EQUILIBRIUM PROPERTIES OF A MULTI-COMPONENT IONIC MIXTURE

I. SUM RULES FOR CORRELATION FUNCTIONS

L.G. SUTTORP and A.J. VAN WONDEREN
Instituut voor Theoretische Fysica, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

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Equilibrium statistical methods are used to derive sum rules for two- and three-particle correlation functions of a multi-component ionic mixture. Some of these rules are general consequences of the electrostatic character of the interaction, whereas others depend on specific thermodynamic properties of the system. The first group of rules follows from the BBGKY hierarchy and a clustering hypothesis for Ursell functions. The sum rules of the second group are obtained by describing the system with the help of a restricted grand-canonical ensemble in which the particle numbers of the various components in the mixture fluctuate under the condition that the total charge in the system remains constant.

I. Introduction

During the first part of this decade a series of papers\textsuperscript{1-7} appeared in which the static properties of systems with a long-range interaction between the constituent particles were studied. In these papers a set of sum rules for Ursell functions was derived by starting from the BBGKY hierarchy and a suitable clustering assumption. In this way well-known features of systems with electrostatic interaction, such as perfect screening and the second moment condition of Stillinger and Lovett\textsuperscript{8}), were established rigorously.

Besides these general electrostatic sum rules it is also of interest to derive sum rules in which the thermodynamic properties of the system are involved. The main reason to study these thermodynamic sum rules on a par with the electrostatic rules is their indispensability in a systematic derivation of fluctuation formulae for charged particle systems by means of equilibrium statistical mechanics\textsuperscript{9,10}). Moreover these sum rules are useful in the evaluation of more complicated fluctuation formulae for the product of three or more fluctuating...
quantities. Such formulae play a role in mode-coupling theories for time
correlation functions and transport properties\textsuperscript{11,12}).

A unified treatment of both types of sum rules has been presented recently
for the special case of a one-component plasma\textsuperscript{9}). In this model the charged
particles, which repel each other according to the Coulomb law, are immersed
in a neutralizing inert background of opposite charge, so that overall neutrality
of the system is ensured. By describing this system with the help of a canonical
ensemble both sum rules and fluctuation formulae were obtained from first
principles. A somewhat different approach to the sum rules and the fluctuation
formulae for a one-component plasma starts by considering the balance
equations for the particle density, the momentum density and the energy
density\textsuperscript{13}).

It is the purpose of the present paper to give a statistical derivation of the
sum rules for the two- and the three-particle Ursell functions of a multi-
component ionic mixture. In such a mixture several species of particles, with
different charges of equal sign and interacting through a Coulomb repulsion,
move in a neutralizing background, as in the one-component case. Although an
ionic mixture thus resembles a one-component plasma, its static properties
differ considerably, since in a mixture the particle density and the charge
density are no longer proportional to each other.

Some time ago\textsuperscript{13}) the properties of the pair correlation functions for
multi-component electrolytes have been studied by statistical methods. To
derive these properties use is made of a statistical description for non-uniform
systems in terms of a grand-canonical partition functional. For systems with
Coulomb interactions the ensuing functional of the free energy is written as the
sum of an electrostatic contribution and a remainder that is assumed to be a
local functional of the density. Whereas the methods used in the present paper
are different, the results will corroborate and complement the findings of ref.
13.

Before considering the thermodynamic sum rules we shall give a review of
the electrostatic sum rules. The derivation of the latter will yield several
ancillary relations that are needed later on. To obtain the thermodynamic sum
rules we shall describe the ionic mixture by a suitably chosen equilibrium
ensemble in which the total charge is kept constant. In this ensemble the
derivatives of the partial densities and the pair correlation functions with
respect to the independent thermodynamic variables of the system lead to
identities from which the thermodynamic sum rules for the two- and three-
particle Ursell functions will follow.

In the second paper of this series\textsuperscript{14}) the fluctuation formulae for the
multi-component ionic mixture will be obtained from the sum rules that are
derived presently.
2. Electrostatic sum rules

The Hamiltonian of a multi-component ionic mixture consisting of \( s \) components and being confined to a vessel of volume \( V \) is given by

\[
H = \sum_{\sigma} \frac{p_{\sigma}^2}{2m_{\sigma}} + \frac{1}{2} \sum_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} v_{\sigma_1 \sigma_2}(r_{\sigma_1 \sigma_3} - r_{\sigma_2 \sigma_4}),
\]

(2.1)

with the potential

\[
v_{\sigma_1 \sigma_2}(r) = \frac{1}{V} \sum_{q \neq 0} \frac{e_{\sigma_1} e_{\sigma_2}}{q^2} e^{iq \cdot r}.
\]

(2.2)

The system contains \( N_\sigma \) particles of species \( \sigma \). The particle \( \alpha \) of the component \( \sigma \) has mass \( m_\sigma \), charge \( e_\sigma \), position \( r_{\sigma \alpha} \) and momentum \( p_{\sigma \alpha} \). The symbol \( \Sigma' \) means that one should sum over all particles under the restriction \( \sigma_i \alpha_i \neq \sigma_j \alpha_j \) \( (i \neq j) \). In the definition of the potential periodic boundary conditions have been assumed. On account of the presence of the neutralizing background the term with \( q = 0 \) is excluded from the expression for \( v_{\sigma_1 \sigma_2}(r) \).

The \( k \)-particle correlation functions, defined as

\[
n_{\sigma_1} \cdots n_{\sigma_k} g^{(k)}_{\sigma_1 \cdots \sigma_k}(r_1, \cdots, r_k) = \left\langle \sum_{\alpha_1 \cdots \alpha_k} \delta(r_1 - r_{\sigma_1 \alpha_1}) \cdots \delta(r_k - r_{\sigma_k \alpha_k}) \right\rangle, \quad k = 2, 3, \ldots,
\]

(2.3)

with the brackets denoting an equilibrium ensemble average and \( n_\sigma = \left\langle N_\sigma \right\rangle / V \) the particle density of species \( \sigma \), satisfy the BBGKY hierarchy equations

\[
n_{\sigma_1} \cdots n_{\sigma_k} \frac{\partial}{\partial r_1} g^{(k)}_{\sigma_1 \cdots \sigma_k}(r_1, \cdots, r_k) = -\beta n_{\sigma_1} \cdots n_{\sigma_k} g^{(k)}_{\sigma_1 \cdots \sigma_k}(r_1, \cdots, r_k) \sum_{\alpha = 2}^{k} \frac{\partial}{\partial r_1} v_{\sigma_1 \alpha}(r_1) \]

\[-\beta n_{\sigma_1} \cdots n_{\sigma_k} \sum_{\sigma} n_\sigma \int \! dr_{k+1} g^{(k+1)}_{\sigma_1 \cdots \sigma \sigma}(r_1, \cdots, r_{k+1}) \frac{\partial}{\partial r_1} v_{\sigma_1 \sigma}(r_{k+1}),
\]

(2.4)

with \( \beta = (k_B T)^{-1} \) determining the temperature \( T \). As usual the correlation functions \( g^{(k)} \) can be expanded in terms of Ursell functions \( h^{(k)}_{\sigma_1 \cdots \sigma_k}(r_1, \cdots, r_k) \) with \( k = 2, 3, \ldots \). We assume that these Ursell functions tend to zero faster than any power \( r_{ij}^{-m} \), with integer \( m \), if the separation \( r_{ij} \) between the positions \( r_i \) and \( r_j \) goes to infinity. This assumption is the usual exponential clustering
hypothesis for charged systems. It will enable us to derive the electrostatic sum rules for an ionic mixture in an analogous way as for the one-component plasma.

The hierarchy (2.4) for \( k = 2 \) yields

\[
\beta \sum_{\alpha_3} n_{\alpha_3} \int \mathrm{d}r_3 \, h_{\alpha_1, \alpha_2, \alpha_3}^{(3)} \frac{\partial v_{\alpha_1, \alpha_2}}{\partial r_1} = -\frac{\partial h_{\alpha_1, \alpha_2}^{(2)}}{\partial r_1} - \beta \sum_{\alpha_3} n_{\alpha_3} \int \mathrm{d}r_3 \, h_{\alpha_2, \alpha_3}^{(3)} \frac{\partial v_{\alpha_1, \alpha_2}}{\partial r_1} - \beta h_{\alpha_1, \alpha_2}^{(2)} \frac{\partial v_{\alpha_1, \alpha_2}}{\partial r_1} - \beta \frac{\partial v_{\alpha_1, \alpha_2}}{\partial r_1}. \tag{2.5}
\]

For convenience we do not write anymore the arguments of a function \( f_{\alpha_1, \ldots, \alpha_k}(r_1, \ldots, r_k) \). The first term at the right-hand side can be simplified with the help of the equality

\[
\int \mathrm{d}r_3 \, h_{\alpha_2, \alpha_3}^{(2)} \frac{\partial v_{\alpha_1, \alpha_3}}{\partial r_1} = \frac{\partial v_{\alpha_1, \alpha_3}(r_{12})}{\partial r_1} \int \mathrm{d}r_{23} \, h_{\alpha_2, \alpha_3}^{(2)}. \tag{2.6}
\]

To understand this relation we note that \( V \) can be chosen such that \( r_{12} \ll V^{1/3} \) and that moreover the main contribution to the integral at the left-hand side arises from the domain defined by \( r_{13} \ll V^{1/3} \). This implies that to a fair approximation the potential \( v_{\alpha_1, \alpha_3}(r) \) may be replaced by the Coulomb form \( e_{\alpha_1} e_{\alpha_3}/(4 \pi r) \).

