SECOND-MOMENT SUM RULES FOR CORRELATION FUNCTIONS IN A CLASSICAL IONIC MIXTURE

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Abstract

The complete set of second-moment sum rules for the correlation functions of arbitrarily high order describing a classical multi-component ionic mixture in equilibrium is derived from the grand-canonical ensemble. The connection of these sum rules with the large-scale behaviour of fluctuations in an ionic mixture is pointed out.

1 Introduction

The equilibrium correlations in classical Coulomb systems are dominated by screening effects, as has first been demonstrated by Debye and Hückel for dilute systems. These screening effects give rise to sum rules that determine the first few moments of the correlation functions. An example of such a sum rule is the second-moment rule obtained by Stillinger and Lovett [1]. For a one-component plasma it gives an exact expression for the second moment of the pair correlation function. If the system is a mixture of several species of charged particles, the Stillinger-Lovett rule contains a weighted sum of partial pair correlation functions for each of the species. A systematic treatment of second-moment sum rules for both two- and three particle correlation functions of ionic mixtures has been given a few years ago [2], [3]. As shown in these papers generalized Stillinger-Lovett sum rules, with different weights entering the summation over the species, can be formulated as well. These generalized sum rules are indispensable in deriving fluctuation formulas for an ionic mixture.

Recently, second-moment sum rules for correlation functions of arbitrarily high order have been discussed for the special case of a one-component plasma [4], [5]. It is the purpose of the present paper to generalize these results and derive the complete set of second-moment sum rules for the higher-order correlation functions of general multi-component ionic mixtures. Moreover, we wish to establish the connection of these sum rules with the large-scale behaviour of the fluctuations in ionic mixtures. An important tool in our derivation will be a set of differentiation formulas that determine the partial derivatives of average physical quantities with respect to the thermodynamic variables characterizing an ionic mixture in equilibrium.

2 Grand-canonical ensemble

A multi-component ionic mixture with s species of charged particles in a neutralizing background is described by the Hamiltonian

$$\begin{aligned} H &= \sum_{\sigma\alpha} \frac{p_{\sigma\alpha}^2}{2m_\sigma} + \frac{1}{2}\int^V d\mathbf{r}\int^V d\mathbf{r}' v(|\mathbf{r}-\mathbf{r}'|)\Bigg[\sum_{\sigma_1\alpha_1,\sigma_2\alpha_2}{}' e_{\sigma_1}e_{\sigma_2}\delta(\mathbf{r}-\mathbf{q}_{\sigma_1\alpha_1})\delta(\mathbf{r}'-\mathbf{q}_{\sigma_2\alpha_2}) \\ &- q_v\sum_{\sigma_1\alpha_1} e_{\sigma_1}\delta(\mathbf{r}-\mathbf{q}_{\sigma_1\alpha_1}) - q_v\sum_{\sigma_2\alpha_2} e_{\sigma_2}\delta(\mathbf{r}'-\mathbf{q}_{\sigma_2\alpha_2}) + q_v^2\Bigg] \quad . \end{aligned} \tag{2.1}$$

The phase space of the system is determined by the positions $\mathbf{q}_{\sigma\alpha}$ and the momenta $\mathbf{p}_{\sigma\alpha}$ of the particles, which are labeled by a double index $\sigma\alpha$, with σ indicating the species. The charges and masses of the particles of species σ are e_σ and m_σ, respectively. The interaction between the particles is given by the Coulomb potential $v(r) = 1/(4\pi r)$. Self-interactions are excluded, as indicated by the prime at the first summation sign between the square brackets. The charge density $-q_v$ of the neutralizing background is uniform throughout the volume V of the system.

Equilibrium averages can be evaluated with the use of the grand-canonical ensemble the weight function of which is

$$\rho_{gr} = Z_{gr}^{-1} \left[\prod_\sigma N_\sigma! h^{3N_\sigma} \right]^{-1} \exp(\beta \sum_\sigma \mu_\sigma N_\sigma - \beta H) \quad , \tag{2.2}$$

with β the inverse temperature, μ_σ the chemical potentials, and Z_{gr} the grand-canonical partition function. Since H depends on q_v, the weight function depends on a thermodynamically overcomplete set of $s+2$ variables, namely β, $\{\beta\mu_\sigma\}$ and q_v. The same is true for the grand-canonical partition function. However, as a consequence of the long-range nature of the Coulomb interactions non-neutral configurations for which $\sum_\sigma e_\sigma N_\sigma$ differs from Vq_v, are strongly suppressed in the thermodynamic limit, so that q_v is in fact determined once β and $\{\beta\mu_\sigma\}$ are given. It can be proved [3] that the grand-canonical partition function is related to the pressure p in the usual way, namely as

