrations. Upon scalar multiplication of (3.6) by \mathbf{k} we find in the limit $\mathbf{k} \rightarrow \mathbf{0}$

$$\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} a_{\sigma_1\sigma_2}^{(0)} = -e_{\sigma_1}, \quad (3.7)$$

where (3.5) has been employed. This relation is the perfect-screening condition for the pair correlation function^{3,5} in Fourier language.

The hierarchy equation for $h^{(4)}$ in Fourier language reads

$$\begin{aligned} \beta e_{\sigma_1} \sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} h_{\sigma_1\sigma_2\sigma_3\sigma_4}^{(4)}(\mathbf{k}, \mathbf{k}', \mathbf{q}) \\ = \beta e_{\sigma_1} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} [e_{\sigma_2} h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{k} - \mathbf{q}, \mathbf{k}') + e_{\sigma_3} h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{k}, \mathbf{k}' - \mathbf{q})] \end{aligned}$$

$$\begin{aligned}
& + (\mathbf{k} + \mathbf{k}') h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{k}, \mathbf{k}') \\
& + \beta e_{\sigma_1} \frac{\mathbf{k}'}{k'^2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k}) \left[e_{\sigma_3} + \sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} h_{\sigma_3 \sigma_4}^{(2)}(\mathbf{k}') \right] \\
& + \beta e_{\sigma_1} \frac{\mathbf{k}}{k^2} h_{\sigma_1 \sigma_3}^{(2)}(\mathbf{k}') \left[e_{\sigma_2} + \sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} h_{\sigma_2 \sigma_4}^{(2)}(\mathbf{k}) \right] \\
& + \beta e_{\sigma_1} \frac{(\mathbf{k} + \mathbf{k}')}{|\mathbf{k} + \mathbf{k}'|^2} \left[\sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} h_{\sigma_2 \sigma_3 \sigma_4}^{(3)}(\mathbf{k}', -\mathbf{k} - \mathbf{k}') \right. \\
& \left. + e_{\sigma_2} h_{\sigma_2 \sigma_3}^{(2)}(\mathbf{k}') + e_{\sigma_3} h_{\sigma_2 \sigma_3}^{(2)}(\mathbf{k}) \right]. \tag{3.8}
\end{aligned}$$

Upon scalar multiplication with $(\mathbf{k} + \mathbf{k}')$ we get in the limit $\mathbf{k}' \rightarrow -\mathbf{k}$

$$\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{k}, \mathbf{0}) = -(e_{\sigma_1} + e_{\sigma_2}) h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k}), \tag{3.9}$$

which is the first of a set of perfect-screening relations for the three-particle Ursell functions^{3,5}). Higher-order perfect-screening relations for $h^{(3)}$ may be derived from (3.8) by considering the Taylor expansion around $\mathbf{K} = \mathbf{k} + \mathbf{k}' = \mathbf{0}$ for fixed \mathbf{k}' . Employing (A.3) to the left-hand side and the first seven terms at the right-hand side of (3.8) we may write all these contributions as linear combinations of traceless tensors of the form $K^n \hat{\mathbf{K}}^l$, for $n \geq 0$, $l \geq 0$, with coefficients depending on \mathbf{k}' . On the other hand, by using (A.4) in the last three terms of (3.8) we deduce that these terms give rise to contributions of the form $K^{-2} \hat{\mathbf{K}}^l$. Since such contributions do not occur in the remainder of (3.8) their coefficients should vanish. As a consequence we are led to the conditions

$$\lim_{k' \rightarrow 0} \hat{\nabla}_{\mathbf{k}'}^l \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{k}, \mathbf{k}') = -e_{\sigma_2} \hat{\nabla}_{\mathbf{k}}^l h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k}), \quad l \geq 1, \tag{3.10}$$

which are the higher-order perfect-screening relations in cartesian form.

Further information on the Ursell functions is obtained by combining the hierarchy equations (3.6) and (3.8) with the symmetry properties (3.4). From the latter we may prove the equality for $h^{(k)}$ with $k \geq 3$,

$$\lim_{Q \rightarrow 0} \nabla_{\mathbf{q}_i}^n h_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{q}_2, \dots, \mathbf{q}_k) = \lim_{Q \rightarrow 0} (\nabla_{\mathbf{q}_i} + \nabla_{\mathbf{q}_k})^n h_{\sigma_k \sigma_2 \dots \sigma_{k-1} \sigma_1}^{(k)}(\mathbf{q}_2, \dots, -\mathbf{q}_k), \tag{3.11}$$

with $Q = \sum_{j=2}^{k-1} \mathbf{q}_j$ and $2 \leq i \leq k-1$. Putting $k=3$ we derive from this equality

$$\begin{aligned}
 & \lim_{\mathbf{k} \rightarrow \mathbf{0}} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} \cdot \nabla_{\mathbf{k}} \nabla_{\mathbf{k}}^n h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{q}, \mathbf{k}) \\
 &= \frac{1}{2} \lim_{\mathbf{k} \rightarrow \mathbf{0}} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \{ \mathbf{q} \cdot \nabla_{\mathbf{q}} (\nabla_{\mathbf{k}} - \nabla_{\mathbf{q}})^n \\
 & \quad - \mathbf{q} \cdot \nabla_{\mathbf{k}} [(\nabla_{\mathbf{k}} - \nabla_{\mathbf{q}})^n - \nabla_{\mathbf{k}}^n] \} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{q}, \mathbf{k}). \tag{3.12}
 \end{aligned}$$

Both sides are symmetric invariant tensors of rank n . Since these vanish trivially for odd n we choose n even and contract the tensor indices pairwise. Subsequently, we transform the left-hand side with the help of the hierarchy equation (3.6) and the expansion (3.5). In this way we get

$$\begin{aligned}
 & \lim_{\mathbf{k} \rightarrow \mathbf{0}} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \{ (\Delta_{\mathbf{k}} - 2\nabla_{\mathbf{k}} \cdot \nabla_{\mathbf{q}} + \Delta_{\mathbf{q}})^n \\
 & \quad + \mathbf{q} \cdot \nabla_{\mathbf{k}} [(\Delta_{\mathbf{k}} - 2\nabla_{\mathbf{k}} \cdot \nabla_{\mathbf{q}} + \Delta_{\mathbf{q}})^n - \Delta_{\mathbf{k}}^n] \} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{q}, \mathbf{k}) \\
 &= -2 \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} e_{\sigma_3} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \Delta_{\mathbf{q}}^n h_{\sigma_1 \sigma_3}^{(2)}(\mathbf{q}) \\
 & \quad - 2(2n+1)!(2n+3) \left[q_v \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} a_{\sigma_1 \sigma_3}^{(n+1)} + \beta^{-1} \sum_{\sigma_1} n_{\sigma_1} a_{\sigma_1 \sigma_3}^{(n)} \right]. \tag{3.13}
 \end{aligned}$$

Both the identities (3.11) and (3.13) are needed to derive some auxiliary relations that have been collected in appendix B.

By choosing $n = 0$ we get from (3.13)

$$\begin{aligned}
 & \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{q}, \mathbf{0}) \\
 &= -2 \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} e_{\sigma_3} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_1 \sigma_3}^{(2)}(\mathbf{q}) \\
 & \quad - 6q_v \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} a_{\sigma_1 \sigma_3}^{(1)} - 6\beta^{-1} \sum_{\sigma_1} n_{\sigma_1} a_{\sigma_1 \sigma_3}^{(0)}. \tag{3.14}
 \end{aligned}$$

Upon summing over σ_3 , with the weights $n_{\sigma_3} e_{\sigma_3}$, and using (3.7) and (3.9) we obtain

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} a_{\sigma_1 \sigma_2}^{(1)} = \beta^{-1}, \tag{3.15}$$

which is the condition of Stillinger and Lovett⁵⁻¹¹ in Fourier language.

The perfect-screening relations (3.7), (3.9), (3.10) and the Stillinger-Lovett

condition (3.15) are equivalent to the ‘electrostatic’ sum rules³⁾ for the Ursell functions in position space. These sum rules are direct consequences of the long-range character of the electrostatic interaction. As stated before, additional ‘thermodynamic’ sum rules for the Ursell functions follow by making use of the precise form of the equilibrium ensemble that describes the ionic mixture³⁾. These will not be considered any further here.

4. Derivation of fluctuation formulae

In this section the equilibrium ensemble averages of products of fluctuations in the partial densities, the pressure and the energy density will be studied. In particular, we shall derive fluctuation formulae that express these averages, for small wavenumbers, in terms of the Ursell functions $h_{\sigma_1\sigma_2}^{(2)}$ and their expansion coefficients $a_{\sigma_1\sigma_2}^{(n)}$.

