

Equilibrium Properties of Ionic Mixtures: Derivation of Fluctuation Formulae from the Grand-Canonical Ensemble

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Abstract

The grand-canonical ensemble is used to derive fluctuation formulae for the particle densities, the pressure and the energy density of a multi-component ionic mixture. As an intermediate step sum rules are established for the two-particle Ursell functions.

1. Introduction

The equilibrium properties of plasmas have been the subject of numerous studies (for some recent reviews see [1–3]). Owing to the long-range character of the Coulomb forces these properties differ qualitatively from those of fluids of neutral particles. In particular, the fluctuations in a plasma in equilibrium are strongly influenced by the effective suppression of non-uniformities in the charge distribution.

Some years ago a statistical derivation of the fluctuation formulae involving the particle density, the pressure and the energy density has been given for the special case of the one-component plasma (OCP), which consists of charged particles in a neutralizing background [4, 5]. Since charge and density fluctuations are proportional in the OCP, all fluctuation expressions containing the particle density tend to zero in the long-wavelength limit, so that fluctuation theory becomes rather degenerate.

Fluctuation theory loses its degenerate character if an ionic mixture consisting of several species of particles in a neutralizing background is considered. Recently [6, 7] we have derived, in the framework of statistical mechanics, the complete set of fluctuation formulae for such a multi-component ionic mixture (MIM). An important role in our derivation was played by a set of sum rules for the Ursell functions, which are related to the correlation functions by a standard cluster expansion. Several of these sum rules could be derived only by specifying the ensemble that describes the ionic mixture in equilibrium. In our treatment we chose a particular ensemble, in which the particle numbers vary, as in the grand-canonical ensemble, whereas the total charge of the particles is strictly kept constant at a value that matches the charge of the background. In view of this restriction on the particle numbers this ensemble may be called a neutral grand-canonical ensemble [8] (cf. also [9]).

For the OCP it has been shown [10] that in choosing the ensemble the condition of overall charge neutrality (which leads in that case to the canonical ensemble) may be dropped, provided that the background charge density is kept constant. Likewise, one may employ for ionic mixtures the ordinary ‘unrestricted’ grand-canonical ensemble,

with a fixed background density, instead of the neutral grand-canonical ensemble [8]. In the following we shall show how the fluctuation formulae for an ionic mixture can be derived in this way. To that end we shall start by introducing the basic formulae for the grand-canonical ensemble description of the ionic mixture (section 2). Subsequently, we shall derive sum rules for the Ursell functions in section 3. Finally, the fluctuation formulae will be established in section 4.

2. Grand-Canonical Ensemble

The Hamiltonian of an ionic mixture consisting of s components of charged particles moving in a neutralizing background is

$$H = \sum_{\alpha\sigma} \frac{p_{\alpha\sigma}^2}{2m_\sigma} + \frac{1}{2} \sum'_{\sigma_1\alpha_1, \sigma_2\alpha_2} e_{\sigma_1} e_{\sigma_2} v(|\mathbf{r}_{\sigma_1\alpha_1} - \mathbf{r}_{\sigma_2\alpha_2}|) - q_v \sum_{\sigma_1\alpha_1} e_{\sigma_1} \int^V d\mathbf{r} v(|\mathbf{r}_{\sigma_1\alpha_1} - \mathbf{r}|) + \frac{1}{2} q_v^2 \int^V d\mathbf{r} \int^V d\mathbf{r}' v(|\mathbf{r} - \mathbf{r}'|). \quad (1)$$

The N_σ particles of the species σ carry charge e_σ and mass m_σ . The position and momentum of particle α of the component σ are denoted by $\mathbf{r}_{\sigma\alpha}$ and $\mathbf{p}_{\sigma\alpha}$, respectively. Furthermore, $v(r)$ is the Coulomb interaction $1/(4\pi r)$. The prime at the summation symbol indicates the restriction $\sigma_i\alpha_i \neq \sigma_j\alpha_j$ ($i \neq j$). The integral terms in (1) represent the interaction with the background which has got a charge density q_v that is uniform through the volume V of the system. It should be noted that the background charge density q_v is an independent parameter in (1); it is not related a priori to the total charge of the particles. Often [4, 6, 7] a Fourier representation for the Coulomb potential is chosen in such a way that the background charge density is determined by the particle numbers. Such a representation is not adequate for our present treatment.