$$p = \lim_{V\to\infty} \frac{1}{\beta V} \log Z_{gr} \quad , \tag{2.3}$$

if the background charge density is chosen such that the constraint

$$\left(\frac{\partial}{\partial q_v} Z_{gr} \right)_{\beta,\{\beta\mu_\sigma\}} = 0 \tag{2.4}$$

is satisfied identically. This constraint fixes q_v as a function of the independent variables β and $\{\beta\mu_\sigma\}$. Likewise, the pressure p is a function of these variables, which fulfils the standard differential relation $d(\beta p) = -u_v d\beta + \sum_\sigma n_\sigma d(\beta\mu_\sigma)$, with u_v the internal energy density and n_σ the partial densities.

On account of the homogeneity of the Coulomb potential the pressure obeys a scaling relation which reads

$$p(\beta, \{\beta\mu_\sigma\}) = \lambda^4 p(\lambda\beta, \{\beta\mu_\sigma - \frac{3}{2}\log\lambda\}) \quad , \tag{2.5}$$

for all positive λ. Likewise, the partial densities fulfil the scaling relation

$$n_\sigma(\beta, \{\beta\mu_\sigma\}) = \lambda^3 n_\sigma(\lambda\beta, \{\beta\mu_\sigma - \frac{3}{2}\log\lambda\}) \quad . \tag{2.6}$$

Differentiation of (2.5) and (2.6) with respect to λ yields the well-known equation of state for Coulomb systems

$$p = \frac{1}{3}u_v + \frac{n}{2\beta} \quad , \tag{2.7}$$

(with n the total particle density) and an identity for the partial densities of the form

$$\left[\beta\frac{\partial}{\partial\beta} - \frac{3}{2}\sum_{\sigma'} \frac{\partial}{\partial\beta\mu_{\sigma'}} + 3 \right] n_\sigma = 0 \quad . \tag{2.8}$$

The equilibrium average $\langle f \rangle$ of a microscopic quantity f depends on the variables β and $\{\beta\mu_\sigma\}$ via the weight function ρ_{gr}. Formal expressions for the partial derivatives of $\langle f \rangle$ follow by employing (2.2). In taking the derivatives one should be careful in accounting for the dependence through the charge density q_v [3]. If the latter is kept fixed differentiation of $\langle f \rangle$ with respect to $\beta\mu_\sigma$ yields the

fluctuation expression $\langle (f - \langle f \rangle)(N_\sigma - \langle N_\sigma \rangle) \rangle$. The complete expression for the partial derivative $\partial \langle f \rangle / \partial \beta \mu_\sigma$ contains an additional term:

$$\left(\frac{\partial \langle f \rangle}{\partial \beta \mu_\sigma} \right)_{\beta, \{\beta \mu_{\sigma'}\}} = \langle (f - \langle f \rangle)(N_\sigma - \langle N_\sigma \rangle) \rangle + \left(\frac{\partial \langle f \rangle}{\partial q_v} \right)_{\beta, \{\beta \mu_{\sigma'}\}} \left(\frac{\partial q_v}{\partial \beta \mu_\sigma} \right)_{\beta, \{\beta \mu_{\sigma'}\}} \quad . \tag{2.9}$$

When this identity is summed over σ, with weights e_σ, the first term at the right-hand side yields an expression involving the fluctuation of the total charge $\sum_\sigma e_\sigma N_\sigma$, which is negligible in the thermodynamic limit. Hence, one may solve for the partial derivative $\partial \langle f \rangle / \partial q_v$. Substitution in (2.9) then gives:

$$\frac{\partial \langle f \rangle}{\partial \beta \mu_\sigma} - \frac{\beta}{S} \frac{\partial q_v}{\partial \beta \mu_\sigma} \sum_{\sigma'} e_{\sigma'} \frac{\partial \langle f \rangle}{\partial \beta \mu_{\sigma'}} = \langle (f - \langle f \rangle)(N_\sigma - \langle N_\sigma \rangle) \rangle \quad , \tag{2.10}$$

with the abbreviation $S = \beta \sum_\sigma e_\sigma \partial q_v / \partial \beta \mu_\sigma$. All partial derivatives are taken with respect to the independent variables β and $\beta \mu_\sigma$. Likewise, one may derive a formal expression for the derivative with respect to β:

$$\frac{\partial \langle f \rangle}{\partial \beta} - \frac{\beta}{S} \frac{\partial q_v}{\partial \beta} \sum_{\sigma} e_{\sigma} \frac{\partial \langle f \rangle}{\partial \beta \mu_\sigma} = -\langle (f - \langle f \rangle)(H - \langle H \rangle) \rangle \quad . \tag{2.11}$$