Fluctuation formulae for the partial densities $n_\sigma(\mathbf{k})$ follow directly from the definitions (2.1) and (3.3)

$$\frac{1}{V} \langle n_{\sigma_1}(\mathbf{k})^* n_{\sigma_2}(\mathbf{k}) \rangle = n_{\sigma_1} [\delta_{\sigma_1\sigma_2} + n_{\sigma_2} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{k})]. \quad (4.1)$$

for $\mathbf{k} \neq \mathbf{0}$. Introducing the fluctuations of the total particle density and of the charge density through

$$n(\mathbf{k}) = \sum_{\sigma} n_{\sigma}(\mathbf{k}), \quad (4.2)$$

$$q_v(\mathbf{k}) = \sum_{\sigma} e_{\sigma} n_{\sigma}(\mathbf{k}), \quad (4.3)$$

we obtain from (4.1)

$$\frac{1}{V} \langle n(\mathbf{k})^* n(\mathbf{k}) \rangle = n + \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} a_{\sigma_1\sigma_2}^{(0)} + \dots, \quad (4.4)$$

$$\frac{1}{V} \langle q_v(\mathbf{k})^* n(\mathbf{k}) \rangle = \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} a_{\sigma_1\sigma_2}^{(1)} k^2 + \dots, \quad (4.5)$$

$$\frac{1}{V} \langle q_v(\mathbf{k})^* q_v(\mathbf{k}) \rangle = \beta^{-1} k^2 + \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} a_{\sigma_1\sigma_2}^{(2)} k^4 + \dots, \quad (4.6)$$

where (3.5), (3.7) and (3.15) have been used.

To derive fluctuation formulae for the product of the partial densities and the energy density we multiply the expressions (2.1) and (2.7), take the average and use the definition (3.3) of the Ursell functions. Considering first

the potential part of the energy density (2.7) we find

$$\begin{aligned} \frac{1}{V} \langle \varepsilon^{\text{pot}}(\mathbf{k})^* n_\sigma(\mathbf{k}) \rangle &= -\frac{1}{2} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q} \cdot (\mathbf{k} - \mathbf{q})}{q^2 |\mathbf{k} - \mathbf{q}|^2} \\ &\times [n_\sigma h_{\sigma_1 \sigma_2 \sigma}^{(3)}(-\mathbf{q}, \mathbf{k}) + \delta_{\sigma_1 \sigma} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + \delta_{\sigma_2 \sigma} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} - \mathbf{q})]. \end{aligned} \quad (4.7)$$

As before, we have taken the thermodynamic limit, so that the discrete summation in (2.7) is transformed to an integration. If \mathbf{k} tends to $\mathbf{0}$ we may use (3.14) to simplify the contribution of $h^{(3)}$ to the integral. As a result we get with the help of (3.5)

$$\frac{1}{V} \langle \varepsilon^{\text{pot}}(\mathbf{k})^* n_\sigma(\mathbf{k}) \rangle = -3\beta^{-1} n_\sigma \sum_{\sigma_1} n_{\sigma_1} (a_{\sigma_1 \sigma}^{(0)} + k_{D\sigma_1}^2 a_{\sigma_1 \sigma}^{(1)}) \quad (4.8)$$

for $\mathbf{k} \rightarrow \mathbf{0}$, with partial Debye wavenumbers given by $k_{D\sigma}^2 = \beta e_\sigma q_v$. Upon adding the contribution of the kinetic energy density, which follows easily from (4.1), we obtain for small \mathbf{k}

$$\frac{1}{V} \langle \varepsilon(\mathbf{k})^* n_\sigma(\mathbf{k}) \rangle = \frac{3}{2} \beta^{-1} n_\sigma \left[1 - \sum_{\sigma_1} n_{\sigma_1} (a_{\sigma_1 \sigma}^{(0)} + 2k_{D\sigma_1}^2 a_{\sigma_1 \sigma}^{(1)}) \right]. \quad (4.9)$$

Summation over σ , with equal weights, gives

$$\frac{1}{V} \langle \varepsilon(\mathbf{k})^* n(\mathbf{k}) \rangle = \frac{3}{2} \beta^{-1} \left[n - \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} (a_{\sigma_1 \sigma_2}^{(0)} + 2k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)}) \right] \quad (4.10)$$

for $\mathbf{k} \rightarrow \mathbf{0}$. On the other hand, upon choosing the weights e_σ , in the summation over σ , we conclude that $V^{-1} \langle \varepsilon(\mathbf{k})^* q_v(\mathbf{k}) \rangle$ vanishes for $\mathbf{k} \rightarrow \mathbf{0}$. To obtain the leading term of this fluctuation expression we return to (4.7). The factor between square brackets inside the integral yields, upon multiplication by e_σ and summation over σ , an expression that is, according to (B.4), of second order in \mathbf{k} . Using the identity (B.5) we then conclude

$$\frac{1}{V} \langle \varepsilon(\mathbf{k})^* q_v(\mathbf{k}) \rangle = \frac{-3k^2}{2\beta^2 q_v} \left(\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)} + 2 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} k_{D\sigma_1}^2 k_{D\sigma_2}^2 a_{\sigma_1 \sigma_2}^{(2)} \right), \quad (4.11)$$

for small \mathbf{k} . Here (3.7) has been used to reduce the kinetic contribution.

Next we consider the fluctuation formulae for the product of the pressure

tensor and the partial densities. Since (2.5) and (2.7) have a similar structure we may proceed as before, to derive on a par with (4.7)

$$\begin{aligned} \frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k})^* n_{\sigma}(\mathbf{k}) \rangle &= \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} [n_{\sigma} h_{\sigma_1 \sigma_2 \sigma}^{(3)}(-\mathbf{q}, \mathbf{k}) \\ &\quad + \delta_{\sigma_1 \sigma} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + \delta_{\sigma_2 \sigma} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} - \mathbf{q})]. \end{aligned} \quad (4.12)$$

Employing the hierarchy equation (3.6) to reduce the integral and inserting the expansion (3.5) we get

$$\begin{aligned} \frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k})^* n_{\sigma}(\mathbf{k}) \rangle \\ = -\beta^{-1} n_{\sigma} \mathbf{k} \sum_{\sigma_1} n_{\sigma_1} [a_{\sigma_1 \sigma}^{(0)} + k_{D\sigma_1}^2 a_{\sigma_1 \sigma}^{(1)} + (a_{\sigma_1 \sigma}^{(1)} + k_{D\sigma_1}^2 a_{\sigma_1 \sigma}^{(2)}) k^2] \end{aligned} \quad (4.13)$$

for small \mathbf{k} . Addition of the kinetic-pressure contribution gives the result

$$\frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k})^* n_{\sigma}(\mathbf{k}) \rangle = \beta^{-1} n_{\sigma} \mathbf{k} \left[1 - \sum_{\sigma_1} n_{\sigma_1} k_{D\sigma_1}^2 (a_{\sigma_1 \sigma}^{(1)} + a_{\sigma_1 \sigma}^{(2)} k^2) \right], \quad (4.14)$$

for $\mathbf{k} \rightarrow \boldsymbol{\theta}$, from which the fluctuation formulae involving the total particle density and the charge density are easily obtained as

$$\frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k})^* n(\mathbf{k}) \rangle = \beta^{-1} \mathbf{k} \left[n - \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)} \right], \quad (4.15)$$

$$\frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k})^* q_v(\mathbf{k}) \rangle = -\beta^{-2} q_v^{-1} \mathbf{k} k^2 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} k_{D\sigma_1}^2 k_{D\sigma_2}^2 a_{\sigma_1 \sigma_2}^{(2)}, \quad (4.16)$$

in leading orders of \mathbf{k} . Here (3.15) has been used to derive the second formula.

The fluctuation formula for the square of the energy density in Fourier space contains contributions arising from the kinetic and the potential parts of $\epsilon(\mathbf{k})$ as given by (2.7). The purely potential contribution to the fluctuation formula is found upon introducing the Fourier transforms of the two-, three- and four-particle Ursell functions and using the symmetry properties of the sums and the integrals:

$$\begin{aligned} \frac{1}{V} \langle \epsilon^{\text{pot}}(\mathbf{k})^* \epsilon^{\text{pot}}(\mathbf{k}) \rangle \\ = \frac{1}{4} \sum_{\sigma_1, \sigma_2, \sigma_3, \sigma_4} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} e_{\sigma_4} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{d\mathbf{q}'}{(2\pi)^3} \frac{\mathbf{q} \cdot (\mathbf{k} - \mathbf{q})}{q^2 |\mathbf{k} - \mathbf{q}|^2} \frac{\mathbf{q}' \cdot (\mathbf{k} - \mathbf{q}')}{q'^2 |\mathbf{k} - \mathbf{q}'|^2} \\ \times [n_{\sigma_3} n_{\sigma_4} h_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}^{(4)}(-\mathbf{q}, \mathbf{k} - \mathbf{q}', \mathbf{q}') + 4n_{\sigma_3} \delta_{\sigma_1 \sigma_4} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \mathbf{q}')] \end{aligned}$$

$$\begin{aligned}
& + 2\delta_{\sigma_1\sigma_3}\delta_{\sigma_2\sigma_4}h_{\sigma_1\sigma_2}^{(2)}(\mathbf{q}-\mathbf{q}') \\
& + \frac{1}{2}\sum_{\sigma_1,\sigma_2,\sigma_3,\sigma_4}n_{\sigma_1}n_{\sigma_2}e_{\sigma_1}e_{\sigma_2}e_{\sigma_3}e_{\sigma_4}\int\frac{d\mathbf{q}}{(2\pi)^3}\frac{[\mathbf{q}\cdot(\mathbf{k}-\mathbf{q})]^2}{q^4|\mathbf{k}-\mathbf{q}|^4} \\
& \times [\delta_{\sigma_1\sigma_3}+n_{\sigma_3}h_{\sigma_1\sigma_3}^{(2)}(\mathbf{q})][\delta_{\sigma_2\sigma_4}+n_{\sigma_4}h_{\sigma_2\sigma_4}^{(2)}(\mathbf{k}-\mathbf{q})]. \tag{4.17}
\end{aligned}$$