In the grand-canonical ensemble the average $\langle f \rangle$ of a microscopic quantity f is given by a sum over the particle numbers $\{N_\sigma\}$ and an integral over phase space. The weight function ϱ_{gr} is proportional to

$$\exp \left(\beta \sum_{\sigma} \mu_{\sigma} N_{\sigma} - \beta H \right), \quad (2)$$

with β the inverse temperature and $\{\mu_{\sigma}\}$ the chemical potentials, and to the inverse of the grand-canonical partition function Z_{gr} . Since H depends on q_v as a parameter, Z_{gr} is a function of β , $\{\mu_{\sigma}\}$, q_v and V . By introducing the auxiliary chemical potentials $\tilde{\mu}_q = \mu_1/e_1$ and $\tilde{\mu}_{\sigma} = \mu_{\sigma} - (e_{\sigma}/e_1)\mu_1$ ($\sigma = 2, \dots, s$) we may write the exponential (2) that occurs in ϱ_{gr} and in Z_{gr} as

$$\exp \left(\beta \tilde{\mu}_q \sum_{\sigma} e_{\sigma} N_{\sigma} + \beta \sum_{\sigma \neq 1} \tilde{\mu}_{\sigma} N_{\sigma} - \beta H \right). \quad (3)$$

As a consequence of the long-range Coulomb interactions the contribution to Z_{gr} of the non-neutral configurations, with $\sum_{\sigma} e_{\sigma} N_{\sigma} \neq q_v V$, are strongly suppressed. Hence we have in the thermodynamic limit

$$\lim_{V \rightarrow \infty} \frac{1}{\beta V} \log Z_{gr} = \tilde{\mu}_q q_v + \tilde{p}, \quad (4)$$

with $\tilde{p}(\beta, \{\tilde{\mu}_{\sigma}\}, q_v)$ given by

$$\tilde{p} = \lim_{V \rightarrow \infty} \frac{1}{\beta V} \log Z. \quad (5)$$

Here Z stands for the partition function in the neutral grand-canonical ensemble which is defined by considering only configurations with $N_1 = (q_v V - \sum_{\sigma \neq 1} e_\sigma N_\sigma) / e_1$, with a weight function proportional to

$$\exp \left(\beta \sum_{\sigma \neq 1} \tilde{\mu}_\sigma N_\sigma - \beta H \right). \tag{6}$$

This ensemble has been discussed before [6–9]. The thermodynamic pressure p of the system follows from \tilde{p} as

$$p = \tilde{p} - q_v \frac{\partial \tilde{p}}{\partial q_v}. \tag{7}$$

Upon using (4) we infer that

$$p = \lim_{V \rightarrow \infty} \frac{1}{\beta V} \log Z_{gr}, \tag{8}$$

provided that one chooses the auxiliary potential $\tilde{\mu}_q$ as $-\partial \tilde{p} / \partial q_v$. Alternatively, this condition may be stated as

$$\left(\frac{\partial}{\partial q_v} \left[\lim_{V \rightarrow \infty} \frac{1}{\beta V} \log Z_{gr} \right] \right)_{\beta, \{\mu_\sigma\}} = 0. \tag{9}$$

Limiting ourselves from now on to those values of $\beta, \{\mu_\sigma\}, q_v$ for which (9) is satisfied we may write the usual Gibbs-Duhem relation

$$d(\beta p) = -u_v d\beta + \sum_\sigma n_\sigma d(\beta \mu_\sigma), \tag{10}$$

with $u_v = \langle H \rangle / V$ the internal energy per unit volume and $n_\sigma = \langle N_\sigma \rangle / V$ the partial densities. The scaling property of the Coulomb potential implies that the pressure p satisfies the equation of state

$$p = \frac{1}{3} u_v + \frac{n}{2\beta}, \tag{11}$$

where $n = \sum_\sigma n_\sigma$ is the total particle density.