From (2.5) and (2.6) we obtain

\[
\beta \sum_{\alpha_3} n_{\alpha_3} \int \mathrm{d}r_3 \, h_{\alpha_1, \alpha_2, \alpha_3}^{(3)} \frac{\partial v_{\alpha_1, \alpha_2}}{\partial r_1} = -\frac{\partial h_{\alpha_1, \alpha_2}^{(2)}}{\partial r_1} - \beta \sum_{\alpha_3} n_{\alpha_3} \frac{\partial v_{\alpha_1, \alpha_3}(r_{12})}{\partial r_1} \int \mathrm{d}r_{23} \, h_{\alpha_2, \alpha_3}^{(2)} - \beta h_{\alpha_1, \alpha_2}^{(2)} \frac{\partial v_{\alpha_1, \alpha_2}}{\partial r_1} - \beta \frac{\partial v_{\alpha_1, \alpha_2}}{\partial r_1}. \tag{2.7}
\]

Because of the fast decay of the Ursell functions we learn from this equation

\[
\sum_{\alpha_2} n_{\alpha_2} e_{\alpha_2} \int \mathrm{d}r_{12} \, h_{\alpha_1, \alpha_2}^{(2)} + e_{\alpha_1} = 0, \tag{2.8}
\]

which is the well-known perfect-screening condition. Some years ago it was proved that the result (2.8) is the first member of a hierarchy of perfect-screening conditions for Ursell functions. The combination of (2.6) and (2.8) gives
\[ \sum_{\sigma_3} n_{\sigma_3} \int dr_3 h^{(2)}_{\sigma_1 \sigma_2 \sigma_3} \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} = -\sum_{\sigma_3} n_{\sigma_3} \frac{\partial v_{\sigma_1 \sigma_2}(r_{12})}{\partial r_1} \int dr_{23} h^{(2)}_{\sigma_1 \sigma_2 \sigma_3} - \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1}. \]  
(2.9)

This relation will be needed presently.

From the hierarchy (2.4) for \( k = 3 \) we deduce

\[ \beta \sum_{\sigma_4} n_{\sigma_4} \int dr_4 h^{(4)}_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} = -\beta \frac{\partial h^{(3)}_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}}{\partial r_1} - \beta h^{(3)}_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} \left[ \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} + \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} \right] \]

\[ -\beta h^{(2)}_{\sigma_1 \sigma_2} \left( \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} + \sum_{\sigma_4} n_{\sigma_4} \int dr_4 h^{(2)}_{\sigma_1 \sigma_2 \sigma_4} \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} \right) \]

\[ -\beta h^{(2)}_{\sigma_1 \sigma_2} \left( \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} + \sum_{\sigma_4} n_{\sigma_4} \int dr_4 h^{(2)}_{\sigma_1 \sigma_2 \sigma_4} \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} \right) \]

\[ -\beta \sum_{\sigma_4} n_{\sigma_4} \int dr_4 h^{(3)}_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} - \beta h^{(2)}_{\sigma_1 \sigma_2 \sigma_3} \left[ \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} + \frac{\partial v_{\sigma_1 \sigma_2}}{\partial r_1} \right], \]  
(2.10)

where (2.5) has been employed. If we take the limit \( r_{12} \to \infty \), the left-hand side and the first seven terms of the right-hand side vanish quickly on account of the fast decay of the Ursell functions and the relation (2.9). So the same holds true for the last three terms at the right-hand side. Using the Legendre expansion

\[ v_{\sigma_1 \sigma_2} = v_{\sigma_1 \sigma_2}(r_{12}) + \sum_{l=1}^{\infty} \frac{e_{\sigma_1} e_{\sigma_2}}{4\pi} \frac{r_{12}^l}{r_{12}^{l+1}} P_l(\hat{r}_{12} \cdot \hat{r}_{32}), \quad r_{12} > r_{23}, \]  
(2.11)

with \( \hat{r} = r/r \) and collecting equal powers of \( r_{12} \) we find as a consequence

\[ \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_3 h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} = -(e_{\sigma_1} + e_{\sigma_2}) h^{(2)}_{\sigma_1 \sigma_2}, \]  
(2.12)

\[ \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_3 h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} r_{13}^l P_l(\hat{r}_{12} \cdot \hat{r}_{13}) = -e_{\sigma_3} h^{(2)}_{\sigma_1 \sigma_2}, \quad l = 1, 2, \ldots. \]  
(2.13)

These are the perfect-screening rules\(^{1-4}\) for \( h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} \).

As in the one-component-plasma case\(^5\) a consistency relation can now be established from (2.5) and (2.13). If we eliminate the second term at the right-hand side of (2.5) with the help of (2.9), we obtain after scalar multiplication by \( r_{12} \) and integration over \( r_{12} \)
\[ -\beta e_{\sigma_1} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_{12} dr_{3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)} \frac{r_{12} \cdot r_{13}}{4 \pi r_{13}^3} \]

\[ = -\beta e_{\sigma_1} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_{23} h_{\sigma_1 \sigma_2 \sigma_3}^{(2)} r_{23}^2 + \beta \int dr_{12} h_{\sigma_1 \sigma_2 \sigma_1}^{(2)} + 3 \int dr_{12} h_{\sigma_1 \sigma_2}^{(2)} \]

(2.14)

On the other hand from (2.13) for \( l = 1 \) it follows after multiplication by \( e_{\sigma_1} / (4 \pi r_{12}^2) \) and integration over \( r_{12} \):

\[ e_{\sigma_1} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_{12} dr_{3} h_{\sigma_1 \sigma_2 \sigma_3}^{(3)} \frac{r_{12} \cdot r_{13}}{4 \pi r_{12}^3} = -\int dr_{12} h_{\sigma_1 \sigma_2 \sigma_1}^{(2)} \]

(2.15)

Comparing (2.14) with (2.15) we obtain upon using (2.8) and the symmetry of \( h^{(2)} \) under the interchange of its variables (see (A.1))

\[ \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_{12} h_{\sigma_1 \sigma_2 \sigma_1}^{(2)} r_{12}^2 = -\frac{6}{\beta} \]

(2.16)

This identity is the second-moment condition formulated by Stillinger and Lovett\(^8\) and thereafter discussed by many authors\(^3,5,7,9,10,13,15-18\).

In the course of the above derivation of the perfect-screening rules and the condition of Stillinger and Lovett there was no need to specify completely the ensemble we work with. However, in order to proceed further some general properties of the ensemble are needed. These will be considered in the next section.

3. Ensemble and thermodynamics

In section 2 we made an assumption on the asymptotic form of the Ursell functions. This form depends on the choice of the ensemble, at least for finite systems. In the neutral case the correlation functions possess the clustering property up to terms of order \( N^{-1} \), with \( N \) the particle number, if the grand-canonical ensemble is adopted\(^10\). On the other hand, for the one-component plasma the canonical ensemble is to be preferred\(^20\), since the total charge of the system has to remain a constant.

To determine the ensemble that is adequate for the multi-component ionic mixture we impose the constraint

\[ Q = \sum_{\sigma} e_{\sigma} N_{\sigma} = \text{constant} \]

(3.1)

In contrast to the one-component plasma the ionic mixture admits fluctuations
in the number of particles of the constituent species. In fact \((s - 1)\) of these particle numbers may vary independently. Assuming \(e_1 \neq 0\) we write relation (3.1) as

\[
N_i = \left[ Q - \sum_{\sigma \neq 1} e_\sigma N_\sigma \right] / e_1 ,
\]

so that \(N_i\) can be considered as a function of \(\{N_\sigma\}, \sigma = 2, \ldots, s\), with \(Q\) a parameter.