It should be remarked that the second integral contains no divergencies in $\mathbf{q}=\mathbf{0}$ or $\mathbf{q}=\mathbf{k}$, as a consequence of the perfect-screening relation (3.7) with (3.5). Taking the limit $\mathbf{k}\rightarrow\mathbf{0}$ we may use the auxiliary relation (B.8) to eliminate $h^{(4)}$. As a result we get

$$\begin{aligned}
& \frac{1}{V}\langle\varepsilon^{\text{pot}}(\mathbf{k})^*\varepsilon^{\text{pot}}(\mathbf{k})\rangle \\
& = -\frac{3}{2}\beta^{-1}\sum_{\sigma_1,\sigma_2,\sigma_3}n_{\sigma_1}n_{\sigma_2}n_{\sigma_3}e_{\sigma_1}e_{\sigma_2}\int\frac{d\mathbf{q}}{(2\pi)^3}h_{\sigma_1\sigma_2\sigma_3}^{(3)}(-\mathbf{q},\mathbf{0}) \\
& - \frac{3}{2}q_v\lim_{\mathbf{k}\rightarrow\mathbf{0}}\frac{1}{k^2}\sum_{\sigma_1,\sigma_2}n_{\sigma_1}n_{\sigma_2}e_{\sigma_1}e_{\sigma_2}\int\frac{d\mathbf{q}}{(2\pi)^3}\frac{1}{q^2} \\
& \times \left[\sum_{\sigma_3}n_{\sigma_3}e_{\sigma_3}h_{\sigma_1\sigma_2\sigma_3}^{(3)}(-\mathbf{q},\mathbf{k})+e_{\sigma_1}h_{\sigma_1\sigma_2}^{(2)}(\mathbf{q})+e_{\sigma_2}h_{\sigma_1\sigma_2}^{(2)}(\mathbf{k}-\mathbf{q})\right] \\
& - \beta^{-1}\sum_{\sigma_1,\sigma_2}n_{\sigma_1}n_{\sigma_2}e_{\sigma_1}e_{\sigma_2}\int\frac{d\mathbf{q}}{(2\pi)^3}\frac{1}{q^2}h_{\sigma_1\sigma_2}^{(2)}(\mathbf{q}) \tag{4.18}
\end{aligned}$$

for $\mathbf{k}\rightarrow\mathbf{0}$. Subsequently we employ the relations (3.14) and (B.5) to evaluate the first and the second integral, respectively. In this way we obtain for small \mathbf{k}

$$\begin{aligned}
\frac{1}{V}\langle\varepsilon^{\text{pot}}(\mathbf{k})^*\varepsilon^{\text{pot}}(\mathbf{k})\rangle & = 9\beta^{-2}\sum_{\sigma_1,\sigma_2}n_{\sigma_1}n_{\sigma_2}(a_{\sigma_1\sigma_2}^{(0)}+2k_{D\sigma_1}^2a_{\sigma_1\sigma_2}^{(1)}+k_{D\sigma_1}^2k_{D\sigma_2}^2a_{\sigma_1\sigma_2}^{(2)}) \\
& + 2\beta^{-1}\sum_{\sigma_1,\sigma_2}n_{\sigma_1}n_{\sigma_2}e_{\sigma_1}e_{\sigma_2}\int\frac{d\mathbf{q}}{(2\pi)^3}\frac{1}{q^2}h_{\sigma_1\sigma_2}^{(2)}(\mathbf{q}). \tag{4.19}
\end{aligned}$$

The mixed kinetic-potential contribution to the fluctuation formula for the energy density follows directly by averaging over the momenta and employing (4.8),

$$\frac{1}{V}\langle\varepsilon^{\text{kin}}(\mathbf{k})^*\varepsilon^{\text{pot}}(\mathbf{k})\rangle = -\frac{9}{2}\beta^{-2}\sum_{\sigma_1,\sigma_2}n_{\sigma_1}n_{\sigma_2}(a_{\sigma_1\sigma_2}^{(0)}+k_{D\sigma_1}^2a_{\sigma_1\sigma_2}^{(1)}), \tag{4.20}$$

for small wavenumbers. Upon adding the purely kinetic contribution we end

up with

$$\begin{aligned} \frac{1}{V} \langle \varepsilon(\mathbf{k})^* \varepsilon(\mathbf{k}) \rangle &= 9\beta^{-2} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} \left(\frac{1}{4} a_{\sigma_1 \sigma_2}^{(0)} + k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)} + k_{D\sigma_1}^2 k_{D\sigma_2}^2 a_{\sigma_1 \sigma_2}^{(2)} \right) \\ &\quad + 2\beta^{-1} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + \frac{15}{4} \beta^{-2} n, \end{aligned} \quad (4.21)$$

for small \mathbf{k} .

Let us turn now to the derivation of a fluctuation formula for the product of the energy density and the pressure tensor. Since both (2.5) and (2.7) consist of a kinetic and a potential part the fluctuation expression falls apart into four terms. Of these the purely potential contribution becomes, upon introducing the Ursell functions,

$$\begin{aligned} \frac{1}{V} \langle \varepsilon^{\text{pot}}(\mathbf{k})^* \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) \rangle &= -\frac{1}{2} \sum_{\sigma_1, \sigma_2, \sigma_3, \sigma_4} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} e_{\sigma_4} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{d\mathbf{q}'}{(2\pi)^3} \frac{\mathbf{q} \cdot (\mathbf{k} - \mathbf{q})}{q^2 |\mathbf{k} - \mathbf{q}|^2} \frac{q'}{q'^2} \\ &\quad \times \{ n_{\sigma_3} n_{\sigma_4} h_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}^{(4)}(-\mathbf{q}, \mathbf{k} - \mathbf{q}', \mathbf{q}') + 2n_{\sigma_3} \delta_{\sigma_1 \sigma_4} [h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \mathbf{q}')] \\ &\quad + h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \mathbf{k} - \mathbf{q}') \} + 2\delta_{\sigma_1 \sigma_3} \delta_{\sigma_2 \sigma_4} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q} - \mathbf{q}') \\ &\quad - \sum_{\sigma_1, \sigma_2, \sigma_3, \sigma_4} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} e_{\sigma_4} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q} \cdot (\mathbf{k} - \mathbf{q})}{q^2 |\mathbf{k} - \mathbf{q}|^2} \frac{\mathbf{q}}{q^2} \\ &\quad \times [\delta_{\sigma_1 \sigma_3} + n_{\sigma_3} h_{\sigma_1 \sigma_3}^{(2)}(\mathbf{q})] [\delta_{\sigma_2 \sigma_4} + n_{\sigma_4} h_{\sigma_2 \sigma_4}^{(2)}(\mathbf{k} - \mathbf{q})]. \end{aligned} \quad (4.22)$$

The four-particle Ursell function is eliminated by rearranging its arguments with the help of (3.4) and using subsequently the hierarchy equation (3.8). Likewise, by means of (3.6), the term with $h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \mathbf{q}')$ is transformed into an expression involving $h^{(2)}$ only. As a result we are left with the identity

$$\begin{aligned} \frac{1}{V} \langle \varepsilon^{\text{pot}}(\mathbf{k})^* \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) \rangle &= \frac{1}{2} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q} \cdot (\mathbf{k} - \mathbf{q})}{q^2 |\mathbf{k} - \mathbf{q}|^2} \\ &\quad \times \left\{ q_v \frac{\mathbf{k}}{k^2} \left[\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \mathbf{k}) + e_{\sigma_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + e_{\sigma_2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} - \mathbf{q}) \right] \right. \\ &\quad \left. + \beta^{-1} \mathbf{k} \sum_{\sigma_3} n_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \mathbf{k}) + \beta^{-1} \mathbf{q} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + \beta^{-1} (\mathbf{k} - \mathbf{q}) h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} - \mathbf{q}) \right\}. \end{aligned} \quad (4.23)$$

From (B.4) we infer that the expression between braces is linear in \mathbf{k} for small

$$\begin{aligned}
 & \frac{1}{V} \langle \varepsilon^{\text{pot}}(\mathbf{k}) * \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) \rangle \\
 &= -\frac{1}{2} \beta^{-1} \mathbf{k} \sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \boldsymbol{\theta}) \\
 & \quad - \frac{1}{2} q_v \mathbf{k} \lim_{k \rightarrow 0} \frac{1}{k^2} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \\
 & \quad \times \left[\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \mathbf{k}) + e_{\sigma_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + e_{\sigma_2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} - \mathbf{q}) \right] \\
 & \quad - \frac{1}{2} \beta^{-1} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \mathbf{k} \cdot \nabla_{\mathbf{q}} [q h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q})]. \quad (4.24)
 \end{aligned}$$

In the last term we perform a partial integration and use the isotropy of $h_{\sigma_1 \sigma_2}^{(2)}$. The other terms may be evaluated with the help of (3.14) and (B.5), as was done below (4.18). This gives the result

$$\begin{aligned}
 & \frac{1}{V} \langle \varepsilon^{\text{pot}}(\mathbf{k}) * \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) \rangle \\
 &= 3\beta^{-2} \mathbf{k} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} (a_{\sigma_1 \sigma_2}^{(0)} + 2k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)} + k_{D\sigma_1}^2 k_{D\sigma_2}^2 a_{\sigma_1 \sigma_2}^{(2)}) \\
 & \quad + \frac{2}{3} \beta^{-1} \mathbf{k} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}), \quad (4.25)
 \end{aligned}$$

up to terms linear in \mathbf{k} .