Since the non-neutral configurations drop out effectively from the averages $\langle f \rangle$, the latter will depend only on $\beta, \{\tilde{\mu}_\sigma\}$ ($\sigma \neq 1$) and on q_v . From the exponential form of the weight function we easily derive the identity

$$\left(\frac{\partial \langle f \rangle}{\partial \beta} \right)_{\{\beta \tilde{\mu}_\sigma\}, q_v} = -\langle f(H - \langle H \rangle) \rangle. \tag{12}$$

Choosing the new variables $\{\mu_\sigma\}$ ($\sigma = 1, \dots, s$) instead of $\{\tilde{\mu}_\sigma\}$ ($\sigma = 2, \dots, s$) and q_v we get from this equality

$$\left(\frac{\partial \langle f \rangle}{\partial \beta} \right)_{\{\beta \mu_\sigma\}} - \frac{1}{S} \left(\frac{\partial q_v}{\partial \beta} \right)_{\{\beta \mu_\sigma\}} \sum_\sigma e_\sigma \left(\frac{\partial \langle f \rangle}{\partial \mu_\sigma} \right)_{\beta, \{\mu_{\sigma'}\}} = -\langle f(H - \langle H \rangle) \rangle, \tag{13}$$

with $S = \sum_\sigma e_\sigma (\partial q_v / \partial \mu_\sigma)$. In deriving (13) we used the transformation matrix

$$\left(\frac{\partial \mu_\sigma}{\partial q_v} \right)_{\beta, \{\tilde{\mu}_\sigma\}} = \frac{e_\sigma}{S}, \quad \left(\frac{\partial \mu_\sigma}{\partial \tilde{\mu}_{\sigma'}} \right)_{\beta, \{\tilde{\mu}_{\sigma''}\}} = \delta_{\sigma\sigma'} - \frac{e_\sigma}{S} \left(\frac{\partial q_v}{\partial \mu_{\sigma'}} \right)_{\beta, \{\mu_{\sigma''}\}}. \tag{14}$$

It should be noted that the second term at the right-hand side of (13) would be missed, if naive differentiation of the grand-canonical average $\langle f \rangle$ would be performed without taking account of the dependence of H on q_v and of the relation (9).

On a par with (13) we may prove

$$\sum_{\sigma'} \left[\delta_{\sigma\sigma'} - \frac{e_{\sigma'}}{S} \left(\frac{\partial q_v}{\partial \mu_{\sigma'}} \right)_{\beta, \{\mu_{\sigma''}\}} \right] \left(\frac{\partial \langle f \rangle}{\partial \mu_{\sigma'}} \right)_{\beta, \{\mu_{\sigma''}\}} = \beta \langle f(N_{\sigma} - \langle N_{\sigma} \rangle) \rangle. \quad (15)$$

The identities (13) and (15) will play an important role in the following.

3. Sum Rules for Ursell Functions

The k -particle correlation functions are defined as

$$n_{\sigma_1} \dots n_{\sigma_k} g_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) = \left\langle \sum'_{\alpha_1, \dots, \alpha_k} \delta(\mathbf{r}_1 - \mathbf{r}_{\sigma_1 \alpha_1}) \dots \delta(\mathbf{r}_k - \mathbf{r}_{\sigma_k \alpha_k}) \right\rangle. \quad (16)$$

They can be expanded in the usual way in terms of Ursell functions $h_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k)$. The latter satisfy an infinite set of integro-differential equations, the so-called hierarchy equations. According to the exponential clustering hypothesis [1–3] the Ursell functions are assumed to decay faster than any inverse power of the interparticle distances if these tend to infinity. On the basis of this hypothesis one may prove from the hierarchy equations relations that express the perfect-screening property. Furthermore the so-called Stillinger-Lovett sum rule can be established [1–3, 6, 7, 11].

