Sum rules for correlation functions of ionic mixtures in arbitrary dimension $d \geq 2$

L G Suttorp

Instituut voor Theoretische Fysica, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

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Abstract
The correlations in classical multi-component ionic mixtures with a spatial dimension $d \geq 2$ are studied by using a restricted grand-canonical ensemble and the associated hierarchy equations for the correlation functions. Sum rules for the first few moments of the two-particle correlation function are derived and their dependence on $d$ is established. By varying $d$ continuously near $d = 2$ it is shown how the sum rules for the two-dimensional mixture are related to those for mixtures at higher $d$.

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1. Introduction

The statistical equilibrium properties of classical many-particle systems with long-range forces have been the subject of an extensive literature (for reviews see [1]–[4]). The simplest models with long-range interactions are Coulomb systems consisting of point particles with charges of the same sign that move in an inert uniform background of opposite sign. For these systems no collapse of particles can occur and stability is guaranteed at all densities and temperatures. Both the one-component plasma, also known as jellium, and ionic mixtures of particles with different charges and masses fall in this class. An important tool in the analysis of the equilibrium behaviour of these systems is furnished by the set of correlation functions and the associated Ursell functions. The first few moments of the latter satisfy sum rules, which are essential for the description of the large-scale fluctuations of local densities.

In studying one-component plasmas and ionic mixtures it has been found that the dimension $d$ of space in which these systems are embedded plays a remarkable role. It turns out that several properties of systems with $d = 2$ and $d = 3$ (which have mainly been considered) are quite similar, whereas occasionally the derivation of these properties proceeds along rather different lines. An example is a recent proof of a second-moment sum rule for correlations near a guest charge in a two-dimensional one-component plasma [5]. Here the use of symmetry properties of the Ursell functions leads to a short proof [6], whereas in deriving...
the analogous sum rule for the three-dimensional case a detailed analysis of the statistical ensemble properties has to be carried out [7]. Sometimes the analogy between the two- and three-dimensional cases gets lost altogether, as seems to be the case for a higher-order sum rule of the two-dimensional one-component plasma [8]. For this sixth-moment rule no counterpart at \( d = 3 \) has been found as yet.

The purpose of the present paper is to postpone any choice of dimension and to derive sum rules that are valid for ionic mixtures in all dimensions \( d \geq 2 \). We shall refrain from a discussion of the case \( d = 1 \), as periodic oscillations in the density lead to complications in that case [2]. We shall concentrate on sum rules for two-particle Ursell functions. Our unified treatment enables one to clearly see how the simplifications in the derivation of these sum rules for \( d = 2 \) come about, and why the proof for \( d > 2 \) (and hence for \( d = 3 \) in particular) is necessarily more complicated. In the course of our analysis we shall obtain several new results for a general Coulomb-type system with \( d > 3 \), which has hardly been discussed in the past [9]–[13]. In deriving our results we shall treat \( d \) as a continuous variable, as is standard practice in the theory of phase transitions [14] and in dimensional regularization of quantum field theory [15]. This method has been used in the context of systems with long-range forces as well [16].

When describing multi-component ionic mixtures attention has to be paid to a suitable choice of the equilibrium ensemble. As in a previous treatment [7], we shall use a restricted grand-canonical ensemble, in which the fluctuating particle numbers are constrained by stipulating that the ensuing total charge matches the fixed charge of the inert background.

2. Ionic mixtures in dimension \( d \geq 2 \)

We consider a \( d \)-dimensional multi-component ionic mixture of \( s \) components, with label \( \sigma = 1, \ldots, s \), in a large volume \( V \). The \( N_\sigma \) particles of species \( \sigma \) carry mass \( m_\sigma \) and positive charge \( e_\sigma \). The system is neutral owing to a uniform background with charge density \( -q_v \equiv -\sum_\sigma e_\sigma N_\sigma / V \).

For arbitrary \( d \) the potential \( \phi \) depending on the distance \( r = |r| \) is proportional to \( 1/r^{d-2} \). It is the solution of the \( d \)-dimensional inhomogeneous Laplace equation \( \Delta \phi(r) = -\delta(r) \), with \( \Delta \) the \( d \)-dimensional Laplace operator and \( \delta(r) \) the Dirac delta function in \( d \) dimensions. Here, it should be noted that in a space with dimension \( d \) the Laplace operator acting on an isotropic function is given by \( r^{-d+1}(\partial/\partial r)r^{d-1}(\partial/\partial r) \). The explicit form of \( \phi(r) \) is

\[
\phi(r) = \frac{\Gamma(d/2 - 1)}{4\pi^{d/2}} \frac{1}{r^{d-2}} + c_d, \tag{2.1}
\]

with \( \Gamma(z) \) the gamma function and with \( c_d \) an arbitrary additive constant. We used the fact that the surface of a unit sphere in \( d \) dimensions equals \( 2\pi^{d/2}/\Gamma(d/2) \) for \( d = 3 \). For \( d = 2 \) the potential has the form \( \phi(r) = 1/(4\pi r) \) (at least for \( c_d = 0 \)), which corresponds to the choice of so-called rationalized Lorentz–Heaviside units in electrodynamics. For \( d = 2 \) the potential \( \phi \) that solves the two-dimensional Laplace equation is logarithmic,