The two mixed kinetic-potential contributions to the fluctuation formula for the product of the energy density and the pressure tensor are obtained by averaging over the momenta and using (4.8) and (4.13),

$$\frac{1}{V} \langle \varepsilon^{\text{kin}}(\mathbf{k}) * \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) \rangle = -\frac{3}{2} \beta^{-2} \mathbf{k} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} (a_{\sigma_1 \sigma_2}^{(0)} + k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)}), \quad (4.26)$$

$$\frac{1}{V} \langle \varepsilon^{\text{pot}}(\mathbf{k}) * \mathbf{k} \cdot \boldsymbol{\tau}^{\text{kin}}(\mathbf{k}) \rangle = -3\beta^{-2} \mathbf{k} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} (a_{\sigma_1 \sigma_2}^{(0)} + k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)}), \quad (4.27)$$

up to first order in \mathbf{k} . The purely kinetic contribution is trivially evaluated. Adding all results we find:

$$\begin{aligned}
 \frac{1}{V} \langle \varepsilon(\mathbf{k}) * \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle &= \left[\frac{3}{2} \beta^{-2} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} (k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)} + 2k_{D\sigma_1}^2 k_{D\sigma_2}^2 a_{\sigma_1 \sigma_2}^{(2)}) \right. \\
 & \quad \left. + \frac{2}{3} \beta^{-1} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + \frac{5}{2} \beta^{-2} n \right] \mathbf{k}, \quad (4.28)
 \end{aligned}$$

for small \mathbf{k} .

Finally we consider the fluctuation formula for the square of the pressure tensor. The evaluation of the purely potential contribution to this fluctuation formula is greatly facilitated by making use of the close similarity of the potential parts of (2.5) and (2.7). Instead of (4.23) we get

$$\begin{aligned} \frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) * \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) \rangle &= - \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} \\ &\times \left\{ q_v \frac{\mathbf{k}}{k^2} \left[\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \mathbf{k}) + e_{\sigma_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + e_{\sigma_2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} - \mathbf{q}) \right] \right. \\ &\left. + \beta^{-1} \mathbf{k} \sum_{\sigma_3} n_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(-\mathbf{q}, \mathbf{k}) + \beta^{-1} \mathbf{q} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + \beta^{-1} (\mathbf{k} - \mathbf{q}) h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} - \mathbf{q}) \right\}. \end{aligned} \quad (4.29)$$

The terms with $h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}$ can be reduced with the help of the hierarchy equation (3.6). The second term at the right-hand side vanishes on account of parity. As a result we obtain

$$\begin{aligned} \frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) * \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) \rangle &= -\beta^{-1} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}\mathbf{q}}{q^2} [h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) - h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} - \mathbf{q})] \\ &+ \beta^{-2} \frac{\mathbf{k}\mathbf{k}}{k^4} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} (k^2 + k_{D\sigma_1}^2)(k^2 + k_{D\sigma_2}^2) h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k}) \\ &+ \beta^{-1} q_v^2 \frac{\mathbf{k}\mathbf{k}}{k^2} + q_v^2 \frac{\mathbf{k}\mathbf{k}}{k^4} \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1}^2. \end{aligned} \quad (4.30)$$

For small \mathbf{k} the integral is simplified by making a Taylor expansion and using the isotropy of the integration. The other terms are evaluated by inserting (3.5), so that we arrive at the expression

$$\begin{aligned} \frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) * \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) \rangle &= \beta^{-2} \mathbf{k}\mathbf{k} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} (a_{\sigma_1 \sigma_2}^{(0)} + 2k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)} + k_{D\sigma_1}^2 k_{D\sigma_2}^2 a_{\sigma_1 \sigma_2}^{(2)}) \\ &+ \frac{1}{5} \beta^{-1} \left(\mathbf{k}\mathbf{k} - \frac{1}{3} k^2 \mathbf{U} \right) \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}), \end{aligned} \quad (4.31)$$

up to second order in \mathbf{k} . Once more the electrostatic sum rules (3.7) and (3.15) have been employed.

The mixed kinetic-potential contribution to the fluctuation formula follows

directly from (4.13) as

$$\frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}^{\text{kin}}(\mathbf{k})^* \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k}) \rangle = -\beta^{-2} \mathbf{k} \mathbf{k} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} (a_{\sigma_1 \sigma_2}^{(0)} + k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)}) \quad (4.32)$$

in leading order of \mathbf{k} . Adding the trivial kinetic contribution we end up with

$$\begin{aligned} \frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k})^* \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle &= \beta^{-2} \mathbf{k} \mathbf{k} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} k_{D\sigma_1}^2 k_{D\sigma_2}^2 a_{\sigma_1 \sigma_2}^{(2)} \\ &+ \frac{1}{5} \beta^{-1} \left(\mathbf{k} \mathbf{k} - \frac{1}{3} k^2 \mathbf{U} \right) \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) \\ &+ n\beta^{-2} (2\mathbf{k} \mathbf{k} + k^2 \mathbf{U}), \end{aligned} \quad (4.33)$$

up to terms of second order in \mathbf{k} .

We have now completed our task to derive the fluctuation formulae for the products of the partial densities, the energy density and the pressure in Fourier space. We have established these formulae on the basis of the BBGKY hierarchy equations and the exponential clustering hypothesis. However, the results obtained so far are not yet in their final form, since they still contain the expansion coefficients $a_{\sigma_1 \sigma_2}^{(n)}$ as defined in (3.5). These coefficients satisfy the conditions (3.7) and (3.15), which are the Fourier transcriptions of the perfect-screening and the Stillinger–Lovett sum rules for the zeroth and second moments of the two-particle Ursell function in coordinate space. A close inspection of the results of this section shows that the ‘electrostatic’ sum rules are of no help in further reducing the fluctuation formulae. To achieve that goal we must employ the ‘thermodynamic’ sum rules derived in a previous paper³).

5. Derivation of fluctuation formulae from the microscopic balance equations

In the previous section fluctuation formulae have been established by expressing the ensemble average of the microscopic fluctuating quantities in terms of the Ursell functions and employing subsequently equalities that follow from the hierarchy equations and the symmetry properties. This method to derive fluctuation formulae is quite general; in principle it may be applied for any fluctuating quantity. However, a somewhat different approach may be adopted if one is interested in particular in the fluctuations of physical quantities that occur in the balance equations of particle density, momentum density and energy density. For the one-component plasma the fluctuation

formulae for the density, the pressure and the energy density have been obtained along these lines²). In this section we shall show that an ionic mixture can be dealt with in an analogous fashion.

Let us start from the momentum balance (2.4), multiply it by $V^{-1}n_\sigma(\mathbf{k})^*$ and take the average. Upon using the hermiticity of the Liouville operator and the continuity equation (2.2) we get

$$\frac{1}{V}\langle n_\sigma(\mathbf{k})^* \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle = n_\sigma k_B T \mathbf{k} \left\{ 1 - \frac{1}{k^2} \sum_{\sigma_1} k_{D\sigma_1}^2 [\delta_{\sigma_1\sigma} + n_{\sigma_1} h_{\sigma_1\sigma}^{(2)}(\mathbf{k})] \right\}. \quad (5.1)$$

Since the left-hand side is finite for $\mathbf{k} \rightarrow \mathbf{0}$ it follows that the term of order k^{-2} at the right-hand side should vanish. Substitution of the expansion (3.5) for $h_{\sigma_1\sigma_2}^{(2)}(\mathbf{k})$ leads directly to the perfect-screening relation (3.7). As a consequence (5.1) reduces to the fluctuation formula (4.14). Subtracting the contribution of the kinetic pressure, which is trivially obtained, we recover (4.13).