These differentiation formulas will be used to evaluate partial derivatives of the correlation functions.

3 Correlation functions

The equilibrium correlation functions $g^{(k)}_{\sigma_1 \ldots \sigma_k}(\mathbf{r}_1, \ldots, \mathbf{r}_k)$ are defined as

$$n_{\sigma_1} \ldots n_{\sigma_k} g^{(k)}_{\sigma_1 \ldots \sigma_k}(\mathbf{r}_1, \ldots, \mathbf{r}_k) = \left\langle \sum_{\alpha_1, \ldots \alpha_k}{}' \; \delta(\mathbf{r}_1 - \mathbf{q}_{\sigma_1 \alpha_1}) \ldots \delta(\mathbf{r}_k - \mathbf{q}_{\sigma_k \alpha_k}) \right\rangle \quad . \tag{3.1}$$

Often we shall abbreviate the left-hand side as $G^{(k)}(1, \ldots, k)$.

The correlation functions depend on β and $\{\beta \mu_\sigma\}$. They satisfy the scaling relation:

$$g^{(k)}_{\sigma_1 \ldots \sigma_k}(\mathbf{r}_1, \ldots, \mathbf{r}_k, \beta, \{\beta \mu_\sigma\}) = g^{(k)}_{\sigma_1 \ldots \sigma_k}(\lambda \mathbf{r}_1, \ldots, \lambda \mathbf{r}_k, \lambda \beta, \{\beta \mu_\sigma - \frac{3}{2} \log \lambda\}) \quad . \tag{3.2}$$

As a consequence the derivatives of the correlation function $g^{(k)}$ are linearly dependent. Using (2.8) we may write the relation of linear dependence as:

$$\left[\sum_{i=1}^{k} \mathbf{r}_i \cdot \nabla_i + \beta \frac{\partial}{\partial \beta} - \frac{3}{2} \sum_\sigma \frac{\partial}{\partial \beta \mu_\sigma} + 3k \right] G^{(k)}(1, \ldots, k) = 0 \quad , \tag{3.3}$$

with $\nabla_i \equiv \partial / \partial \mathbf{r}_i$.

The spatial partial derivatives in (3.3) are determined by the hierarchy equations:

$$\begin{aligned} &\left\{ \beta^{-1} \nabla_j + \sum_{i=1 (i \neq j)}^{k} [\nabla_j v(i,j)] \right\} G^{(k)}(1, \ldots, k) = \\ &= - \sum_{\sigma_{k+1}} \int d\mathbf{r}_{k+1} G^{(1|k)}(k+1|1, \ldots, k) \nabla_j v(j, k+1) \quad , \end{aligned} \tag{3.4}$$

with $v(i,j) \equiv e_{\sigma_i} e_{\sigma_j} v(|\mathbf{r}_i - \mathbf{r}_j|)$ and with the truncated correlation function defined as

$$G^{(1|k)}(k+1|1, \ldots, k) = n_{\sigma_1} \ldots n_{\sigma_{k+1}} \left[g^{(k+1)}_{\sigma_1 \ldots \sigma_{k+1}}(\mathbf{r}_1, \ldots, \mathbf{r}_{k+1}) - g^{(k)}_{\sigma_1 \ldots \sigma_k}(\mathbf{r}_1, \ldots, \mathbf{r}_k) \right] \quad . \tag{3.5}$$