An ensemble density for a multi-component ionic mixture with the constraint (3.1) has been discussed before\(^{21}\). Here we shall derive it by employing the maximum-entropy method. We introduce the functional

\[
S[\rho] = -k_B \sum_{N_2, \ldots, N_s} \int dr^{N_1} \cdots dr^{N_s} dp^{N_1} \cdots dp^{N_s} \rho \log(N_1! \cdots N_s! h^{3N}\rho) ,
\]

with \(\rho(r^{N_1}, \ldots, r^{N_s}, p^{N_1}, \ldots, p^{N_s}, N_2, \ldots, N_s)\) the density in the phase space \(\Gamma\) and \(N = \sum N_\sigma\) the total number of particles. Of course the sum must be carried out under the condition \(N_i \geq 0\), which is indicated by the prime at the summation symbol. The density \(\rho\) will be varied under the constraints

\[
\langle 1 \rangle = 1 , \quad \frac{1}{V} \langle H \rangle = u_\sigma , \quad \frac{1}{V} \langle N_\sigma \rangle = n_\sigma , \quad \sigma = 2, \ldots, s ,
\]

with the brackets indicating an average with the density \(\rho\). Here \(u_\sigma = U/V\) is the internal energy per unit of volume; in general we shall use the notation \(A_\sigma = A/V\) for any global quantity \(A\). The stationary value of \(S[\rho]\) under variations of \(\rho\) with the constraints (3.4) may be identified with the thermodynamic entropy \(S\). The phase space density corresponding to this stationary value has the general form:

\[
\rho(r^{N_1}, \ldots, r^{N_s}, p^{N_1}, \ldots, p^{N_s}, N_2, \ldots, N_s)
\]

\[
= \frac{1}{N_1! \cdots N_s! h^{3N}Z} \exp \left( \beta \sum_{\sigma \neq 1} \tilde{\mu}_\sigma N_\sigma - \beta H \right) ,
\]

with the partition function

\[
Z = \sum_{N_2, \ldots, N_s} \frac{1}{N_1! \cdots N_s! h^{3N}} \int dr^{N_1} \cdots dr^{N_s} dp^{N_1} \cdots dp^{N_s}
\]

\[
\times \exp \left( \beta \sum_{\sigma \neq 1} \tilde{\mu}_\sigma N_\sigma - \beta H \right) .
\]
Here \( \beta \) and \( \{ \beta \tilde{\mu}_\sigma \} \), with \( \sigma = 2, \ldots, s \) are Lagrange multipliers. In the usual way \( \beta \) may be identified with \( (k_B T)^{-1} \), with \( T \) the temperature. Combining (3.3) with the constraints (3.4) we readily find

\[
\lim_{V \rightarrow \infty} \frac{1}{BV} \log Z(\beta, \{ \beta \tilde{\mu}_\sigma \}, q_e, V) = TS_e - u_e + \sum_{\sigma = 1} \tilde{\mu}_\sigma n_\sigma .
\]  

(3.7)

Differentiation of (3.7), with (3.6) inserted, yields

\[
T \, ds_e = du_e - \sum_{\sigma = 1} \tilde{\mu}_\sigma \, dn_\sigma - \tilde{\mu}_q \, dq_e .
\]  

(3.8)

with \( \tilde{\mu}_q \) an additional parameter. This relation shows that the Lagrange multipliers \( \{ \tilde{\mu}_\sigma \} \) may be interpreted as chemical potentials of the system with the constraint (3.1). An alternative form of (3.8) is

\[
T \, ds_e = du_e - \sum_{\sigma} \mu_\sigma \, dn_\sigma ,
\]  

(3.9)

where we defined \( \mu_1 - e_1 \tilde{\mu}_q \) and \( \mu_\sigma - \tilde{\mu}_\sigma + c_\sigma \tilde{\mu}_q \) for \( \sigma = 2, \ldots, s \). Putting

\[
\beta \tilde{\rho}(\beta, \{ \beta \tilde{\mu}_\sigma \}, q_e) := \lim_{V \rightarrow \infty} \frac{1}{V} \log Z(\beta, \{ \beta \tilde{\mu}_\sigma \}, q_e, V) ,
\]  

(3.10)

we can calculate all thermodynamic quantities of the system by starting from the relations

\[
u_e = - \frac{\partial \beta \tilde{\rho}}{\partial \beta} , \quad n_\sigma = - \frac{\partial \beta \tilde{\rho}}{\partial \beta \mu_\sigma} , \quad \sigma = 2, \ldots, s , \quad \tilde{\mu}_q = - \frac{\partial \tilde{\rho}}{\partial q_e} .
\]  

(3.11)

In writing a partial derivative with respect to a variable of the set \( \beta, \{ \beta \tilde{\mu}_\sigma \}, q_e \), the variables of the set that are meant to remain constant are suppressed.

From now on we shall assume that the exponential clustering hypothesis holds in the ensemble defined by (3.5), so that we may use the results of the preceding section. In the remainder of this section we shall derive some consequences of the ensemble (3.5) by using the scaling law

\[
H^{\text{pot}}(r^N, \ldots, r^N, V) = \lambda H^{\text{pot}}(\lambda r^N, \ldots, \lambda r^N, \lambda^3 V) , \quad \lambda > 0 .
\]  

(3.12)

Here the superscript 'pot' indicates the potential part of the hamiltonian (2.1) with (2.2). From (3.10) with (3.6) one can now verify

\[
\beta \tilde{\rho}(\beta, \{ \beta \tilde{\mu}_\sigma \}, q_e) = - \frac{3q_e \log \lambda}{2e_1} + \lambda^3 \beta \tilde{\rho}(\lambda \beta, \{ \beta \tilde{\mu}_\sigma - \frac{3}{2} \left( 1 - e_\sigma \right) \log \lambda \}, \lambda^{-3} q_e) .
\]  

(3.13)
Choosing $\lambda = \beta^{-1}$ we get the scaling property
\[
\beta \tilde{p}(\beta, (\beta \tilde{\mu}_\sigma), q_v) = \frac{3q_v \log \beta}{2e_i} + q_v \psi \left( \frac{3}{2} \left( 1 - \frac{e_v}{e_i} \right) \log \beta \right), \beta^3 q_v,
\]
(3.14)

with a function $\psi$ that depends on $s$ variables only. As a consequence the $(s+1)$ partial derivatives (3.11) are not independent
\[
\beta \frac{\partial \beta \tilde{p}}{\partial \beta} = \frac{3}{2} \sum_{\sigma \neq 1} \left( 1 - \frac{e_v}{e_i} \right) \frac{\partial \beta \tilde{p}}{\partial \beta \tilde{\mu}_\sigma} + 3q_v \frac{\partial \beta \tilde{p}}{\partial q_v} + \frac{3q_v}{2e_i} - 3\beta \tilde{p}.
\]
(3.15)

On substitution of the relations (3.11) we find
\[
p = \frac{n}{2\beta} + \frac{1}{3} \mu_v,
\]
(3.16)

with
\[
p := \tilde{p} + \tilde{\mu}_v q_v.
\]
(3.17)

With this definition we can cast (3.7) into the familiar Euler form.

If we differentiate (3.16), with (3.17) inserted, with respect to $\beta \tilde{\mu}_\sigma$ for $\sigma = 2, \ldots, s$ and use (3.11) we get
\[
\beta \frac{\partial n_\sigma}{\partial \beta} = \frac{3}{2} \frac{\partial n}{\partial \beta \tilde{\mu}_\sigma} + 3q_v \frac{\partial n_\sigma}{\partial q_v} - 3n_\sigma,
\]
(3.18)

The derivative $\partial n_i / \partial \beta$ follows by applying (3.2)
\[
\beta \frac{\partial n_i}{\partial \beta} = \frac{3}{2} \sum_{\sigma \neq i} \frac{e_v}{e_i} \frac{\partial n_i}{\partial \beta \tilde{\mu}_\sigma} + 3q_v \frac{\partial n_i}{\partial q_v} - 3n_i.
\]
(3.19)

Defining the operator $D/D\beta \tilde{\mu}_\sigma$ by
\[
\frac{D}{D\beta \tilde{\mu}_\sigma} = (1 - \delta_{\sigma 1}) \frac{\partial}{\partial \beta \tilde{\mu}_\sigma} - \delta_{\sigma 1} \sum_{\sigma' \neq 1} \frac{e_{\sigma'}}{e_i} \frac{\partial}{\partial \beta \tilde{\mu}_{\sigma'}}.
\]
(3.20)

we can combine the results (2.18) and (2.19) into the equation
\[
\beta \frac{\partial n_\sigma}{\partial \beta} = \frac{3}{2} \frac{Dn}{D\beta \tilde{\mu}_\sigma} + 3q_v \frac{\partial n_\sigma}{\partial q_v} - 3n_\sigma.
\]
(3.21)

Incidentally, we remark that it may be proved from (3.2) and (3.11) that $Dn_\sigma / D\beta \tilde{\mu}_\sigma$ is symmetric in $(\sigma, \sigma')$. 
Finally, differentiation of (3.16) with respect to $\beta$ yields

$$
\frac{\partial u_v}{\partial \beta} = 9q_v \frac{\partial \rho}{\partial q_v} - \frac{9q_v}{2\beta} \frac{\partial n}{\partial q_v} - \frac{3}{2} \frac{\partial n}{\partial \beta} - 4u_v,
$$

(3.22)

where again (3.11) has been employed. Both (3.21) and (3.22) will be needed in the following.