An alternative way to obtain relations for the Ursell functions starts from the identities (13) and (15). As it turns out one may derive in this way more general equalities that imply the perfect-screening relations and the Stillinger-Lovett sum rule as special cases. Let us first choose $f = N_{\sigma}/V$ in (15). Then the right-hand side reduces to an integral over the Ursell function $h^{(2)}$, so that we get immediately

$$n_{\sigma_1} n_{\sigma_2} \int d\mathbf{r}_{12} h_{\sigma_1 \sigma_2}^{(2)} = \beta^{-1} \left(\frac{\partial n_{\sigma_1}}{\partial \mu_{\sigma_2}} - \frac{1}{S} \frac{\partial q_v}{\partial \mu_{\sigma_1}} \frac{\partial q_v}{\partial \mu_{\sigma_2}} \right) - n_{\sigma_1} \delta_{\sigma_1 \sigma_2}. \quad (17)$$

Multiplying both sides by e_{σ_2} and summing over σ_2 we find

$$\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_{12} h_{\sigma_1 \sigma_2}^{(2)} = -e_{\sigma_1}, \quad (18)$$

which is the perfect-screening relation for $h^{(2)}$.

Likewise, by substituting $f = N_{\sigma}/V$ in (13) and inserting the Hamiltonian (1) we obtain

$$\begin{aligned} & n_{\sigma_1} \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int d\mathbf{r}_{12} d\mathbf{r}_{13} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)} v_{23} \\ & + n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \int d\mathbf{r}_{12} h_{\sigma_1 \sigma_2}^{(2)} \left(2e_{\sigma_1} e_{\sigma_2} v_{12} + \frac{3}{\beta} \right) \\ & = -2 \left(\frac{\partial n_{\sigma_1}}{\partial \beta} - \frac{1}{S} \frac{\partial q_v}{\partial \beta} \frac{\partial q_v}{\partial \mu_{\sigma_1}} \right) - \frac{3}{\beta} n_{\sigma_1}, \end{aligned} \quad (19)$$

where the differentiations with respect to β are taken at constant $\{\beta \mu_{\sigma}\}$. The integral with $h^{(3)}$ can be reduced to an expression involving pair correlation functions only by

employing the symmetry properties of $h^{(3)}$ and the hierarchy equations. Indeed, one may prove [6]

$$\begin{aligned} & \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_{12} d\mathbf{r}_{13} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)} v_{12} \\ &= \sum_{\sigma_1} n_{\sigma_1} \int d\mathbf{r}_{13} h_{\sigma_1 \sigma_3}^{(2)} \left(q_v e_{\sigma_1} r_{13}^2 - 2 e_{\sigma_1} e_{\sigma_3} v_{13} - \frac{6}{\beta} \right). \end{aligned} \tag{20}$$

Using furthermore (17) we arrive at the equality

$$n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_{12} h_{\sigma_1 \sigma_2}^{(2)} r_{12}^2 = - \frac{6}{\beta S} \frac{\partial q_v}{\partial \mu_{\sigma_1}}. \tag{21}$$

This relation implies the Stillinger-Lovett result as a special case, since we get upon multiplication by e_{σ_1} and summation over σ_1

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_{12} h_{\sigma_1 \sigma_2}^{(2)} r_{12}^2 = - \frac{6}{\beta}, \tag{22}$$

which is indeed the sum rule of Stillinger and Lovett.

Additional relations can be derived from (11) and (13) by substitution of $f = \sum'_{\alpha_1, \alpha_2} \delta(\mathbf{r}_1 - \mathbf{r}_{\sigma_1 \alpha_1}) \delta(\mathbf{r}_2 - \mathbf{r}_{\sigma_2 \alpha_2})$. In this way one gets equalities containing the derivatives of $h_{\sigma_1 \sigma_2}^{(2)}$ with respect to β and $\{\mu_{\sigma}\}$. From these one may prove [6] a sum rule for the fourth moment of $h^{(2)}$, viz.

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_{12} h_{\sigma_1 \sigma_2}^{(2)} r_{12}^4 = - \frac{120}{\beta S}. \tag{23}$$

Alternative forms of the identities (17), (21) and (23) result by introducing the Fourier transform of the two-particle Ursell function and expanding it around $\mathbf{k} = 0$

$$h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{k}) = a_{\sigma_1 \sigma_2}^{(0)} + a_{\sigma_1 \sigma_2}^{(1)} k^2 + a_{\sigma_1 \sigma_2}^{(2)} k^4 + \dots \tag{24}$$

Constraints on the coefficients follow directly from (17), (21) and (23), viz.