The derivatives with respect to the thermodynamic variables in (3.3) can be evaluated with the help of the diferentiation formulas (2.10) and (2.11). Let us first consider (2.10). Writing N_σ as the integral of $\sum_\alpha \delta(\mathbf{r}-\mathbf{q}_{\sigma\alpha})$ over the volume one may express the fluctuation expression at the right-hand side in terms of correlation functions as well, with the result:

$$\left[\frac{\partial}{\partial\beta\mu_{\sigma_{k+1}}} - \frac{\beta}{S}\frac{\partial q_v}{\partial\beta\mu_{\sigma_{k+1}}}\sum_\sigma e_\sigma \frac{\partial}{\partial\beta\mu_\sigma}\right] G^{(k)}(1,\ldots,k) =$$
$$= \; G^{(k)}(1,\ldots,k)\sum_{j=1}^{k}\delta_{\sigma_j,\sigma_{k+1}} + \int d\mathbf{r}_{k+1} G^{(1|k)}(k+1|1,\ldots,k) \quad . \tag{3.6}$$

These are $s-1$ independent relations for the s partial derivatives with respect to the chemical potentials. Upon summing over σ_{k+1}, with a weight factor $e_{\sigma_{k+1}}$, the left-hand side yields 0, so that one finds

$$\sum_{\sigma_{k+1}} e_{\sigma_{k+1}} \int d\mathbf{r}_{k+1} G^{(1|k)}(k+1|1,\ldots,k) = -\left(\sum_{j=1}^{k} e_{\sigma_j}\right) G^{(k)}(1,\ldots,k) \quad . \tag{3.7}$$

This is the well-known charge sum rule, which may be derived from the hierarchy equations as well.

We now turn to the derivative of $G^{(k)}$ with respect to β as given by (2.11). Substituting (2.1) at the right-hand side and rewriting the average in terms of correlation functions we find

$$\left[\frac{\partial}{\partial\beta} - \frac{\beta}{S}\frac{\partial q_v}{\partial\beta}\sum_\sigma e_\sigma \frac{\partial}{\partial\beta\mu_\sigma}\right] G^{(k)}(1,\ldots,k) =$$
$$= \; -\frac{3}{2\beta}\left[kG^{(k)}(1,\ldots,k) + \sum_{\sigma_{k+1}}\int d\mathbf{r}_{k+1} G^{(1|k)}(k+1|1,\ldots,k)\right]$$
$$- \; \frac{1}{2}\sum_{\sigma_{k+1},\sigma_{k+2}}\int d\mathbf{r}_{k+1}d\mathbf{r}_{k+2} G^{(2|k)}(k+1,k+2|1,\ldots,k) v(k+1,k+2)$$
$$- \; \sum_{\sigma_{k+1}}\sum_{j=1}^{k}\int d\mathbf{r}_{k+1} G^{(1|k)}(k+1|1,\ldots,k) v(j,k+1)$$
$$- \; \frac{1}{2}G^{(k)}(1,\ldots,k)\sum_{i,j=1(i\neq j)}^{k} v(i,j) \quad . \tag{3.8}$$

Here we introduced the generalized truncated correlation function

$$G^{(2|k)}(k+1,k+2|1,\ldots,k) = n_{\sigma_1}\ldots n_{\sigma_{k+2}}\Big[g^{(k+2)}_{\sigma_1\ldots\sigma_{k+2}}(\mathbf{r}_1,\ldots,\mathbf{r}_{k+2})$$
$$- \; g^{(k+1)}_{\sigma_1\ldots\sigma_{k+1}}(\mathbf{r}_1,\ldots,\mathbf{r}_{k+1}) - g^{(k+1)}_{\sigma_1\ldots\sigma_k\sigma_{k+2}}(\mathbf{r}_1,\ldots,\mathbf{r}_k,\mathbf{r}_{k+2})$$
$$- \; g^{(2)}_{\sigma_{k+1}\sigma_{k+2}}(\mathbf{r}_{k+1},\mathbf{r}_{k+2}) g^{(k)}_{\sigma_1\ldots\sigma_k}(\mathbf{r}_1,\ldots,\mathbf{r}_k) + 2g^{(k)}_{\sigma_1\ldots\sigma_k}(\mathbf{r}_1,\ldots,\mathbf{r}_k)\Big] \quad . \tag{3.9}$$