4. Derivatives of the partial densities and the pair correlation functions

As we now have at our disposal the expression (3.5) for the phase space density, we can calculate the partial derivatives of an ensemble average with respect to the chemical potentials and the temperature

$$
\frac{D}{D\beta \mu_\alpha} \langle f \rangle = \langle f(N_\alpha - \langle N_\alpha \rangle) \rangle, \quad (4.1)
$$

$$
\frac{\partial}{\partial \beta} \langle f \rangle = -\langle f(H - \langle H \rangle) \rangle, \quad (4.2)
$$

for any function $f$ in phase space. In carrying out the partial differentiations the appropriate independent variables of the set $\beta$, $\{\beta \mu_\alpha\}$, $q_v$, and also $V$, have to be kept constant. In the following we shall derive sum rules by choosing suitable functions $f$ and expressing the right-hand sides of (4.1) and (4.2) in terms of Ursell functions.

For the choice $f = N_{\alpha_1}/V$ the identity (4.1) becomes upon using (2.3) and the cluster expansion

$$
\frac{Dn_{\alpha_1}}{D\beta \mu_{\alpha_2}} = n_{\alpha_1} n_{\alpha_2} \int dr_{12} h_{\alpha_1 \alpha_2}^{(2)} + n_{\alpha_1} \delta_{\alpha_1, \alpha_2}, \quad (4.3)
$$

Likewise, (4.2) yields, with the use of the expression

$$
\frac{1}{V} \langle H \rangle = \frac{1}{2} \sum_{\alpha_1, \alpha_2} n_{\alpha_1} n_{\alpha_2} \int dr_{12} h_{\alpha_1 \alpha_2}^{(2)} v_{\alpha_1 \alpha_2} + \frac{3n}{2\beta} = u_v \quad (4.4)
$$

for the average hamiltonian, the relation

$$
\beta \frac{\partial n_{\alpha_1}}{\partial \beta} = -\frac{1}{2} \beta n_{\alpha_1} \sum_{\alpha_2, \alpha_3} n_{\alpha_2} n_{\alpha_3} \int dr_{23} h_{\alpha_1 \alpha_2 \alpha_3}^{(3)} v_{\alpha_1 \alpha_2 \alpha_3} + n_{\alpha_1} \sum_{\alpha_2} n_{\alpha_2} \int dr_{12} h_{\alpha_1 \alpha_2}^{(2)} v_{\alpha_1 \alpha_2} - \frac{3}{2} n_{\alpha_1} \sum_{\alpha_2} n_{\alpha_2} \int dr_{12} h_{\alpha_1 \alpha_2}^{(2)} - \frac{3}{2} n_{\alpha_1}, \quad (4.5)
$$
The first term of the right-hand side can be reduced to an expression with pair correlation functions by employing the symmetry properties of \( h^{(3)} \) that are discussed in appendix A. Insertion of (A.4) gives

\[
\beta \frac{\delta n_{\alpha_1}}{\delta \beta} = -\frac{1}{2} \beta q n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \varepsilon_{\sigma_2} \int dr_{12} h^{(2)}_{\alpha_1 \alpha_2} r_{12}^2 + \frac{3}{2} n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \int dr_{12} h^{(2)}_{\alpha_1 \sigma_2} - \frac{3}{2} n_{\sigma_1}.
\]

(4.6)

Next we consider (4.1) and (4.2) for the case \( f = \Sigma_{\alpha_1 \alpha_2} \delta(r_1 - r_{\sigma_1 \alpha_1}) \delta(r_2 - r_{\sigma_2 \alpha_2}) \). From (4.1) we now learn

\[
\frac{\delta}{\delta \beta \mu_{\alpha_1}} (n_{\sigma_1} n_{\sigma_2} h^{(2)}_{\sigma_1 \sigma_2}) = n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} \int dr_1 h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} + n_{\sigma_2} n_{\sigma_3} h^{(2)}_{\sigma_2 \sigma_3} (\delta_{\sigma_1 \sigma_2} + \delta_{\sigma_1 \sigma_3}),
\]

(4.7)

where we used (4.3) and the definition of the Ursell functions, as before. Similarly, we can prove from (4.2) with (4.5)

\[
\beta \frac{\delta}{\delta \beta} (n_{\sigma_1} n_{\sigma_2} h^{(2)}_{\sigma_1 \sigma_2}) = -\frac{1}{2} \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} \int dr_3 dr_4 h^{(4)}_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} u_{\sigma_3 \sigma_4}
\]

\[-\frac{3}{2} n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} \int dr_3 h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} - \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} \int dr_3 h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} (v_{\sigma_1 \sigma_3} + v_{\sigma_2 \sigma_3})
\]

\[-3 n_{\sigma_1} n_{\sigma_2} h^{(2)}_{\sigma_1 \sigma_2} - \beta n_{\sigma_1} n_{\sigma_2} h^{(2)}_{\sigma_1 \sigma_2} u_{\sigma_1 \sigma_2}
\]

\[-\frac{1}{2} \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} \int dr_3 dr_4 (h^{(2)}_{\alpha_1 \sigma_3} h^{(2)}_{\sigma_2 \sigma_4} + h^{(2)}_{\sigma_1 \sigma_3} h^{(2)}_{\sigma_2 \sigma_4}) v_{\sigma_3 \sigma_4}
\]

\[-\beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} \int dr_3 (h^{(2)}_{\sigma_1 \sigma_3} v_{\sigma_2 \sigma_4} + h^{(2)}_{\sigma_2 \sigma_3} v_{\sigma_1 \sigma_4}) - \beta n_{\sigma_1} n_{\sigma_2} v_{\sigma_1 \sigma_2}.
\]

(4.8)

The left-hand side and the first six terms of the right-hand side vanish quickly if \( r_{12} \to \infty \). So the same should hold for the last five terms of the right-hand side. We shall prove that this is indeed the case.

The terms with a product of \( h^{(2)} \) functions are equal to each other, as follows by the symmetry of the sums and the integrals under the interchange of the labels 3 and 4. Inserting the identity

\[
v_{\sigma_3 \sigma_4} = (r_{13} - r_{14}) \frac{\partial v_{\sigma_3 \sigma_4}}{\partial r_{34}},
\]

(4.9)
and employing (2.9) we find that the sum of these terms can be written as

\[
\begin{align*}
\beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} & \int dr_3 h^{(2)}_{\sigma_3 \sigma_3} \frac{1}{4 \pi r_{13}} \left( e_{\sigma_1} + \sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} \right) \int_{r_{14}^2/r_{13}} dr_{14} h^{(2)}_{\sigma_1 \sigma_4} \\
+ \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} & \int dr_3 h^{(2)}_{\sigma_3 \sigma_3} \frac{r_{13} \cdot r_{23}}{4 \pi r_{23}^3} \left( e_{\sigma_2} + \sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} \right) \int_{r_{24}^2/r_{23}} dr_{24} h^{(2)}_{\sigma_2 \sigma_4}.
\end{align*}
\]

(4.10)

Finally, using the identity \( r_{13} = r_{12} + r_{23} \) and (2.9) to simplify the third term of (4.10) we can show that the last five terms of (4.8) are equal to

\[
\begin{align*}
\beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} & \int dr_3 h^{(2)}_{\sigma_3 \sigma_3} \cdot \frac{\partial v_{\sigma_3 \sigma_4}(r_{13})}{\partial r_3} \int_{r_{24}^2/r_{21}} dr_{24} h^{(2)}_{\sigma_4 \sigma_4} \\
+ \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} & \int dr_3 h^{(2)}_{\sigma_3 \sigma_3} v_{\sigma_3 \sigma_4}(r_{13}) \int_{r_{14}^2/r_{13}} dr_{14} h^{(2)}_{\sigma_4 \sigma_4} \\
+ \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} v_{\sigma_3 \sigma_3}(r_{12}) & \int_{r_{13}^2/r_{12}} dr_{13} h^{(2)}_{\sigma_3 \sigma_3}.
\end{align*}
\]

(4.11)

These terms are manifestly of short range for \( r_{12} \to \infty \).