Returning to the momentum balance equation (2.4) we now multiply it by $V^{-1} \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k})^*$ and take the average. Employing the hermiticity of L , as before, the left-hand side of the resulting equation becomes after substitution of $\mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k})$, as given by (2.5), and averaging over the momenta,

$$k_B T \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \left\{ \frac{\mathbf{q}\mathbf{q}}{q^2} [h_{\sigma_1\sigma_2}^{(2)}(\mathbf{q}) - h_{\sigma_1\sigma_2}^{(2)}(\mathbf{k} - \mathbf{q})] - \frac{\mathbf{q}\mathbf{k}}{q^2} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{q}) \right\}. \quad (5.2)$$

For small \mathbf{k} the integral can be evaluated by Taylor expansion of $h_{\sigma_1\sigma_2}^{(2)}(\mathbf{k} - \mathbf{q})$ and a partial integration. In this way we get

$$\begin{aligned} & \frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}^{\text{pot}}(\mathbf{k})^* \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle \\ &= \frac{\mathbf{k}\mathbf{k}}{k^2} (k_B T)^2 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} k_{D\sigma_1}^2 [a_{\sigma_1\sigma_2}^{(0)} + k_{D\sigma_2}^2 a_{\sigma_1\sigma_2}^{(1)} + k^2 (a_{\sigma_1\sigma_2}^{(1)} + k_{D\sigma_2}^2 a_{\sigma_1\sigma_2}^{(2)})] \\ & \quad + \frac{1}{5} k_B T \left(\mathbf{k}\mathbf{k} - \frac{1}{3} k^2 \mathbf{U} \right) \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{q}), \end{aligned} \quad (5.3)$$

up to second order in \mathbf{k} . Since the left-hand side is quadratic in \mathbf{k} it follows that the coefficient of $\mathbf{k}\mathbf{k}/k^2$ at the right-hand side must vanish,

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} k_{D\sigma_1}^2 (a_{\sigma_1\sigma_2}^{(0)} + k_{D\sigma_2}^2 a_{\sigma_1\sigma_2}^{(1)}) = 0. \quad (5.4)$$

Use of the perfect-screening relation (3.7) now leads to the Stillinger-Lovett condition (3.15).

The kinetic counterpart $V^{-1} \langle \mathbf{k} \cdot \boldsymbol{\tau}^{\text{kin}}(\mathbf{k}) * \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle$ is easily derived since we have (4.13) (and hence (4.32)) at our disposal. Upon adding it to (5.3), with (5.4) inserted, we arrive at (4.33) once more.

The outline given above shows how the fluctuation formulae for the pressure may be obtained by a systematic use of the momentum balance equation and the continuity equations. In the course of the derivation both the perfect-screening property and the Stillinger-Lovett condition were proved as well. We may proceed, as in ref. 2, with a consideration of the fluctuation formulae for the energy density. These follow from the relation between the potential part of the energy density and the trace of the potential pressure tensor. In this way the complete set of fluctuation formulae involving the energy density, viz. (4.9)–(4.11), (4.21) and (4.28), are found again. Since the arguments are closely analogous to those used for the one-component plasma the details will not be given here.

6. Partial density fluctuations

The fluctuation formulae derived in sections 4 and 5 are not yet in a suitable form, since they still contain the expansion coefficients $a_{\sigma_1 \sigma_2}^{(n)}$ of the two-particle Ursell functions $h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q})$ for small wavenumber \mathbf{q} . In ref. 3 (also to be referred to as I) we have derived sum rules for the pair correlation functions in terms of macroscopic thermodynamic quantities. These ‘thermodynamic’ sum rules can be used to obtain expressions for the sums over $a_{\sigma_1 \sigma_2}^{(n)}$ that occur in the fluctuation formulae. In fact, by using (3.2) and (3.5), we find from the sum rules (I.5.3), (I.5.5) and (I.5.8)

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} a_{\sigma_1 \sigma_2}^{(0)} = \frac{2}{3} \beta \frac{\partial n}{\partial \beta} - 2q_v \frac{\partial n}{\partial q_v} + n, \tag{6.1}$$

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} k_{D\sigma_1}^2 a_{\sigma_1 \sigma_2}^{(1)} = q_v \frac{\partial n}{\partial q_v}, \tag{6.2}$$

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} k_{D\sigma_1}^2 k_{D\sigma_2}^2 a_{\sigma_1 \sigma_2}^{(2)} = -\beta q_v \frac{\partial p}{\partial q_v}, \tag{6.3}$$

where the partial derivatives at the right-hand side are defined in terms of the independent set $\beta, \tilde{\mu}_\sigma$ ($\sigma = 2, \dots, s$) and q_v , as introduced in ref. 3. With the help of these identities the fluctuation formulae (4.4)–(4.6) for the particle and

the charge density become

$$\frac{1}{V} \langle n(\mathbf{k})^* n(\mathbf{k}) \rangle = \frac{2}{3} \beta \frac{\partial n}{\partial \beta} - 2q_v \frac{\partial n}{\partial q_v} + 2n, \quad (6.4)$$

$$\frac{1}{V} \langle q_v(\mathbf{k})^* n(\mathbf{k}) \rangle = \frac{1}{\beta} \frac{\partial n}{\partial q_v} k^2, \quad (6.5)$$

$$\frac{1}{V} \langle q_v(\mathbf{k})^* q_v(\mathbf{k}) \rangle = \frac{1}{\beta} k^2 - \frac{1}{\beta q_v} \frac{\partial p}{\partial q_v} k^4, \quad (6.6)$$

in leading orders of the wavenumber. As one would expect for a multi-component ionic mixture, in which the particle density and the charge density are independent quantities, the particle density fluctuations remain finite in the long-wavelength limit, whereas the charge density fluctuations are suppressed for $k \rightarrow 0$.

The fluctuation formulae (6.4)–(6.6) may be cast into an alternative form by choosing as the independent thermodynamic variables β and μ_σ with $\sigma = 1, \dots, s$. The sum rules (I.5.11)–(I.5.13) in terms of these variables yield on a par with (6.4)–(6.6)

$$\frac{1}{V} \langle n(\mathbf{k})^* n(\mathbf{k}) \rangle = \frac{S_{nn} S - S_n^2}{\beta S}, \quad (6.7)$$

$$\frac{1}{V} \langle q_v(\mathbf{k})^* n(\mathbf{k}) \rangle = \frac{S_n}{\beta S} k^2, \quad (6.8)$$

$$\frac{1}{V} \langle q_v(\mathbf{k})^* q_v(\mathbf{k}) \rangle = \frac{1}{\beta} k^2 - \frac{1}{\beta S} k^4, \quad (6.9)$$

with the abbreviations $S := \sum_\sigma e_\sigma \partial q_v / \partial \mu_\sigma$, $S_n := \sum_\sigma \partial q_v / \partial \mu_\sigma$ and $S_{nn} := \sum_\sigma \partial n / \partial \mu_\sigma$.

It may be remarked that formulae analogous to (6.4) and (6.5), or (6.7) and (6.8), can be derived for the fluctuations $m_v(\mathbf{k})$ in the equilibrium mass density $m_v = \sum_\sigma m_\sigma n_\sigma$. From the sum rules one easily derives for small k

$$\frac{1}{V} \langle m_v(\mathbf{k})^* m_v(\mathbf{k}) \rangle = \frac{S_{mm} S - S_m^2}{\beta S}, \quad (6.10)$$

$$\frac{1}{V} \langle q_v(\mathbf{k})^* m_v(\mathbf{k}) \rangle = \frac{S_m}{\beta S} k^2, \quad (6.11)$$

with $S_m := \sum_\sigma m_\sigma \partial q_v / \partial \mu_\sigma$ and $S_{mm} := \sum_\sigma m_\sigma \partial m_v / \partial \mu_\sigma$. As (6.10) shows the fluctuations in the mass density are in general finite in the long-wavelength limit, even for ionic mixtures in which all species carry the same charge. An

obvious exception is the ionic mixture for which the ratio e_σ/m_σ is equal for all species, since then $S_m = m/e S$ and $S_{mm} = (m/e)^2 S$.