The truncated correlation function $G^{(2|k)}$ can be eliminated from (3.8) by using the hierarchy equation (3.4). In fact, writing (3.4) for $k+1$ instead of k, and choosing $j=k+1$ one derives an expression for the derivative of $G^{(1|k)}$ (defined in (3.5)) with respect to $\mathbf{r}_{k+1}$. It contains an integral with a function $G^{(1|k+1)}(k+2|1,\ldots,k+1)$ that can be written as a linear combination of $G^{(2|k)}(k+1,k+2|1,\ldots,k)$, $G^{(1|k)}(k+2|1,\ldots,k)$ and $G^{(k)}(1,\ldots,k)$. In this way one finds the auxiliary relation:

$$\sum_{\sigma_{k+2}}\int d\mathbf{r}_{k+2} G^{(2|k)}(k+1,k+2|1,\ldots,k)\nabla_{k+1} v(k+1,k+2) =$$
$$= \; -\beta^{-1}\nabla_{k+1} G^{(1|k)}(k+1|1,\ldots,k)$$
$$- \; G^{(1|k)}(k+1|1,\ldots,k)\sum_{j=1}^{k}\nabla_{k+1} v(j,k+1)$$

$$
\begin{aligned}
&- \; n_{\sigma_{k+1}} \nabla_{k+1} \Bigg[G^{(k)}(1,\ldots,k) \sum_{j=1}^{k} v(j,k+1) \\
&+ \; \sum_{\sigma_{k+2}} \int d\mathbf{r}_{k+2} G^{(1|k)}(k+2|1,\ldots,k) v(k+1,k+2) \Bigg] \quad . \qquad (3.10)
\end{aligned}
$$

We now take the inner product of this vector identity with $\mathbf{r}_{k+1}$, integrate over $\mathbf{r}_{k+1}$ and sum over σ_{k+1}. At the left-hand side we use the symmetry with respect to the interchange of $k+1$ and $k+2$, and the homogeneity of the potential function. As a result we find an expression that is equal to the term with $G^{(2|k)}$ in (3.8). In the first, third and fourth terms at the right-hand a partial integration can be performed, while the second term at the right-hand side may be transformed with the use of the identity

$$
\mathbf{r}_{k+1} \cdot \nabla_{k+1} v(j,k+1) = -v(j,k+1) - \mathbf{r}_j \cdot \nabla_j v(j,k+1) \quad . \qquad (3.11)
$$

The contribution with $\nabla_j v(j,k+1)$ that arises in this way can be rewritten once more with the help of (3.4). The identity that is finally obtained from (3.10) may be used to eliminate $G^{(2|k)}$ from (3.8). As a result the latter gets the form

$$
\begin{aligned}
&\left[\frac{\partial}{\partial \beta} - \frac{\beta}{S} \frac{\partial q_v}{\partial \beta} \sum_{\sigma} e_\sigma \frac{\partial}{\partial \beta \mu_\sigma} \right] G^{(k)}(1,\ldots,k) = \\
&= \; -\frac{3}{2\beta} \left[k G^{(k)}(1,\ldots,k) - \sum_{\sigma_{k+1}} \int d\mathbf{r}_{k+1} G^{(1|k)}(k+1|1,\ldots,k) \right] \\
&- \; \beta^{-1} \sum_{j=1}^{k} \mathbf{r}_j \cdot \nabla_j G^{(k)}(1,\ldots,k) \\
&+ \; 3 \sum_{\sigma_{k+1}} n_{\sigma_{k+1}} \int d\mathbf{r}_{k+1} \Bigg[G^{(k)}(1,\ldots,k) \sum_{j=1}^{k} v(j,k+1) \\
&+ \; \sum_{\sigma_{k+2}} \int d\mathbf{r}_{k+2} G^{(1|k)}(k+2|1,\ldots,k) v(k+1,k+2) \Bigg] \quad . \qquad (3.12)
\end{aligned}
$$

The term with the spatial derivatives in (3.12) can be eliminated with the help of the scaling relation (3.3). The derivative with respect to β then drops out as well. Furthermore, the last two terms in (3.12) may be transformed with the help of the Legendre expansion for the electrostatic potential. In doing so it is convenient to choose as the integration domain for the integral over $\mathbf{r}_{k+1}$ a large sphere S around the origin (with a radius tending to ∞). Using moreover the charge sum rule (3.7) we write the last two terms of (3.12) in such a way that the integral over $\mathbf{r}_{k+1}$ can be carried out, with the result:

$$
-\frac{1}{2} q_v \left[G^{(k)}(1,\ldots,k) \sum_{j=1}^{k} e_{\sigma_j} r_j^2 + \sum_{\sigma_{k+2}} e_{\sigma_{k+2}} \int d\mathbf{r}_{k+2} G^{(1|k)}(k+2|1,\ldots,k) r_{k+2}^2 \right] \quad . \qquad (3.13)
$$