The first term at the right-hand side of (4.8) can be expressed in terms of two- and three-particle Ursell functions by using the symmetry properties of \( h^{(1)} \) and the hierarchy equation (2.10), as demonstrated in appendix B. On substitution of (B.6) and (4.11) into (4.8) we are left with the identity

\[
\beta \frac{\partial}{\partial \beta} (\beta n_{\sigma_1} n_{\sigma_2} h^{(2)}_{\sigma_1 \sigma_2}) = -\frac{1}{2} \beta q_{\sigma_1} n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_3 h^{(3)}_{\sigma_3 \sigma_3} \int_{r_{23}^2/r_{23}} \frac{\partial h^{(2)}_{\sigma_1 \sigma_2}}{\partial r_{12}}
\]

\[
+ \frac{3}{2} n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} \int dr_3 h^{(3)}_{\sigma_3 \sigma_3} - n_{\sigma_1} n_{\sigma_2} r_{12} \cdot \frac{\partial h^{(2)}_{\sigma_1 \sigma_2}}{\partial r_{12}}
\]

\[
- \frac{1}{2} \beta q_{\sigma_1} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} h^{(2)}_{\sigma_1 \sigma_2} r_{12}^2 - 3 n_{\sigma_1} n_{\sigma_2} h^{(2)}_{\sigma_1 \sigma_2}.
\]

(4.12)

The derivatives of the partial densities and the pair correlation functions have now been written in terms of Ursell functions. In the following two sections some consequences of the results (4.3), (4.6), (4.7) and (4.12) will be derived.
5. Thermodynamic sum rules for pair correlation functions

In the previous section the integral of \( h^{(2)}_{\sigma_1, \sigma_2} \) has been expressed in terms of thermodynamic derivatives

\[
n_{\sigma_1} n_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} = \frac{Dn_{\sigma_1}}{D\beta \mu_{\sigma_2}} - n_{\sigma_1} \delta_{\sigma_1, \sigma_2}.
\]  

(5.1)

Multiplying (5.1) by \( e_{\sigma_2} \) and summing over \( \sigma_2 \) we recover the perfect screening condition (2.8). If we repeat this procedure without the weights \( e_{\sigma_2} \) and employ the auxiliary relation (3.21), a new equality, which is independent of (2.8), emerges:

\[
n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} = \frac{2}{3} \beta \frac{\partial n_{\sigma_1}}{\partial \beta} - 2q_v \frac{\partial n_{\sigma_1}}{\partial q_v} + n_{\sigma_1}.
\]  

(5.2)

Since this identity holds for all species \( \sigma_1 \), it may be summed over \( \sigma_1 \) with arbitrary weights. Once again a perfect-screening relation is recovered, if the weights \( e_{\sigma_1} \) are used. However, if the sum is taken with equal weights we get

\[
\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} = \frac{2}{3} \beta \frac{\partial n_{\sigma_1}}{\partial \beta} - 2q_v \frac{\partial n_{\sigma_1}}{\partial q_v} + n.
\]  

(5.3)

A sum rule of a different type is obtained on insertion of the result (5.2) into the right-hand side of (4.6)

\[
n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} r_{12}^2 = -\frac{6}{\beta} \frac{\partial n_{\sigma_1}}{\partial q_v}.
\]  

(5.4)

Summing over \( \sigma_1 \) with the weights \( e_{\sigma_1} \), we obtain the second-moment condition (2.16) of Stillinger and Lovett. It should be emphasized however that (5.4) is a stronger equality. In particular, it implies the following variant of the Stillinger–Lovett condition:

\[
\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} r_{12}^2 = -\frac{6}{\beta} \frac{\partial n}{\partial q_v}.
\]  

(5.5)

as follows by summing (5.4) over \( \sigma_1 \) with equal weights. Of course, for a one-component plasma the second-moment conditions (2.16), (5.4) and (5.5) coincide.

An alternative way to derive a second-moment sum rule for the pair correlation function starts from (4.7). Let us multiply (4.7) by \( v_{\sigma_2, \sigma_1} \), integrate
over $r_{12}$ and sum over $\sigma_1$ and $\sigma_2$. The result of this operation for the first term at the right-hand side can be reduced with the help of (A.4), while at the left-hand side the potential internal energy shows up. In this way we get

$$\frac{D\mu^{\text{pot}}}{D\beta_{\mu}} = -\frac{3}{\beta} n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1\sigma_2} + \frac{1}{2} q_{\sigma_1} n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1\sigma_2} r_{12}^2.$$  

(5.6)

Using (3.11) and (4.4) we may write the left-hand side as $-\partial n_{\sigma_1}/\partial \beta - \frac{1}{2} \beta^{-1} Dn/D(\beta \mu)$. The first term at the right-hand side can be rewritten with the use of (5.2). On simplifying the resulting thermodynamic expression by means of (3.21) we recover (5.4). To complete the picture we should mention that (5.4) can be obtained from (4.12) as well, namely on integration over $r_{12}$, summation over $\sigma_1$ with the weights $e_{\sigma_1}$ and use of (2.8), (2.12) and (5.2).

Finally, we wish to derive a fourth-moment sum rule for the pair correlation function. We again start from (4.12), multiply it by $v_{\sigma_1\sigma_2}$ and sum over $\sigma_1$ and $\sigma_2$. Then the left-hand side becomes equal to $2\beta \partial u^{\text{pot}}/\partial \beta$, while the first two terms of the right-hand side can be reduced to expressions involving $h^{(2)}$ only by employing (A.4) and (A.7), which follow from the symmetry of $h^{(3)}$. In this way we are led to the identity

$$\frac{3q_v^2}{40} \sum_{\sigma_1,\sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1\sigma_2} r_{12}^4 = \frac{9q_v}{4\beta} \sum_{\sigma_1,\sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} \int dr_{12} h^{(2)}_{\sigma_1\sigma_2} r_{12}^2$$

$$- \frac{9}{2\beta^2} \sum_{\sigma_1,\sigma_2} n_{\sigma_1} n_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1\sigma_2} - \frac{\partial u^{\text{pot}}}{\partial \beta} - \frac{4}{\beta} u^{\text{pot}}.$$  

(5.7)

At the right-hand side we now substitute the sum rules (5.3) and (5.5). Subsequently we can employ the thermodynamic identity (3.22). As a result we obtain the fourth-moment sum rule

$$\sum_{\sigma_1,\sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1\sigma_2} r_{12}^4 = -\frac{120}{\beta q_v} \frac{\partial p}{\partial q_v}.$$  

(5.8)

For the one-component plasma this sum rule reduces to the well-known compressibility sum rule$^{9, 10, 33}$.

The choice of $N_i$ to be the particle number that depends on the other ones is reflected in the asymmetry of the expression (5.1). This asymmetry disappears if we choose as independent variables the symmetric set $\beta, \{\mu_\alpha\}, \sigma = 1, \ldots, s$, as defined below (3.9). The transformation matrix reads

$$\frac{\partial \mu_\alpha}{\partial q_v} = e_\alpha S^{-1}.$$  

(5.9)
\begin{equation}
\frac{\partial \mu_{\sigma_1}}{\partial \beta \tilde{\mu}_{\sigma_2}} = \frac{1}{\beta} \delta_{\sigma_1 \sigma_2} - \frac{e_{\sigma_1}}{\beta S} \frac{\partial q_{\sigma_1}}{\partial \mu_{\sigma_2}}, \quad \sigma_2 = 2, \ldots, s,
\end{equation}

with the abbreviation \( S := \sum_\sigma e_{\sigma} \frac{\partial q_{\sigma}}{\partial \mu_{\sigma}} \). At the left-hand side of (5.9) and (5.10) the independent variables are \( \beta, \{ \beta \tilde{\mu}_\sigma \}, \sigma = 2, \ldots, s \) and \( q_{\sigma} \), while at the right-hand side they are \( \beta, \{ \mu_\sigma \}, \sigma = 1, \ldots, s \); in writing the partial derivatives the independent variables that are kept constant are suppressed, as before. After transformation to the symmetric set \( \beta, \{ \mu_\sigma \} \) the sum rules (5.1), (5.4) and (5.8) become

\begin{equation}
n_{\sigma_1} n_{\sigma_2} \int \text{d}r_{12} h_{\sigma_1 \sigma_2}^{1(2)} = k_B T \left[ \frac{\partial n_{\sigma_1}}{\partial \mu_{\sigma_1}} - S^{-1} \frac{\partial q_{\sigma_1}}{\partial \mu_{\sigma_1}} \frac{\partial q_{\sigma_1}}{\partial \mu_{\sigma_2}} \right] - n_{\sigma_1} \delta_{\sigma_1 \sigma_2},
\end{equation}

\begin{equation}
n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \text{d}r_{12} h_{\sigma_1 \sigma_2}^{2(2)} r_{12}^2 = -6k_B TS^{-1} \frac{\partial q_{\sigma_1}}{\partial \mu_{\sigma_1}},
\end{equation}

\begin{equation}
\sum_{\sigma_1} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \text{d}r_{12} h_{\sigma_1 \sigma_2}^{2(2)} r_{12}^4 = -120k_B TS^{-1}.
\end{equation}

Some years ago the thermodynamic properties of a multi-component electrolyte, without a background, have been discussed\(^{13}\) with the use of the statistical mechanics of non-uniform systems formulated in terms of a grand-canonical partition functional. In this way the sum rules (5.11) and (5.13) have been found. However, for the second moments only the Stillinger-Lovett rule (2.16) is obtained in ref. 13. It should be remarked here that the stronger second-moment sum rule (5.4), or (5.12), is essential in the derivation of the complete set of fluctuation formulae of a multi-component ionic mixture, as will be shown in the accompanying paper\(^{14}\).