The fluctuation expressions for the partial densities $n_\sigma(\mathbf{k})$ can be combined conveniently in a matrix representation^{8,9}):

$$\frac{1}{V} \langle n_{\sigma_1}(\mathbf{k})^* n_{\sigma_2}(\mathbf{k}) \rangle = (n_{\sigma_1} n_{\sigma_2})^{1/2} [\delta_{\sigma_1 \sigma_2} + H_{\sigma_1 \sigma_2}(\mathbf{k})], \quad (6.12)$$

with the symmetric matrix $H_{\sigma_1 \sigma_2} = (n_{\sigma_1} n_{\sigma_2})^{1/2} h_{\sigma_1 \sigma_2}^{(2)}$. Writing the Taylor expansion

$$\mathbf{H}(\mathbf{k}) = \sum_{n=0}^{\infty} \mathbf{H}^{(n)} k^{2n}, \quad (6.13)$$

we get from the sum rules (I.5.11)–(I.5.13)

$$\delta_{\sigma_1 \sigma_2} + H_{\sigma_1 \sigma_2}^{(0)} = \frac{1}{\beta (n_{\sigma_1} n_{\sigma_2})^{1/2}} \left(\frac{\partial n_{\sigma_1}}{\partial \mu_{\sigma_2}} - \frac{1}{S} \frac{\partial q_v}{\partial \mu_{\sigma_1}} \frac{\partial q_v}{\partial \mu_{\sigma_2}} \right), \quad (6.14)$$

$$\sum_{\sigma_1} e_{\sigma_1} n_{\sigma_1}^{1/2} H_{\sigma_1 \sigma_2}^{(1)} = \frac{1}{\beta n_{\sigma_2}^{1/2} S} \frac{\partial q_v}{\partial \mu_{\sigma_2}}, \quad (6.15)$$

$$\sum_{\sigma_1, \sigma_2} e_{\sigma_1} e_{\sigma_2} (n_{\sigma_1} n_{\sigma_2})^{1/2} H_{\sigma_1 \sigma_2}^{(2)} = -\frac{1}{\beta S}. \quad (6.16)$$

The representation (6.12) is particularly suitable if one is interested in the direct correlation functions $c_{\sigma_1 \sigma_2}(\mathbf{k})$ that are defined through the Ornstein–Zernike equation

$$\sum_{\sigma_3} (\delta_{\sigma_1 \sigma_3} + H_{\sigma_1 \sigma_3})(\delta_{\sigma_3 \sigma_2} - C_{\sigma_3 \sigma_2}) = \delta_{\sigma_1 \sigma_2}, \quad (6.17)$$

with $C_{\sigma_1 \sigma_2}(\mathbf{k}) = (n_{\sigma_1} n_{\sigma_2})^{1/2} c_{\sigma_1 \sigma_2}(\mathbf{k})$. In contrast to \mathbf{H} the small-wavenumber expansion of \mathbf{C} is singular for a Coulomb system,

$$\mathbf{C}(\mathbf{k}) = \sum_{n=-1}^{\infty} \mathbf{C}^{(n)} k^{2n}. \quad (6.18)$$

The matrix $\mathbf{1} + \mathbf{H}^{(0)}$ is singular, as follows from the perfect-screening property contained in (6.14). Its null-space is spanned by the vector \bar{e} , with components $n_\sigma^{1/2} e_\sigma / (\sum_{\sigma'} n_{\sigma'} e_{\sigma'}^2)^{1/2}$. The Ornstein–Zernike equation in order k^{-2} and k^0 yields directly

$$C_{\sigma_1 \sigma_2}^{(-1)} = -\beta (n_{\sigma_1} n_{\sigma_2})^{1/2} e_{\sigma_1} e_{\sigma_2}. \quad (6.19)$$

Defining the projector $\mathbf{P} = \mathbf{1} - \bar{e}\bar{e}$ we may derive from (6.17) in order k^0 and k^2 ,

$$\mathbf{P} \cdot (\mathbf{1} - \mathbf{C}^{(0)}) \cdot \mathbf{P} = \mathbf{P} \cdot [\mathbf{P} \cdot (\mathbf{1} + \mathbf{H}^{(0)}) \cdot \mathbf{P}]^{-1} \cdot \mathbf{P}, \quad (6.20)$$

$$\bar{e} \cdot (\mathbf{1} - \mathbf{C}^{(0)}) \cdot \mathbf{P} = -[\bar{e} \cdot \mathbf{H}^{(1)} \cdot \bar{e}]^{-1} \bar{e} \cdot \mathbf{H}^{(1)} \cdot \mathbf{P} \cdot [\mathbf{P} \cdot (\mathbf{1} + \mathbf{H}^{(0)}) \cdot \mathbf{P}]^{-1} \cdot \mathbf{P}, \quad (6.21)$$

$$\begin{aligned} \bar{e} \cdot (\mathbf{1} - \mathbf{C}^{(0)}) \cdot \bar{e} &= -[\bar{e} \cdot \mathbf{H}^{(1)} \cdot \bar{e}]^{-1} \bar{e} \cdot \mathbf{H}^{(2)} \cdot \bar{e} [\bar{e} \cdot \mathbf{H}^{(1)} \cdot \bar{e}]^{-1} \\ &\quad + [\bar{e} \cdot \mathbf{H}^{(1)} \cdot \bar{e}]^{-1} \bar{e} \cdot \mathbf{H}^{(1)} \cdot \mathbf{P} \cdot [\mathbf{P} \cdot (\mathbf{1} + \mathbf{H}^{(0)}) \cdot \mathbf{P}]^{-1} \\ &\quad \cdot \mathbf{P} \cdot \mathbf{H}^{(1)} \cdot \bar{e} [\bar{e} \cdot \mathbf{H}^{(1)} \cdot \bar{e}]^{-1}. \end{aligned} \quad (6.22)$$

Here the matrix inverses are defined in the space orthogonal to \bar{e} . Evaluation of these expressions with the help of (6.14)–(6.16) gives

$$\delta_{\sigma_1\sigma_2} - C_{\sigma_1\sigma_2}^{(0)} = \beta (n_{\sigma_1} n_{\sigma_2})^{1/2} \frac{\partial \mu_{\sigma_1}}{\partial n_{\sigma_2}}, \quad (6.23)$$

with partial derivatives at constant β and n_σ ($\sigma \neq \sigma_2$). By summing over all species, with the weights $(n_{\sigma_1} n_{\sigma_2})^{1/2}$, we arrive at the equality^{9,12)}

$$n - \sum_{\sigma_1, \sigma_2} (n_{\sigma_1} n_{\sigma_2})^{1/2} C_{\sigma_1\sigma_2}^{(0)} = \beta \left[n^{-1} \frac{\partial n}{\partial p} \right]^{-1}, \quad (6.24)$$

which contains at the right-hand side the isothermal compressibility $n^{-1} \partial n / \partial p$ at constant concentrations n_σ / n .

From the Ornstein–Zernike relation (6.17), with (6.18), (6.19) and (6.23) inserted, we obtain an alternative form for the fluctuations (6.12) of the partial densities,

$$\frac{1}{V} \langle n_{\sigma_1}(\mathbf{k})^* n_{\sigma_2}(\mathbf{k}) \rangle = \beta^{-1} \left(e_{\sigma_1} e_{\sigma_2} k^{-2} + \frac{\partial \mu_{\sigma_1}}{\partial n_{\sigma_2}} + \dots \right)^{-1}. \quad (6.25)$$

In ref. 9 this formula has been derived in a different way. Often the partial density fluctuations have been considered for the special case of a binary mixture^{12,13)}, and more in particular for a binary mixture consisting of particles with charges of equal magnitude and opposite sign^{14–16)}.

7. Energy and pressure fluctuations

In sections 4 and 5 we have derived fluctuation formulae for the energy density $\varepsilon(\mathbf{k})$ and the pressure tensor $\boldsymbol{\tau}(\mathbf{k})$ in Fourier space. From the microscopic expressions (2.5) and (2.7) for these quantities we obtain the equilibrium values of their long-wavelength limits as

$$\lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \langle \varepsilon(\mathbf{k}) \rangle = u_v, \quad (7.1)$$

$$\lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \langle \hat{\mathbf{k}} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle = \left(\frac{1}{3} u_v + \frac{1}{2} \beta^{-1} n \right) \hat{\mathbf{k}}, \quad (7.2)$$

with $\hat{\mathbf{k}} = \mathbf{k}/k$ and u_v the internal energy per particle,

$$u_v = \frac{3}{2} \beta^{-1} n + \frac{1}{2} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}). \quad (7.3)$$

Since the scaling properties of the Coulomb interaction imply the thermodynamic equation of state³⁾

$$p = \frac{1}{3} u_v + \frac{1}{2} \beta^{-1} n, \quad (7.4)$$

the equality (7.2) expresses the usual connexion between the mechanical pressure tensor $\boldsymbol{\tau}$ and the thermodynamic pressure p .

By differentiation of the equation of state (7.4) with respect to β the auxiliary identity

$$u_v = \frac{9}{4} q_v \frac{\partial p}{\partial q_v} - \frac{3}{4} \beta \frac{\partial p}{\partial \beta} - \frac{9}{8} \frac{q_v}{\beta} \frac{\partial n}{\partial q_v} - \frac{3}{8} \frac{n}{\beta}, \quad (7.5)$$

which will be useful in reducing the fluctuation formulae, is easily derived (see also (I.3.22)).