$$n_{\sigma_1} n_{\sigma_2} a_{\sigma_1 \sigma_2}^{(0)} = \beta^{-1} \left(\frac{\partial n_{\sigma_1}}{\partial \mu_{\sigma_2}} - \frac{1}{S} \frac{\partial q_v}{\partial \mu_{\sigma_1}} \frac{\partial q_v}{\partial \mu_{\sigma_2}} \right) - n_{\sigma_1} \delta_{\sigma_1 \sigma_2}, \tag{25}$$

$$n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} a_{\sigma_1 \sigma_2}^{(1)} = \frac{1}{\beta S} \frac{\partial q_v}{\partial \mu_{\sigma_1}}, \tag{26}$$

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} a_{\sigma_1 \sigma_2}^{(2)} = - \frac{1}{\beta S}. \tag{27}$$

These results are helpful in obtaining the fluctuation formulae.

4. Fluctuation formulae

To derive fluctuation formulae for the partial densities, the pressure tensor and the energy density we start by considering the microscopic balance equations. The continuity equation for the partial density

$$n_{\sigma}(\mathbf{r}) = \sum_{\alpha} \delta(\mathbf{r} - \mathbf{r}_{\sigma \alpha}) \tag{28}$$

reads

$$iLn_{\sigma}(\mathbf{r}) = -\frac{1}{m_{\sigma}} \nabla \cdot \mathbf{g}_{\sigma}(\mathbf{r}) \quad (29)$$

with the partial momentum density

$$\mathbf{g}_{\sigma}(\mathbf{r}) = \sum_{\alpha} \mathbf{p}_{\sigma\alpha} \delta(\mathbf{r} - \mathbf{r}_{\sigma\alpha}) \quad (30)$$

and L the Liouville operator. The balance equation for the total momentum density has the form

$$iL \sum_{\sigma} \mathbf{g}_{\sigma}(\mathbf{r}) = -\nabla \cdot \boldsymbol{\tau}(\mathbf{r}) + \mathbf{F}(\mathbf{r}). \quad (31)$$

The divergence of the pressure tensor $\boldsymbol{\tau}(\mathbf{r})$ is defined as

$$\begin{aligned} \nabla \cdot \boldsymbol{\tau}(\mathbf{r}) &= \nabla \cdot \sum_{\sigma\alpha} \frac{\mathbf{p}_{\sigma\alpha} \mathbf{p}_{\sigma\alpha}}{m_{\sigma}} \delta(\mathbf{r} - \mathbf{r}_{\sigma\alpha}) \\ &\quad + \int^V d\mathbf{r}' [\nabla_{\mathbf{r}'} v(|\mathbf{r} - \mathbf{r}'|)] \left[\sum_{\sigma_1\alpha_1, \sigma_2\alpha_2} e_{\sigma_1} e_{\sigma_2} \delta(\mathbf{r} - \mathbf{r}_{\sigma_1\alpha_1}) \delta(\mathbf{r}' - \mathbf{r}_{\sigma_2\alpha_2}) \right. \\ &\quad \left. - q_v \sum_{\sigma_1\alpha_1} e_{\sigma_1} \delta(\mathbf{r} - \mathbf{r}_{\sigma_1\alpha_1}) - q_v \sum_{\sigma_2\alpha_2} e_{\sigma_2} \delta(\mathbf{r}' - \mathbf{r}_{\sigma_2\alpha_2}) + q_v^2 \right]. \quad (32) \end{aligned}$$

As can be seen from the integral the interparticle interaction terms have been supplemented by contributions representing the interaction with the background, as in (1). The source term in (31) reads

$$\mathbf{F}(\mathbf{r}) = -q_v \int^V d\mathbf{r}' [\nabla_{\mathbf{r}'} v(|\mathbf{r} - \mathbf{r}'|)] \left[\sum_{\sigma_1\alpha_1} e_{\sigma_1} \delta(\mathbf{r}' - \mathbf{r}_{\sigma_1\alpha_1}) - q_v \right]. \quad (33)$$