6. Thermodynamic sum rules for three-particle Ursell functions

In this section a collection of sum rules for the three-particle Ursell functions \( h^{(3)} \) will be derived from the identities of the previous sections. We shall limit ourselves to the zeroth-, second- and fourth moment sum rules for \( h^{(3)} \). As remarked already in the introduction, these sum rules are useful for theories in which higher-order fluctuation formulae for the product of three or more microscopic physical quantities show up. An example is the mode-coupling theory for time correlation functions and transport properties. To evaluate the mode-coupling amplitudes higher-order fluctuation formulae are needed\(^{11,12}\).

Trivial examples of sum rules for \( h^{(3)} \) follow by starting from (5.1), (5.4) or
(5.8) and introducing the three-particle Ursell function with the help of the perfect-screening relation (2.12). Sum rules of a different type may be derived from the identities of section 4. These will be studied in the present section.

Let us integrate (4.7) over \( r_{23} \), and insert (5.1). In this way we get

\[
n_{\sigma_1}n_{\sigma_2}n_{\sigma_3} \int dr_{12} \int dr_3 \ h^{(3)}_{\sigma_1\sigma_2\sigma_3} = \left( \frac{D}{D\beta \tilde{\mu}_{\sigma_1}} - \delta_{\sigma_1\sigma_2} - \delta_{\sigma_1\sigma_3} \right) \left( \frac{D}{D\beta \tilde{\mu}_{\sigma_2}} - \delta_{\sigma_2\sigma_3} \right) n_{\sigma_3}.
\]

(6.1)

If we sum (6.1) over \( \sigma_3 \), with the weights \( e_{\sigma_3} \), a relation is found, which is also generated in a trivial way from (5.1) with (7.12). A different result emerges by summing (6.1) with equal weights and using (3.21)

\[
\sum_{\sigma_3} n_{\sigma_1}n_{\sigma_2}n_{\sigma_3} \int dr_{12} \int dr_3 \ h^{(3)}_{\sigma_1\sigma_2\sigma_3} = \left( \frac{D}{D\beta \tilde{\mu}_{\sigma_1}} - \delta_{\sigma_1\sigma_2} \right) \left( \frac{2}{3} \beta \frac{\partial}{\partial \beta} - 2q_v \frac{\partial}{\partial q_v} \right) n_{\sigma_3}.
\]

(6.2)

Instead of integrating (4.7) over \( r_{23} \), directly, we now perform the integration after multiplication by \( r_{23}^2 \). Upon summing over \( \sigma_3 \), with the weights \( e_{\sigma_3} \), the left-hand side can be simplified with the help of (5.4), so that we find

\[
\sum_{\sigma_3} n_{\sigma_1}n_{\sigma_2}n_{\sigma_3}e_{\sigma_3} \int dr_{12} \int dr_3 \ h^{(3)}_{\sigma_1\sigma_2\sigma_3}r_{23}^2 = -6 \left( \frac{D}{D\beta \tilde{\mu}_{\sigma_1}} - \delta_{\sigma_1\sigma_2} \right) \frac{\partial n_{\sigma_3}}{\partial q_v} - n_{\sigma_1}n_{\sigma_2}e_{\sigma_2} \int dr_{13} \ h^{(2)}_{\sigma_1\sigma_2\sigma_3} r_{13}^2.
\]

(6.3)

An alternative way to derive this relation consists in integrating (4.12) over \( r_{12} \) and using subsequently (5.1) and (6.2).

To eliminate the last term of (6.3) by means of (5.4) we may sum either over \( \sigma_3 \), with weights \( e_{\sigma_3} \), or over \( \sigma_1 \), with equal weights. In this way we obtain the two sum rules

\[
\sum_{\sigma_2\sigma_3} n_{\sigma_1}n_{\sigma_2}n_{\sigma_3}e_{\sigma_2}e_{\sigma_3} \int dr_{12} \int dr_3 \ h^{(3)}_{\sigma_1\sigma_2\sigma_3}r_{23}^2 - \frac{12}{\beta} e_{\sigma_2} \frac{\partial n_{\sigma_3}}{\partial q_v} = 0,
\]

(6.4)

\[
\sum_{\sigma_1\sigma_2} n_{\sigma_1}n_{\sigma_2}n_{\sigma_3}e_{\sigma_2} \int dr_{12} \int dr_3 \ h^{(3)}_{\sigma_1\sigma_2\sigma_3}r_{23}^2 = -4 \frac{\partial n_{\sigma_2}}{\partial q_v} + \frac{12q_v}{\beta} \frac{\partial^2 n_{\sigma_2}}{\partial q_v^2} + \frac{12}{\beta} \frac{\partial n_{\sigma_3}}{\partial q_v},
\]

(6.5)

where (3.21) has been used.
A different approach to derive second-moment sum rules for $h^{(3)}$ starts from the perfect-screening rule (2.13) for $l = 1$. As before there are two ways of summation, both leading to equalities in which (5.4) may be employed; we may either multiply (2.13) by $n_{\sigma_1} e_{\sigma_1}$ and sum over $\sigma_1$ or we multiply by $n_{\sigma_2}$ and sum over $\sigma_2$. This leads to the following two sum rules:

$$\sum_{\sigma_1, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int dr_{12} dr_{3} h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} r_{12} \cdot r_{13} = \frac{6}{\beta} e_{\sigma_2} \frac{\partial n_{\sigma_2}}{\partial q_v}, \quad (6.6)$$

$$\sum_{\sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int dr_{12} dr_{3} h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} r_{12} \cdot r_{13} = \frac{6}{\beta} \frac{\partial n_{\sigma_1}}{\partial q_v}. \quad (6.7)$$

However, the sum rule (6.6) is not new; upon interchanging the labels 1 and 3 we recover (6.4). On the other hand the sum rules (6.5) and (6.7) are independent.

Additional second-moment sum rules for $h^{(3)}$ are obtained by exploiting in a systematic way the trivial identity $r_{12} + r_{23} + r_{31} = \theta$ and the symmetry of $h^{(3)}_{\sigma_1 \sigma_2 \sigma_3}(r_1, r_2, r_3)$ under a permutation of its labels and variables. To classify these rules we define $\rho_i = r_{jk}$, with $i, j, k$ a cyclic permutation of 1, 2, 3. It turns out that two types of sum rules may be derived from (2.12), (6.4), (6.5) and (6.7)

$$\sum_{\sigma_1, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int dr_{12} dr_{3} h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} \rho_i \cdot \rho_j = a_{ij}^{(2)} \frac{1}{\beta} e_{\sigma_1} \frac{\partial n_{\sigma_1}}{\partial q_v} + b_{ij}^{(2)} S_{\sigma_1}^{(2)}, \quad (6.8)$$

$$\sum_{\sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int dr_{12} dr_{3} h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} \rho_i \cdot \rho_j$$

$$= c_{ij}^{(2)} \frac{1}{\beta} \frac{\partial n_{\sigma_1}}{\partial q_v} + d_{ij}^{(2)} \frac{\partial^2 n_{\sigma_1}}{\partial q_v^2} + e_{ij}^{(2)} \frac{q_v}{\beta} \frac{\partial^2 n_{\sigma_1}}{\partial q_v^2} + f_{ij}^{(2)} S_{\sigma_1}^{(2)}, \quad (6.9)$$

where we introduced the abbreviations

$$S_{\sigma_1}^{(2)} = \sum_{\sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_2}^2 \int dr_{12} h^{(2)}_{\sigma_1 \sigma_2} r_{12}^2, \quad (6.10)$$

$$S_{\sigma_1}^{(2)'} = \sum_{\sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} \int dr_{12} h^{(2)}_{\sigma_1 \sigma_2} r_{12}^2. \quad (6.11)$$

It should be remarked that in general neither of these combinations may be reduced to purely thermodynamic expressions, since the weights in the sums differ from those of (5.4). The coefficients in (6.8) and (6.9) have been
collected in table I. Inspection shows that three of the six sum rules of the type (6.8) do not contain \( S^{(2)}_{\sigma_i} \) and are thus purely thermodynamic. Likewise three of the sum rules (6.9) are purely thermodynamic; the remaining three contain \( S^{(2)}_{\sigma_i} \).

Having discussed the zeroth- and second-moment sum rules for \( h^{(3)} \) we now focus on the derivation of fourth-moment sum rules. These can be generated by multiplying (4.7) by \( r_{23}^4 \), integrating over \( r_{23} \) and summing over \( \sigma_1, \sigma_2, \) and \( \sigma_3 \) with the weights \( e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \). The expressions with the pair correlation functions \( h^{(2)} \) can then be reduced to thermodynamic derivatives by means of (5.8). As a result we get

\[
\sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} \int dr_{12} dr_3 h^{(3)}_{\sigma_1, \sigma_2, \sigma_3} r_{12}^4 = \frac{120}{\beta^2} \frac{\partial n}{\partial q_v} + \frac{240}{\beta q_v} \frac{\partial p}{\partial q_v}, \quad (6.12)
\]

where (3.11) and (3.17) have been used.