Insertion of this expression in (3.12) finally leads to the identity

$$
\begin{aligned}
&\sum_{\sigma} \left[\frac{3}{2} - \frac{\beta^2}{S} e_\sigma \frac{\partial q_v}{\partial \beta} \right] \frac{\partial}{\partial \beta \mu_\sigma} G^{(k)}(1,\ldots,k) = \\
&= \; \frac{3}{2} \left[k G^{(k)}(1,\ldots,k) + \sum_{\sigma_{k+1}} \int d\mathbf{r}_{k+1} G^{(1|k)}(k+1|1,\ldots,k) \right] \\
&- \; \frac{1}{2} \beta q_v \left[G^{(k)}(1,\ldots,k) \sum_{j=1}^{k} e_{\sigma_j} r_j^2 + \sum_{\sigma_{k+1}} e_{\sigma_{k+1}} \int d\mathbf{r}_{k+1} G^{(1|k)}(k+1|1,\ldots,k) r_{k+1}^2 \right] \quad . \qquad (3.14)
\end{aligned}
$$

This identity comes in addition to the $s-1$ relations (3.6) found before. Together they constitute s relations from which the partial derivatives of $G^{(k)}$ with respect to the chemical potentials can be found.

Solution of the s linear equations (3.6) and (3.14) for the partial derivatives $\partial G^{(k)}/\partial\beta\mu_\sigma$ yields the following result

$$\frac{\partial}{\partial\beta\mu_{\sigma_{k+1}}}G^{(k)}(1,\ldots,k) = G^{(k)}(1,\ldots,k)\sum_{j=1}^{k}\delta_{\sigma_j,\sigma_{k+1}} + \int d\mathbf{r}_{k+1}G^{(1|k)}(k+1|1,\ldots,k)$$
$$-\frac{\beta}{6}\frac{\partial q_v}{\partial\beta\mu_{\sigma_{k+1}}}\left[G^{(k)}(1,\ldots,k)\sum_{j=1}^{k}e_{\sigma_j}r_j^2 + \sum_{\sigma_{k+2}}e_{\sigma_{k+2}}\int d\mathbf{r}_{k+2}G^{(1|k)}(k+2|1,\ldots,k)r_{k+2}^2\right] \quad , \quad (3.15)$$

where we used the equality

$$\beta\frac{\partial q_v}{\partial\beta} = \frac{3}{2}\sum_\sigma\frac{\partial q_v}{\partial\beta\mu_\sigma} - 3q_v \quad , \quad (3.16)$$

which follows from (2.8).

The complete set of partial derivatives of the correlation functions $G^{(k)}$ with respect to the chemical potentials has now been found. The expressions for these derivatives contain integrals of the truncated correlation functions $G^{(1|k)}$.

4 Second-moment sum rules

A different way to present the results of the previous section consists in writing them as sum rules for the zeroth and second moments of the truncated correlation functions. In fact, the zeroth moment of $G^{(1|k)}$ is found directly from (3.6). Returning to the notation of (3.1) we get

$$n_{\sigma_1}\ldots n_{\sigma_{k+1}}\int d\mathbf{r}_{k+1}\left[g^{(k+1)}_{\sigma_1\ldots\sigma_{k+1}}(\mathbf{r}_1,\ldots,\mathbf{r}_{k+1}) - g^{(k)}_{\sigma_1\ldots\sigma_k}(\mathbf{r}_1,\ldots,\mathbf{r}_k)\right] =$$
$$= -n_{\sigma_1}\ldots n_{\sigma_k}g^{(k)}_{\sigma_1\ldots\sigma_k}(\mathbf{r}_1,\ldots,\mathbf{r}_k)\sum_{j=1}^{k}\delta_{\sigma_j,\sigma_{k+1}}$$
$$+ \left[\frac{\partial}{\partial\beta\mu_{\sigma_{k+1}}} - \frac{\beta}{S}\frac{\partial q_v}{\partial\beta\mu_{\sigma_{k+1}}}\sum_\sigma e_\sigma\frac{\partial}{\partial\beta\mu_\sigma}\right]n_{\sigma_1}\ldots n_{\sigma_k}g^{(k)}_{\sigma_1\ldots\sigma_k}(\mathbf{r}_1,\ldots,\mathbf{r}_k) \quad . \quad (4.1)$$

As remarked already below (3.6) this sum rule leads to the charge sum rule for the truncated correlation functions if a suitable weighted sum over the species is carried out. The zeroth-order sum rule found here does not contain such a sum: it is valid for each species separately. We will refer to it as a *generalized charge sum rule*. Alternatively, we may write it in terms of the Ursell functions $h^{(k)}_{\sigma_1\ldots\sigma_k}$ that are related to the correlation functions through the standard cluster decomposition.