The energy density of the ionic mixture is defined as [4]

$$\begin{aligned} \varepsilon(\mathbf{r}) &= \sum_{\sigma\alpha} \frac{p_{\sigma\alpha}^2}{2m_{\sigma}} \delta(\mathbf{r} - \mathbf{r}_{\sigma\alpha}) + \frac{1}{2} \int d\mathbf{r}' v(|\mathbf{r} - \mathbf{r}'|) \\ &\quad \times \left[\sum_{\sigma_1\alpha_1, \sigma_2\alpha_2} e_{\sigma_1} e_{\sigma_2} \delta(\mathbf{r} - \mathbf{r}_{\sigma_1\alpha_1}) \delta(\mathbf{r}' - \mathbf{r}_{\sigma_2\alpha_2}) - q_v \sum_{\sigma_1\alpha_1} e_{\sigma_1} \delta(\mathbf{r} - \mathbf{r}_{\sigma_1\alpha_1}) \right. \\ &\quad \left. - q_v \sum_{\sigma_2\alpha_2} e_{\sigma_2} \delta(\mathbf{r}' - \mathbf{r}_{\sigma_2\alpha_2}) + q_v^2 \right]. \quad (34) \end{aligned}$$

Again background terms occur on a par with the direct interparticle interactions. The integral of $\varepsilon(\mathbf{r})$ over the volume V yields again (1), as expected. The energy density (34) fulfils an energy balance equation

$$iL\varepsilon(\mathbf{r}) = -\nabla \cdot \mathbf{j}_{\varepsilon}(\mathbf{r}), \quad (35)$$

with an energy-current density $\mathbf{j}_{\varepsilon}(\mathbf{r})$, which is not needed in the following.

Formulae for products of fluctuations in the partial densities, the pressure and the energy density can be obtained by first expressing the average of products of these fluctuations in terms of the Ursell functions and their expansion coefficients $a_{\sigma_1\sigma_2}^{(n)}$ in Fourier space. In particular, the fluctuations of the partial densities are given by the equality

$$\langle [n_{\sigma_1}(\mathbf{r}_1) - n_{\sigma_1}] [n_{\sigma_2}(\mathbf{r}_2) - n_{\sigma_2}] \rangle = n_{\sigma_1} n_{\sigma_2} h_{\sigma_1\sigma_2}^{(2)}(r_{12}) + \delta_{\sigma_1\sigma_2} n_{\sigma_1} \delta(\mathbf{r}_{12}), \quad (36)$$

which follows from the definition of $n_{\sigma}(\mathbf{r})$ and of $h_{\sigma_1\sigma_2}^{(2)}$. Its Fourier transform yields upon substitution of (24)

$$\frac{1}{V} \langle n_{\sigma_1}(-\mathbf{k}) n_{\sigma_2}(\mathbf{k}) \rangle = \delta_{\sigma_1\sigma_2} n_{\sigma_1} + n_{\sigma_1} n_{\sigma_2} (a_{\sigma_1\sigma_2}^{(0)} + a_{\sigma_1\sigma_2}^{(1)} k^2 + a_{\sigma_1\sigma_2}^{(2)} k^4 + \dots). \quad (37)$$

Explicit thermodynamic expressions for the fluctuations $n(\mathbf{k}) = \sum_{\sigma_1} n_{\sigma_1}(\mathbf{k})$ and $q_v(\mathbf{k}) = \sum_{\sigma_1} e_{\sigma_1} n_{\sigma_1}(\mathbf{k})$ follow with the help of (25)–(26). It turns out that fluctuation formulae involving $q_v(\mathbf{k})$ are of order k^2 . One gets for instance

$$\frac{1}{V} \langle q_v(-\mathbf{k}) q_v(\mathbf{k}) \rangle = \beta^{-1} k^2 - \beta^{-1} S^{-1} k^4 + \dots \tag{38}$$

The average of the product of fluctuations in the partial densities and the energy density can be expressed in Ursell functions $h^{(2)}$ and $h^{(3)}$, as follows from the definitions (28) and (34). Using the hierarchy and the symmetry of the Ursell functions we can eliminate $h^{(3)}$, at least if we confine ourselves to the first few moments of the fluctuation expression in position space, or alternatively, to the first few terms in the small-wavenumber expansion in Fourier space. In zeroth order in \mathbf{k} we get