A second fourth-moment rule for \( h^{(3)} \) is obtained from (4.12) on multiplication by \( r_{12}^4 \), integration over \( r_{12} \) and summation over \( \sigma_1, \sigma_2, \) and \( \sigma_3 \), with weights \( e_{\sigma_2} \). Using (6.5) to eliminate the expression resulting from the second term at the right-hand side of (4.12) and employing moreover (5.5) and (5.8) to transform the terms with \( h^{(2)} \) we get

\[
\sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} \int dr_{12} dr_3 h^{(3)}_{\sigma_1, \sigma_2, \sigma_3} r_{12}^2 r_{23}^2 = \frac{36}{\beta^2} \frac{\partial^2 n}{\partial q_v^2} + \frac{120}{\beta q_v} \frac{\partial p}{\partial q_v}, \quad (6.13)
\]

A third result follows by multiplying (2.13) for \( l = 1 \) with \( r_{12}^4 \), integrating over \( r_{12} \) and summing over \( \sigma_1, \sigma_2, \) and \( \sigma_3 \) with the weights \( n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} \). Again inserting (5.8) we get

\[
\sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} \int dr_{12} dr_3 h^{(3)}_{\sigma_1, \sigma_2, \sigma_3} r_{12}^2 r_{13}^2 r_{23}^2 = \frac{120}{\beta q_v} \frac{\partial p}{\partial q_v}. \quad (6.14)
\]

### Table 1

Coefficients of the second-moment sum rules (6.8) and (6.9) for \( h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} \)

<table>
<thead>
<tr>
<th>ij</th>
<th>( a^{(2)}_{ij} )</th>
<th>( b^{(2)}_{ij} )</th>
<th>( c^{(2)}_{ij} )</th>
<th>( d^{(2)}_{ij} )</th>
<th>( e^{(2)}_{ij} )</th>
<th>( f^{(2)}_{ij} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>12</td>
<td>0</td>
<td>-6</td>
<td>-4</td>
<td>12</td>
<td>-1</td>
</tr>
<tr>
<td>22</td>
<td>6</td>
<td>-1</td>
<td>12</td>
<td>-4</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>33</td>
<td>6</td>
<td>-1</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>12</td>
<td>-6</td>
<td>0</td>
<td>-6</td>
<td>4</td>
<td>-17</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>-6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0</td>
<td>1</td>
<td>-6</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The fourth-moment sum rules (6.12)–(6.14) may be transformed to rules of a different appearance by using the symmetry of $h^{(3)}$ and the identity $r_{12} + r_{23} + r_{31} = 0$, as before. In this way we get sum rules of the general form

$$\sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int dr_{12} dr_{3} h^{(3)}_{\sigma_1 \sigma_2 \sigma_3 \sigma_4} \rho_i \cdot \rho_i \rho_j \cdot \rho_j = a_{ijkl}^{(4)} \frac{\partial^2 n}{\partial q_{ijkl}^2} + b_{ijkl}^{(4)} \frac{\partial p}{\partial q_{ijkl}} + c_{ijkl}^{(4)} S^{(4)},$$  

(6.15)

with the same $\rho_i$ as in (6.8) and (6.9). The quantity $S^{(4)}$, defined as

$$S^{(4)} = \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 \int dr_{12} h^{(2)}_{\sigma_1 \sigma_2} r_{12}^4,$$

(6.16)

cannot be expressed in thermodynamic partial derivatives. It is easily seen to show up in the sum rule that results by starting from (2.12). By using the trivial symmetries of (6.15) under the interchanges $2 \leftrightarrow 3$, $i \leftrightarrow j$, $k \leftrightarrow l$ and $(ik) \leftrightarrow (j l)$ it follows that there are 13 different sum rules of the form (6.15). The coefficients of these rules are given in table II. Nine sum rules are purely thermodynamic, whereas four contain the combination $S^{(4)}$.

The sum rules (6.8), (6.9) and (6.15) simplify considerably for the degenerate case of the one-component plasma. Then (6.8) and (6.9) are equivalent. Moreover the quantities $S^{(2)}$ and $S^{(4)}$ defined in (6.10) (or (6.11)) and (6.16) can all be reduced to thermodynamic derivatives by employing the sum rules of section 5 for the one-component plasma.

| Table II |
|-----------------|-----------------|-----------------|-----------------|
| $ijkl$ | $a_{ijkl}^{(4)}$ | $b_{ijkl}^{(4)}$ | $c_{ijkl}^{(4)}$ |
| 1111 | 120 | 240 | 0 |
| 2222 | 0 | 120 | -1 |
| 1122 | 36 | 120 | 0 |
| 2233 | 36 | 0 | -1 |
| 1112 | -60 | -120 | 0 |
| 1123 | 24 | 0 | 0 |
| 2212 | 0 | -120 | 0 |
| 2213 | -36 | 0 | 0 |
| 2223 | 0 | 0 | 1 |
| 1212 | 12 | 120 | 0 |
| 2323 | 12 | 0 | -1 |
| 1213 | 48 | 0 | 0 |
| 1223 | -12 | 0 | 0 |
Appendix A

Symmetry properties for $h_{a_1a_2a_3}^{(3)}$

The Ursell functions are invariant under the interchange of particles

$$h_{a_1\ldots a_i\ldots a_j \ldots a_k}^{(k)}(r_1, \ldots, r_i, \ldots, r_j, \ldots, r_k) = h_{a_1\ldots a_j\ldots a_i \ldots a_k}^{(k)}(r_1, \ldots, r_j, \ldots, r_i, \ldots, r_k)$$ \hspace{1cm} (A.1)

for $i \neq j$. From this property we learn that

$$\sum_{a_1,a_2} n_{a_1} n_{a_2} e_{a_1} e_{a_2} \int dr_{12} \int dr_3 \ h_{a_1a_2a_3}^{(3)} \psi(r_{12}) (r_{13}^2 - r_{12} \cdot r_{13})^p (r_{12}^2 - 2r_{12} \cdot r_{13}) = 0,$$ \hspace{1cm} (A.2)

for an arbitrary non-negative integer $p$ and for each $\psi$ that leads to a convergent integral. If we choose $p = 0$ and $\psi(r) = (4\pi r^3)^{-1}$, (A.2) yields

$$\sum_{a_1,a_2} n_{a_1} n_{a_2} \int dr_{12} \int dr_3 \ h_{a_1a_2a_3}^{(3)} \psi(r_{12}) \frac{\partial \psi_{a_1a_2}}{\partial r_{12}} = 0.$$ \hspace{1cm} (A.3)

We can apply (2.14) to the right-hand side; in this way we get

$$\sum_{a_1,a_2} n_{a_1} n_{a_2} \int dr_{12} \int dr_3 \ h_{a_1a_2a_3}^{(3)} \psi_{a_1a_2} = q_0 \sum_{a_2} n_{a_2} e_{a_2} \int dr_3 \ h_{a_2a_3}^{(2)} r_{13}^2$$

$$-2 \sum_{a_1} n_{a_1} \int dr_{13} \ h_{a_1a_3}^{(2)} \psi_{a_1a_3} - \frac{6}{p} \sum_{a_1} n_{a_1} \int dr_{13} \ h_{a_1a_3}^{(2)}.$$ \hspace{1cm} (A.4)

The choice $p = 1$ in (A.2) gives upon using (2.13) for $l = 1, 2$

$$\sum_{a_1,a_2,a_3} n_{a_1} n_{a_2} n_{a_3} e_{a_1} e_{a_2} e_{a_3} \int dr_{12} \int dr_3 \ h_{a_1a_2a_3}^{(3)} \psi(r_{12}) (\frac{2}{3} r_{12}^2 r_{13}^2 - 2r_{12} \cdot r_{13} r_{13}^2)$$

$$= \frac{1}{3} \sum_{a_1,a_2} n_{a_1} n_{a_2} e_{a_1} e_{a_2} \int dr_{12} \ h_{a_1a_2}^{(2)} \psi(r_{12}) r_{12}^2.$$ \hspace{1cm} (A.5)

Putting $\psi(r) = (4\pi r^3)^{-1}$ we can simplify the second term at the left-hand side by performing the integral over $r_{12}$ by means of the hierarchy (2.5), with (2.9) inserted. Then this term becomes equal to
\[
\frac{2}{\beta} \sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} e_{\sigma_3} \int dr_{12} \left[ S h^{(2)}_{\sigma_1, \sigma_2} r_{12}^2 + \frac{\beta}{4 \pi} e_{\sigma_1} e_{\sigma_2} h^{(2)}_{\sigma_1, \sigma_2} r_{12} \right] \\
- \frac{\beta}{4 \pi} e_{\sigma_1} r_{12} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int_{r_{23}^2 - r_{12}^2} dr_{23} h^{(2)}_{\sigma_{23}}.
\] (A.6)

The double integral in the last term of (A.6) can be reduced easily to a single integral. Inserting (A.6) in (A.5) we get

\[
\sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_3} \int dr_{12} dr_{3} h^{(3)}_{\sigma_1, \sigma_2, \sigma_3} r_{13}^2 \psi_{\sigma_1, \sigma_2}
= \frac{3}{10} q_u \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} r_{12}^4 - \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} r_{12}^4
- \frac{1}{4 \pi} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} r_{12}^2.
\] (A.7)

The relations (A.4) and (A.7) have been employed in sections 4 and 5.