The second-moment sum rule for the truncated correlation functions follows from (3.15). The simplest form is obtained by summing that equation over σ_{k+1}, with weights e_{k+1}, since then the first two terms at the right-hand side drop out on account of the charge sum rule (3.7). Adopting again the notation of (3.1) we get

$$n_{\sigma_1}\ldots n_{\sigma_k}\sum_{\sigma_{k+1}}e_{\sigma_{k+1}}n_{\sigma_{k+1}}\int d\mathbf{r}_{k+1}\left[g^{(k+1)}_{\sigma_1\ldots\sigma_{k+1}}(\mathbf{r}_1,\ldots,\mathbf{r}_{k+1}) - g^{(k)}_{\sigma_1\ldots\sigma_k}(\mathbf{r}_1,\ldots,\mathbf{r}_k)\right]r_{k+1}^2 =$$
$$= -n_{\sigma_1}\ldots n_{\sigma_k}g^{(k)}_{\sigma_1\ldots\sigma_k}(\mathbf{r}_1,\ldots,\mathbf{r}_k)\sum_{j=1}^{k}e_{\sigma_j}r_j^2 - \frac{6}{S}\sum_\sigma e_\sigma\frac{\partial}{\partial\beta\mu_\sigma}n_{\sigma_1}\ldots n_{\sigma_k}g^{(k)}_{\sigma_1\ldots\sigma_k}(\mathbf{r}_1,\ldots,\mathbf{r}_k) \; . \; (4.2)$$

By using the cluster decomposition one may rewrite this identity in terms of the Ursell functions. The second-moment sum rule found here may be called a *generalized Stillinger-Lovett relation*. The

reason for that becomes obvious if the special case $k = 1$ is considered. Using translation invariance and isotropy we may write (4.2) in that case as

$$n_{\sigma_1} \sum_{\sigma_2} e_{\sigma_2} n_{\sigma_2} \int d\mathbf{r}_{12} h^{(2)}_{\sigma_1\sigma_2}(r_{12}) r_{12}^2 = -\frac{6}{S} \frac{\partial q_v}{\partial \beta \mu_{\sigma_1}} \quad . \tag{4.3}$$

This relation has been derived before [2]. Summation over σ_1, with weights e_{σ_1}, leads to the identity

$$\sum_{\sigma_1,\sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_{12} h^{(2)}_{\sigma_1\sigma_2}(r_{12}) r_{12}^2 = -\frac{6}{\beta} \quad , \tag{4.4}$$

which is the well-known Stillinger-Lovett relation [1] for a mixture. It should be noted that (4.3) is valid for each species σ_1 separately, so that it is more general than (4.4). Likewise, (4.2) contains k independent species labels.

A useful alternative form for the sum rule (4.2) is obtained by adopting a different set of independent thermodynamic variables, namely the charge density q_v and a set of reduced thermodynamic potentials defined as [6]

$$\bar{\mu}_\sigma = \mu_\sigma - e_\sigma \frac{\sum_{\sigma'} e_{\sigma'} \mu_{\sigma'}}{\sum_{\sigma'} e_{\sigma'}^2} \quad , \tag{4.5}$$

which satisfy the constraint $\sum_\sigma e_\sigma \bar{\mu}_\sigma = 0$. In terms of these variables the combination of partial derivatives occurring in (4.2) gets a simple form, since one has

$$\frac{1}{S} \sum_\sigma e_\sigma \left(\frac{\partial}{\partial \beta \mu_\sigma} \right)_{\beta, \{\beta \mu_{\sigma'}\}} = \frac{1}{\beta} \left(\frac{\partial}{\partial q_v} \right)_{\beta, \{\beta \bar{\mu}_\sigma\}} \quad . \tag{4.6}$$

For the special case of the one-component plasma (with $s = 1$) the zeroth-moment sum rule (4.1) is completely equivalent to the standard charge sum rules for the correlation or Ursell functions. The second-moment sum rule (4.2) reduces then to the sum rule found before by Alastuey [4] and by Vieillefosse and Brajon [5] for the one-component plasma.