Employing the sum rules (6.1)–(6.3) in Fourier space, the expression (7.3) for u_v and the thermodynamic identity (7.5) we can transform the right-hand sides of the fluctuation formulae of section 4 to linear combinations of the density n and the derivatives of the pressure p and the density n with respect to the inverse temperature β and the charge density q_v . In leading orders of \mathbf{k} we get

$$\frac{1}{V} \langle \varepsilon(\mathbf{k})^* n(\mathbf{k}) \rangle = - \frac{\partial n}{\partial \beta}, \quad (7.6)$$

$$\frac{1}{V} \langle \varepsilon(\mathbf{k})^* q_v(\mathbf{k}) \rangle = \left(\frac{3}{\beta} \frac{\partial p}{\partial q_v} - \frac{3}{2\beta^2} \frac{\partial n}{\partial q_v} \right) k^2, \quad (7.7)$$

$$\frac{1}{V} \langle \hat{\mathbf{k}} \cdot \boldsymbol{\tau}(\mathbf{k})^* n(\mathbf{k}) \rangle = \left(-\frac{q_v}{\beta} \frac{\partial n}{\partial q_v} + \frac{n}{\beta} \right) \hat{\mathbf{k}}, \quad (7.8)$$

$$\frac{1}{V} \langle \hat{\mathbf{k}} \cdot \boldsymbol{\tau}(\mathbf{k})^* q_v(\mathbf{k}) \rangle = \frac{1}{\beta} \frac{\partial p}{\partial q_v} k^2 \hat{\mathbf{k}}, \quad (7.9)$$

$$\frac{1}{V} \langle \varepsilon(\mathbf{k})^* \varepsilon(\mathbf{k}) \rangle = -3 \frac{\partial p}{\partial \beta} + \frac{3}{2\beta} \frac{\partial n}{\partial \beta} - \frac{3}{2} \frac{n}{\beta^2}, \quad (7.10)$$

$$\frac{1}{V} \langle \varepsilon(\mathbf{k})^* \hat{\mathbf{k}} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle = -\frac{\partial p}{\partial \beta} \hat{\mathbf{k}}, \quad (7.11)$$

$$\begin{aligned} \frac{1}{V} \langle \hat{\mathbf{k}} \cdot \boldsymbol{\tau}(\mathbf{k})^* \hat{\mathbf{k}} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle &= -\frac{3}{10} \frac{\partial p}{\partial \beta} (\hat{\mathbf{k}}\hat{\mathbf{k}} - \frac{1}{3}\mathbf{U}) - \frac{1}{10} \frac{q_v}{\beta} \frac{\partial p}{\partial q_v} (\hat{\mathbf{k}}\hat{\mathbf{k}} + 3\mathbf{U}) \\ &\quad - \frac{9}{20} \frac{q_v}{\beta^2} \frac{\partial n}{\partial q_v} (\hat{\mathbf{k}}\hat{\mathbf{k}} - \frac{1}{3}\mathbf{U}) + \frac{5}{4} \frac{n}{\beta^2} (\hat{\mathbf{k}}\hat{\mathbf{k}} + \mathbf{U}). \end{aligned} \quad (7.12)$$

As before the partial derivatives are taken with respect to the variables of the set β , $\tilde{\mu}_\sigma$ ($\sigma = 2, \dots, s$) and q_v . Alternatively, one may introduce partial derivatives with respect to the set β , μ_σ ($\sigma = 1, \dots, s$) by eliminating $\partial n / \partial q_v$ and $\partial p / \partial q_v$ with the help of the identities

$$\frac{\partial n}{\partial q_v} = \frac{S_n}{S}, \quad \frac{\partial p}{\partial q_v} = \frac{q_v}{S}, \quad (7.13)$$

with S and S_n defined below (6.9). Furthermore we remark that the equation of state (7.4) can be used to eliminate derivatives of p in favour of those of u_v . For example, (7.10) then gets the simpler form

$$\frac{1}{V} \langle \varepsilon(\mathbf{k})^* \varepsilon(\mathbf{k}) \rangle = -\frac{\partial u_v}{\partial \beta}. \quad (7.14)$$

For a one-component plasma the particle density n and the charge density q_v are proportional, so that then $\partial n / \partial \beta = 0$ and $\partial n / \partial q_v = n / q_v$. In that case the fluctuation formulae then reduce to those derived earlier^{1,2}). The fluctuation formulae (7.6)–(7.9) for the ionic mixture show the different reactions of the system to fluctuations in the particle and the charge density. Whereas the fluctuation expressions containing the former remain finite in the long-wavelength limit, the expressions containing the charge density tend to zero for $\mathbf{k} \rightarrow \mathbf{0}$. The fluctuation formulae (7.10)–(7.12) for the energy density and the pressure have a finite limit for $\mathbf{k} \rightarrow \mathbf{0}$.

The complete set of formulae for the long-wavelength fluctuations of the

partial densities, the energy density and the pressure tensor of an ionic mixture have now been derived from equilibrium statistical mechanics. Both the electrostatic and the thermodynamic sum rules for the pair correlation functions, which have been studied in the first paper of this series, turned out to be indispensable for the derivation of the fluctuation formulae.

Appendix A

Irreducible cartesian tensors

To derive the higher-order perfect-screening relations for the three-particle Ursell functions we need some properties of the irreducible parts of polyadic tensors \mathbf{a}^n that can be built on the basis of a vector \mathbf{a} . Although studies on irreducible cartesian tensors are available in the literature¹⁷⁻¹⁹), we prefer to summarize in the following the formulae that are useful to obtain the results of section 3.

The irreducible part of the highest rank included in \mathbf{a}^n is the completely traceless tensor $\hat{\mathbf{a}}^n$ the components of which are given by

$$\hat{a}_{i_1 \dots i_n}^n = \sum_{k=0}^{[n/2]} \frac{(-1)^k (2n - 2k - 1)!!}{(2n - 1)!! k! 2^k (n - 2k)!} a^{2k} \times \sum_P \delta_{P_{i_1}, P_{i_2}} \dots \delta_{P_{i_{2k-1}}, P_{i_{2k}}} \hat{a}_{P_{i_{2k+1}} \dots P_{i_n}}^{n-2k}, \quad (\text{A.1})$$

with $\{P_{i_k}\}$ a permutation of the indices $\{i_k\}$. Inversion of this formula leads to the expansion

$$a_{i_1 \dots i_n}^n = \sum_{k=0}^{[n/2]} \frac{(2n - 4k + 1)!!}{(2n - 2k + 1)!! k! 2^k (n - 2k)!} a^{2k} \times \sum_P \delta_{P_{i_1}, P_{i_2}} \dots \delta_{P_{i_{2k-1}}, P_{i_{2k}}} \hat{a}_{P_{i_{2k+1}} \dots P_{i_n}}^{n-2k}, \quad (\text{A.2})$$

which gives the decomposition of \mathbf{a}^n in its irreducible parts. Both (A.1) and (A.2) can be proved by contraction with $\delta_{i_1 i_2}$ and subsequent solution of the ensuing recursion relations for the expansion coefficients.

With the help of (A.2) we may transform the vectorial Taylor expansion of a function $f(\mathbf{x} + \mathbf{a})$ in the following way:

$$f(\mathbf{x} + \mathbf{a}) = \sum_{n=0}^{\infty} \frac{1}{n!} \mathbf{a}^n : \nabla^n f(\mathbf{x}) = \sum_{l=0}^{\infty} \sum_{s=0}^{\infty} \frac{(2l + 1)!!}{(2s)!! (2l + 2s + 1)!! l!} a^{2s} \hat{\mathbf{a}}^l : \hat{\nabla}^l \Delta^s f(\mathbf{x}). \quad (\text{A.3})$$

An equivalent form of this expansion follows by writing $f(\mathbf{x} + \mathbf{a}) = \exp(\mathbf{a} \cdot \nabla) f(\mathbf{x})$ and applying the Rayleigh expansion to the exponential.

An auxiliary relation needed in section 3 is obtained on multiplying (A.1) by $a_{i_{n+1}}$ and inserting (A.2),

$$\begin{aligned} \hat{a}_{i_1 \dots i_n}^n a_{i_{n+1}} &= \hat{a}_{i_1 \dots i_{n+1}}^{n+1} + \frac{a^2}{(2n+1)(n-1)!} \sum_P \delta_{P i_1 \dots i_{n+1}} \hat{a}_{P i_2 \dots P i_n}^{n-1} \\ &\quad - \frac{a^2}{(2n+1)(2n-1)(n-2)!} \sum_P \delta_{P i_1, P i_2} \hat{a}_{P i_3 \dots P i_n, i_{n+1}}^{n-1}. \end{aligned} \quad (\text{A.4})$$

In the spherical-tensor formalism this equality expresses the coupling of two irreducible tensors, one of rank n and the other of rank 1.

Appendix B

Auxiliary relations for $h^{(3)}$ and $h^{(4)}$

In this appendix a few useful equalities for the Ursell functions $h^{(3)}$ and $h^{(4)}$ will be derived from the hierarchy equations (3.6), (3.8) and the identities (3.11) and (3.13).