$$\frac{1}{V} \langle n_{\sigma_1}(-\mathbf{k}) \varepsilon(\mathbf{k}) \rangle = \frac{3}{\beta} n_{\sigma_1} - \frac{3}{2\beta^2} \frac{\partial n}{\partial \mu_{\sigma_1}} + \frac{3}{2\beta S} \left(\frac{S_n}{\beta} - 2q_v \right) \frac{\partial q_v}{\partial \mu_{\sigma_1}}, \tag{39}$$

with $S_n = \sum_{\sigma} \partial q_v / \partial \mu_{\sigma}$. The fluctuation formula involving the charge density $q_v(\mathbf{k})$ is of second order in k , as before

$$\frac{1}{V} \langle q_v(-\mathbf{k}) \varepsilon(\mathbf{k}) \rangle = -\frac{3}{2\beta^2 S} k^2 (S_n - 2\beta q_v) + \dots \tag{40}$$

Again (25)–(27) have been used to express the right-hand side in thermodynamic quantities.

Fluctuation formulae involving the products of fluctuations $n\tau$, $\varepsilon\varepsilon$, $\varepsilon\tau$, $\tau\tau$ can likewise be derived. In leading order of the wavenumber the results are the following

$$\frac{1}{V} \langle n_{\sigma_1}(-\mathbf{k}) \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle = \beta^{-1} \left(n_{\sigma_1} - \frac{q_v}{S} \frac{\partial q_v}{\partial \mu_{\sigma_1}} \right) \mathbf{k}, \tag{41}$$

$$\frac{1}{V} \langle q_v(-\mathbf{k}) \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle = \frac{q_v}{\beta S} k^2 \mathbf{k}, \tag{42}$$

$$\frac{1}{V} \langle \varepsilon(-\mathbf{k}) \varepsilon(\mathbf{k}) \rangle = \frac{9}{4\beta^3} \left(S_{nn} - \frac{S_n^2}{S} + 4\beta q_v \frac{S_n}{S} - \frac{4\beta^2 q_v^2}{S} - 2\beta n \right) + \frac{4u_v}{\beta}, \tag{43}$$

$$\frac{1}{V} \langle \varepsilon(-\mathbf{k}) \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle = \left(\frac{3q_v S_n}{2\beta^2 S} - \frac{3q_v^2}{\beta S} + \frac{4u_v}{3\beta} + \frac{n}{2\beta^2} \right) \mathbf{k}, \tag{44}$$

$$\frac{1}{V} \langle \mathbf{k} \cdot \boldsymbol{\tau}(-\mathbf{k}) \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle = \left(-\frac{q_v^2}{\beta S} + \frac{2u_v}{5\beta} + \frac{7n}{5\beta^2} \right) \mathbf{k}\mathbf{k} + \left(-\frac{2u_v}{15\beta} + \frac{6n}{5\beta^2} \right) k^2 \mathbf{U}, \tag{45}$$

with \mathbf{U} the unit tensor and $S_{nn} = \sum_{\sigma} \partial n / \partial \mu_{\sigma}$. It should be noted that alternative forms for the right-hand sides of these formulae may be obtained by using thermodynamic identities. For instance, by introducing again the variables $\{\tilde{\mu}_{\sigma}\}$ ($\sigma = 2, \dots, s$) and q_v instead of $\{\mu_{\sigma}\}$ ($\sigma = 1, \dots, s$) one may prove from (43) and (44)

$$\frac{1}{V} \langle \varepsilon(-\mathbf{k}) \varepsilon(\mathbf{k}) \rangle = -\frac{\partial u_v}{\partial \beta}, \tag{46}$$

$$\frac{1}{V} \langle \varepsilon(-\mathbf{k}) \mathbf{k} \cdot \boldsymbol{\tau}(\mathbf{k}) \rangle = -\frac{\partial p}{\partial \beta} \mathbf{k}, \tag{47}$$

where the differentiations should be taken now at constant $\{\beta\tilde{\mu}_\sigma\}$ and q_ν . The formulae (46) and (47) are identical to those obtained in [7]. Likewise one may establish the equivalence of the other fluctuation formulae found here with their counterparts in our earlier treatment. We have thus arrived at the conclusion that the unrestricted grand-canonical ensemble leads to the same fluctuation formulae for the multi-component ionic mixture as the neutral grand-canonical ensemble, which we employed before.

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