The sum rules derived here are useful in studying the behaviour of large-scale fluctuations in an ionic mixture. In particular, they can be employed to establish the small-wavenumber behaviour of the Fourier transform of cross-fluctuation expressions containing the product of the local partial density $n_\sigma(\mathbf{r}) = \sum_\alpha \delta(\mathbf{r} - \mathbf{q}_{\sigma\alpha})$ of species σ or of the local charge density $q_v(\mathbf{r}) = \sum_\sigma e_\sigma n_\sigma(\mathbf{r})$ of the particles on one hand, and an arbitrary localized microscopic configurational quantity $f(\mathbf{r})$ on the other hand. In general, the latter may be written as a linear combination of k-particle sum variables of the form

$$f(\mathbf{r}) = \sum_{\sigma_1\alpha_1,\ldots,\sigma_k\alpha_k}{}' \; f_{\sigma_1\ldots\sigma_k}(\mathbf{q}_{\sigma_1\alpha_1}, \ldots, \mathbf{q}_{\sigma_k\alpha_k}; \mathbf{r}) \quad . \tag{4.7}$$

The Fourier-transformed fluctuation expressions we are interested in have the form

$$\frac{1}{V} \langle [n_\sigma(\mathbf{k})]^* f(\mathbf{k}) \rangle \quad , \tag{4.8}$$

and

$$\frac{1}{V} \langle [q_v(\mathbf{k})]^* f(\mathbf{k}) \rangle \quad , \tag{4.9}$$

with the Fourier transform of the microscopic quantity $f(\mathbf{r})$ defined as $f(\mathbf{k}) \equiv \int^V d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r}) f(\mathbf{r})$.

Writing the fluctuation expression (4.8) in terms of correlation functions and using the zeroth-order sum rule (4.1) one easily derives the identity

$$\lim_{\mathbf{k}\to 0} \frac{1}{V} \langle [n_\sigma(\mathbf{k})]^* f(\mathbf{k}) \rangle = \frac{\partial \langle f \rangle}{\partial \beta \mu_\sigma} - \frac{\beta}{S} \frac{\partial q_v}{\partial \beta \mu_\sigma} \sum_{\sigma'} e_{\sigma'} \frac{\partial \langle f \rangle}{\partial \beta \mu_{\sigma'}} \quad . \tag{4.10}$$

Summing over σ, with weights e_σ, one finds that all cross-fluctuation expressions containing the Fourier transform of the local charge density $q_v(\mathbf{r})$ of the particles as a factor vanish in the long-wavelength limit:

$$\lim_{\mathbf{k}\to 0} \frac{1}{V} \langle [q_v(\mathbf{k})]^* f(\mathbf{k}) \rangle = 0 \quad . \tag{4.11}$$

This result is equivalent to the charge sum rule for the k-point correlation function.

The first non-vanishing contribution in the small-wavenumber expansion of a cross-fluctuation expression with the charge density is of second order in k. The coefficient of the second-order term can be evaluated by employing the second-moment sum rule (4.2). One finds

$$\lim_{\mathbf{k}\to 0} \frac{1}{k^2} \frac{1}{V} \langle [q_v(\mathbf{k})]^* f(\mathbf{k}) \rangle = \frac{1}{S} \sum_\sigma e_\sigma \frac{\partial \langle f \rangle}{\partial \beta \mu_\sigma} \quad . \tag{4.12}$$

In particular, putting $f(\mathbf{k})$ equal to the Fourier transform of the local partial density $n_\sigma(\mathbf{r})$ or of the local charge density $q_v(\mathbf{r})$ of the particles one finds identities that are equivalent to (4.3) and (4.4). A suggestive form for (4.12) is obtained by using a different set of variables as in (4.6):

$$\lim_{\mathbf{k}\to 0} \frac{1}{k^2} \frac{1}{V} \langle [q_v(\mathbf{k})]^* f(\mathbf{k}) \rangle = \frac{1}{\beta} \left(\frac{\partial \langle f \rangle}{\partial q_v} \right)_{\beta, \{\beta \bar{\mu}_\sigma\}} \quad . \tag{4.13}$$

This identity is somewhat similar to the differentiation formulas that have been discussed in section 2. However, the similarity is superficial only: the present identity determines the second-order contribution in the long-wavelength expansion of a fluctuation expression, whereas the identities of section 2 fix the leading zeroth-order contributions of fluctuation expressions.

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