Upon choosing $n = 1$ in (3.13) and performing some partial integrations we get

$$\begin{aligned} \lim_{\mathbf{k} \rightarrow \mathbf{0}} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \left[\Delta_{\mathbf{q}} + \left(-3\mathbf{U} + \frac{2\mathbf{q}\mathbf{q}}{q^2} \right) : \nabla_{\mathbf{q}} \nabla_{\mathbf{k}} \right. \\ \left. + \left(3\mathbf{U} - \frac{4\mathbf{q}\mathbf{q}}{q^2} \right) : \nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \right] h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{q}, \mathbf{k}) \\ = -2 \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} e_{\sigma_3} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \Delta_{\mathbf{q}} h_{\sigma_1 \sigma_3}^{(2)}(\mathbf{q}) - 60 q_v \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} a_{\sigma_1 \sigma_3}^{(2)} \\ - 60 \beta^{-1} \sum_{\sigma_1} n_{\sigma_1} a_{\sigma_1 \sigma_3}^{(1)}. \end{aligned} \quad (\text{B.1})$$

After multiplication by $n_{\sigma_3} e_{\sigma_3}$ and summation over σ_3 we may use the perfect-screening relations (3.9) and (3.10) to transform the left-hand side. In this way we obtain

$$\begin{aligned} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \left[\left(3\mathbf{U} - \frac{2\mathbf{q}\mathbf{q}}{q^2} \right) : \nabla_{\mathbf{q}} \nabla_{\mathbf{q}} \right. \\ \left. - \left(3\mathbf{U} - \frac{4\mathbf{q}\mathbf{q}}{q^2} \right) : \left(\nabla_{\mathbf{q}} \nabla_{\mathbf{q}} - \frac{1}{3} \mathbf{U} \Delta_{\mathbf{q}} \right) \right] h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) \end{aligned}$$

$$\begin{aligned}
 & + \frac{5}{3} \lim_{k \rightarrow 0} \sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \Delta_k h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{q}, \mathbf{k}) \\
 & = -60q_v \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} a_{\sigma_1 \sigma_2}^{(2)} - 60\beta^{-1} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} a_{\sigma_1 \sigma_2}^{(1)}. \quad (\text{B.2})
 \end{aligned}$$

Employing the isotropy of the integral over \mathbf{q} we arrive at the identity

$$\begin{aligned}
 & \lim_{k \rightarrow 0} \sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \Delta_k h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{q}, \mathbf{k}) \\
 & \quad + \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \Delta_q h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) \\
 & = -36q_v \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} a_{\sigma_1 \sigma_2}^{(2)} - 36\beta^{-1} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} a_{\sigma_1 \sigma_2}^{(1)}. \quad (\text{B.3})
 \end{aligned}$$

Since (3.9) and (3.10) for $l = 1, 2$ imply that the combination

$$\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{q}, \mathbf{k}) + e_{\sigma_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + e_{\sigma_2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} + \mathbf{q}) \quad (\text{B.4})$$

has the form $c(\mathbf{q})k^2$ for small \mathbf{k} , with a scalar function $c(\mathbf{q})$, we may write (B.3) as

$$\begin{aligned}
 & \lim_{k \rightarrow 0} \frac{1}{k^2} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \\
 & \quad \times \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \left[\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{q}, \mathbf{k}) + e_{\sigma_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{q}) + e_{\sigma_2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k} + \mathbf{q}) \right] \\
 & = -6q_v \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} a_{\sigma_1 \sigma_2}^{(2)} - 6\beta^{-1} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} a_{\sigma_1 \sigma_2}^{(1)}. \quad (\text{B.5})
 \end{aligned}$$

The identity (3.11) for $k = 4$ and the hierarchy (3.8), can be combined to yield a useful relation for $h^{(4)}$. Let us start from (3.11) for $n = 0$. In an analogous way as followed in deriving (3.12) we may prove

$$\begin{aligned}
 & \lim_{k' \rightarrow -k} \sum_{\sigma_1, \sigma_4} n_{\sigma_1} n_{\sigma_4} e_{\sigma_1} e_{\sigma_4} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} \cdot \nabla_{\mathbf{k}'} h_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}^{(4)}(\mathbf{k}, \mathbf{k}', \mathbf{q}) \\
 & = \frac{1}{2} \sum_{\sigma_1, \sigma_4} n_{\sigma_1} n_{\sigma_4} e_{\sigma_1} e_{\sigma_4} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} \cdot \nabla_{\mathbf{q}} h_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}^{(4)}(\mathbf{k}, -\mathbf{k}, \mathbf{q}). \quad (\text{B.6})
 \end{aligned}$$

The right-hand side is reduced by performing a partial integration. At the left-hand side we employ the hierarchy (3.8) with the result

$$\begin{aligned}
& \lim_{\mathbf{k}' \rightarrow -\mathbf{k}} \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\mathbf{q}}{q^2} \nabla_{\mathbf{k}'} [e_{\sigma_2} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{k} - \mathbf{q}, \mathbf{k}') + e_{\sigma_3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{k}, \mathbf{k}' - \mathbf{q})] \\
& + 3\beta^{-1} \sum_{\sigma_1} n_{\sigma_1} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{k}, -\mathbf{k}) + k^{-2} \left[\sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k}) \right] \\
& \times \left[e_{\sigma_3} + \sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} h_{\sigma_3 \sigma_4}^{(2)}(\mathbf{k}) \right] - e_{\sigma_2} k^{-2} \mathbf{k} \cdot \nabla_{\mathbf{k}} \left[\sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} h_{\sigma_3 \sigma_4}^{(2)}(\mathbf{k}) \right] \\
& + \lim_{\mathbf{k}' \rightarrow -\mathbf{k}} \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \nabla_{\mathbf{k}'} \cdot \left\{ \frac{(\mathbf{k} + \mathbf{k}')}{|\mathbf{k} + \mathbf{k}'|^2} \left[\sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} h_{\sigma_2 \sigma_3 \sigma_4}^{(3)}(\mathbf{k}', -\mathbf{k} - \mathbf{k}') \right. \right. \\
& \left. \left. + e_{\sigma_2} h_{\sigma_2 \sigma_3}^{(2)}(\mathbf{k}') + e_{\sigma_3} h_{\sigma_2 \sigma_3}^{(2)}(\mathbf{k}) \right] \right\}. \tag{B.7}
\end{aligned}$$

In the first two terms we transform the derivative $\nabla_{\mathbf{k}'}$ to a linear combination of $\nabla_{\mathbf{k}}$ and $\nabla_{\mathbf{q}}$ such that the limit $\mathbf{k}' \rightarrow -\mathbf{k}$ can be carried out. Subsequently we perform a partial integration to remove the differentiation with respect to \mathbf{q} , while the contribution with the derivative $\nabla_{\mathbf{k}}$ is evaluated by means of (3.6). In the last three terms of (B.7) we use the fact that the expression between square brackets is, according to (B.4), proportional to $(\mathbf{k} + \mathbf{k}')^2$ for $\mathbf{k}' \rightarrow -\mathbf{k}$. As a consequence the differentiation with respect to \mathbf{k}' is trivially carried out.

Collecting the results obtained from (B.7) and substituting them in (B.6) we finally arrive at the identity

$$\begin{aligned}
& \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}^{(4)}(\mathbf{q}, \mathbf{k}, -\mathbf{k}) \\
& = -2 \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} \\
& \quad \times [e_{\sigma_3} h_{\sigma_2 \sigma_3 \sigma_4}^{(3)}(\mathbf{k} - \mathbf{q}, -\mathbf{k}) + e_{\sigma_4} h_{\sigma_2 \sigma_3 \sigma_4}^{(3)}(\mathbf{k}, -\mathbf{k} - \mathbf{q})] \\
& \quad - 6q_v \lim_{\mathbf{q} \rightarrow \mathbf{0}} \frac{1}{q^2} \left[\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} h_{\sigma_2 \sigma_3 \sigma_4}^{(3)}(\mathbf{k}, -\mathbf{k} + \mathbf{q}) \right. \\
& \quad \left. + e_{\sigma_3} h_{\sigma_3 \sigma_4}^{(2)}(\mathbf{k} - \mathbf{q}) + e_{\sigma_4} h_{\sigma_3 \sigma_4}^{(2)}(\mathbf{k}) \right] \\
& \quad - 6\beta^{-1} \sum_{\sigma_2} n_{\sigma_2} h_{\sigma_2 \sigma_3 \sigma_4}^{(3)}(\mathbf{k}, -\mathbf{k}) - 2e_{\sigma_3} e_{\sigma_4} \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{1}{q^2} h_{\sigma_3 \sigma_4}^{(2)}(\mathbf{k} - \mathbf{q}) \\
& \quad - 2\beta^{-1} \mathbf{k} \cdot \nabla_{\mathbf{k}} h_{\sigma_3 \sigma_4}^{(2)}(\mathbf{k}) - 2k^{-2} \left[e_{\sigma_3} + \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} h_{\sigma_1 \sigma_3}^{(2)}(\mathbf{k}) \right] \\
& \quad \times \left[e_{\sigma_4} + \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} h_{\sigma_2 \sigma_4}^{(2)}(\mathbf{k}) \right] - 6\beta^{-1} h_{\sigma_3 \sigma_4}^{(2)}(\mathbf{k}), \tag{B.8}
\end{aligned}$$

which has been used to eliminate $h^{(4)}$ from (4.17).

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