Parenthetically, we remark that from (A.5) other relations between integrals of \( h^{(2)} \) and \( h^{(3)} \) can be obtained. In fact, choosing \( \psi(r) = 1 \), we may apply (2.13) for \( l = 1 \) to the second integral with the result

\[
\sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int dr_{12} dr_{3} h^{(3)}_{\sigma_1, \sigma_2, \sigma_3} r_{12}^2 r_{13}^2
\]

\[
- \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} r_{12}^4.
\] (A.8)

This relation is not contained in the set (6.15), since the weights of the summation over \( \sigma_1 \) differ. In a similar vein, by choosing \( \psi(r) = r^{-2} \) in (A.5) and employing (2.12) we arrive at the rather exotic equality

\[
\sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int dr_{12} dr_{3} h^{(3)}_{\sigma_1, \sigma_2, \sigma_3} \frac{r_{13}^2}{r_{12}^2} r_{12} \cdot r_{13}
\]

\[
= \frac{11}{6} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_{12} h^{(2)}_{\sigma_1, \sigma_2} r_{12}^2.
\] (A.9)

Appendix B

An auxiliary relation for \( h^{(4)}_{\sigma_1, \sigma_2, \sigma_3, \sigma_4} \)

In section 4 we needed an expression for the integral of \( h^{(4)}_{\sigma_1, \sigma_2, \sigma_3, \sigma_4} \) multiplied by the potential \( v_{\sigma_4} \). To derive this expression we start by writing on the basis
of (A.1)

\[
\frac{1}{2} \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} \int dr_3 \, dr_4 \, h^{(4)}_{\sigma_3 \sigma_4} v_{\sigma_3} v_{\sigma_4} = \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} \int dr_3 \, dr_4 \, h^{(4)}_{\sigma_3 \sigma_4} \frac{\partial v_{\sigma_3} v_{\sigma_4}}{\partial r_3} . \tag{B.1}
\]

With the help of (2.6) and (2.10) we then get

\[
\frac{1}{2} \beta \sum_{\alpha_3, \alpha_4} n_{\alpha_3} n_{\alpha_4} \int dr_3 \, dr_4 \, h^{(4)}_{\alpha_3 \alpha_4} \frac{\partial}{\partial r_3} h^{(3)}_{\alpha_3 \alpha_4} = -\sum_{\alpha_3} n_{\alpha_3} \int dr_3 \, \frac{\partial}{\partial r_3} r_3 \, h^{(3)}_{\alpha_3 \alpha_3} \left( v_{\alpha_3} + v_{\alpha_3} \right) + \beta \sum_{\alpha_3} n_{\alpha_3} \int dr_3 \, h^{(2)}_{\alpha_3 \alpha_3} \sum_{\alpha_4} n_{\alpha_4} r_{13} \frac{\partial v_{\alpha_3} v_{\alpha_4}(r_{23})}{\partial r_3} \int dr_{23} h^{(2)}_{\alpha_3 \alpha_4} + \beta \sum_{\alpha_3} n_{\alpha_3} \int dr_3 \, h^{(2)}_{\alpha_3 \alpha_3} \sum_{\alpha_4} n_{\alpha_4} r_{13} \frac{\partial v_{\alpha_3} v_{\alpha_4}(r_{14})}{\partial r_3} \int dr_{14} h^{(2)}_{\alpha_3 \alpha_4} + \beta \sum_{\alpha_3} n_{\alpha_3} \int dr_3 \, r_{13} \, \frac{\partial}{\partial r_3} \sum_{\alpha_4} n_{\alpha_4} \int dr_4 \, h^{(3)}_{\alpha_3 \alpha_4} v_{\alpha_4} + \beta \sum_{\alpha_3} n_{\alpha_3} \int dr_3 \, r_{13} \, \frac{\partial}{\partial r_3} \sum_{\alpha_4} n_{\alpha_4} \int dr_4 \, h^{(3)}_{\alpha_3 \alpha_4} v_{\alpha_4} + h^{(2)}_{\alpha_3 \alpha_3} \left( v_{\alpha_3} + v_{\alpha_3} \right) \right) . \tag{B.2}
\]

Several terms at the right-hand side can be reduced further. In the first term we carry out a partial integration. The third term becomes upon using the identity \( r_{13} = r_{12} + r_{23} \) and the relations (2.5) and (2.9)

\[
-\beta \sum_{\alpha_3} n_{\alpha_3} \int dr_3 \, h^{(1)}_{\alpha_3 \alpha_3} v_{\alpha_3} + r_{12} \frac{\partial h^{(1)}_{\alpha_3 \alpha_3}}{\partial r_{12}} + 1 \beta \sum_{\alpha_3} n_{\alpha_3} v_{\alpha_3} r_{12} \int dr_{12} h^{(1)}_{\alpha_3 \alpha_3} v_{\alpha_3} . \tag{B.3}
\]

The last three terms at the right-hand side of (B.2) contain divergencies. However, from (2.10) it has been shown that the integrand decays quickly for \( r_{13} \to \infty \). So we may perform a partial integration with respect to \( r_3 \). Using the
Legendre expansion (2.11) we get from the last three terms of (B.2)

\[
\begin{align*}
&\frac{-3\beta}{4\pi} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_{23} \left[ \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int dr_{24} h_{\sigma_1,\sigma_2,\sigma_3}^{(3)} \sum_{l=0}^{\infty} r_{24}^l \frac{r_{23}^l}{r_{23}^{l+1}} P_l(\hat{r}_{23} \cdot \hat{r}_{24}) \right. \\
&\left. + \sum_{\sigma_4} n_{\sigma_4} e_{\sigma_4} \int dr_{24} h_{\sigma_1,\sigma_2,\sigma_4}^{(3)} \sum_{l=0}^{\infty} r_{24}^l \frac{r_{23}^l}{r_{24}^{l+1}} P_l(\hat{r}_{23} \cdot \hat{r}_{24}) + h_{\sigma_1,\sigma_2}^{(2)} \left( \frac{e_{\sigma_1}}{r_{13}} + \frac{e_{\sigma_2}}{r_{23}} \right) \right].
\end{align*}
\]

(B.4)

The integral over \( r_{23} \) may be confined to a large sphere, chosen in such a way that the integrand is negligible outside the sphere. This choice of the integration domain enables us to integrate all terms in (B.4) separately. Owing to the isotropy of the \( r_{23} \), integration all terms containing a Legendre polynomial with \( l \neq 0 \) vanish. The remaining terms can be integrated easily with the use of (2.12). In this way the following result for (B.4) is obtained:

\[
\begin{align*}
&\frac{1}{2} \beta q_{\nu} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_{23} h_{\sigma_1,\sigma_2,\sigma_3}^{(3)} r_{23}^2 + \frac{1}{2} \beta q_{\nu} e_{\sigma_1} h_{\sigma_1,\sigma_2}^{(2)} r_{12}^2.
\end{align*}
\]

(B.5)

Collecting the results we have found now

\[
\begin{align*}
&\frac{1}{2} \beta \sum_{\sigma_3} n_{\sigma_3} n_{\sigma_3} \int dr_3 dr_4 h_{\sigma_1,\sigma_2,\sigma_3}^{(4)} v_{\sigma_3,\sigma_4} \\
&= -\beta \sum_{\sigma_3} n_{\sigma_3} \int dr_3 h_{\sigma_1,\sigma_2,\sigma_3}^{(3)} (v_{\sigma_1,\sigma_3} + v_{\sigma_2,\sigma_3}) \\
&+ \frac{1}{2} \beta q_{\nu} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_3 h_{\sigma_1,\sigma_2,\sigma_3}^{(3)} r_{23}^2 - 3 \sum_{\sigma_3} n_{\sigma_3} \int dr_3 h_{\sigma_1,\sigma_2,\sigma_3}^{(3)} \\
&+ \frac{1}{2} \beta q_{\nu} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int dr_3 h_{\sigma_1,\sigma_2,\sigma_3}^{(3)} r_{23}^2 - \frac{1}{2} \beta q_{\nu} e_{\sigma_1} h_{\sigma_1,\sigma_2}^{(2)} r_{12}^2.
\end{align*}
\]

(B.6)

This is the relation we set out to prove.
References