\[
\phi(r) = -\frac{1}{2\pi} \log(r) + c, \tag{2.2}
\]

with a constant \( c \) that can be used to render the argument of the logarithm dimensionless by writing \( c = \log(L)/(2\pi) \) with an arbitrary length \( L \). This potential can be obtained from (2.1) by taking the limit \( d \to 2 \), if \( c_d \) is chosen as

\[
c_d = -\frac{\Gamma(d/2 - 1)}{4\pi^{d/2}} + c. \tag{2.3}
\]
Indeed, in the limit $d \to 2$ one finds
\[
\lim_{d \to 2} \phi(r) = \lim_{d \to 2} \frac{\Gamma(d/2 - 1)}{4\pi^{d/2}} \left( \frac{1}{r^{d-2}} - 1 \right) + c = -\frac{1}{2\pi} \log(r) + c. \tag{2.4}
\]

It should be noted that the shift in energy $c_d$ as given by (2.3) becomes infinite, when $d$ tends to 2. This does not come as a surprise since the potential (2.2) grows without bound for large $r$, whereas the potential (2.1) for $d > 2$ tends to $c_d$ at large $r$. If desired, one may choose $c_d$ to be given by (2.3) for all $d$. However, we shall see that for $d > 2$ many formulae simplify by choosing $c_d = 0$, so that the choice (2.3) is somewhat artificial in that case. For that reason we shall postpone a specific choice of $c_d$ and leave it arbitrary as yet.

The Hamiltonian of the ionic mixture is the sum of the kinetic energy $T$ and the potential energy $U$,
\[
H = T + U = \sum_{\sigma_1} \frac{p_{\sigma_1}^2}{2m_\sigma} + \frac{1}{2} \sum_{\sigma_1, \sigma_2} e_{\sigma_1} e_{\sigma_2} \phi(|r_{\sigma_1} - r_{\sigma_2}|) \\
- q_1 \sum_{\sigma} e_\sigma \int V \phi(|r_{\sigma} - r|) + \frac{1}{2} q_1^2 \int V \phi(|r - r'|). \tag{2.5}
\]

The particle $\sigma$ of species $\sigma$ has position $r_{\sigma}$ and momentum $p_{\sigma}$. The prime at the summation sign indicates the condition $\sigma_1 \sigma_2 \neq \sigma_2 \sigma_1$, so that self-interactions among the point particles are excluded. As said above, the constant $c_d$ in the potential is left arbitrary for the time being. The integrals representing the interactions involving the background are taken over the $d$-dimensional volume $V$.

As was shown by Lieb and Narnhofer [17] for the one-component plasma in dimension $d = 3$, the potential energy $U$ in $H$ is bounded from below, so that the stability of the system is warranted in that case. Generalizing their argument so as to be applicable to a mixture in arbitrary dimension one may prove stability for any $d \geq 2$, as is shown in appendix A.

3. Electrostatic sum rules

The $k$-particle equilibrium correlation functions $g^{(k)}_{\sigma_1, \sigma_2, \ldots, \sigma_k}$ satisfy the BGY hierarchy equations [2]
\[
\frac{\partial}{\partial r_i} g^{(k)}_{\sigma_1, \sigma_2, \ldots, \sigma_k}(r_1, \ldots, r_k) = -\beta e_{\sigma_1} g^{(k)}_{\sigma_1, \sigma_2, \ldots, \sigma_k}(r_1, \ldots, r_k) \left( k T \right)^{-1} \sum_{j=2}^{k} e_{\sigma_j} \frac{\partial}{\partial r_j} \phi(|r_1 - r_j|) \\times \sum_{\sigma_{k+1}} n_{\sigma_{k+1}} e_{\sigma_{k+1}} \int V \phi(|r_1 - r_{k+1}|), \tag{3.1}
\]
For \( k = 2 \), the hierarchy equation reads in terms of the Ursell functions
\[
\beta e_{\sigma_1} \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int d\mathbf{r}_1 h^{(3)}_{\sigma_1\sigma_1\sigma_1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{\partial \phi(r_{13})}{\partial r_{1}} = -\frac{\partial h^{(2)}_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1}
\]
\[
-\beta e_{\sigma_2} \frac{\partial}{\partial r_1} \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int d\mathbf{r}_1 h^{(2)}_{\sigma_1\sigma_2}(\mathbf{r}_2, \mathbf{r}_3) \phi(r_{13})
\]
\[
-\beta e_{\sigma_2} \frac{\partial}{\partial r_1} \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int d\mathbf{r}_1 h^{(2)}_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial \phi(r_{12})}{\partial r_1}
\]
(3.2)

with \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \).

The second term at the right-hand side can be rewritten by expanding the potential in terms of Gegenbauer polynomials. For \( r > r' \) one has [20]
\[
\phi(|\mathbf{r} - \mathbf{r}'|) = \phi(r) + \frac{\Gamma(d/2 - 1)}{4\pi^{d/2}r^{d-2}} \sum_{\ell=1}^{\infty} \frac{r^{(d-2)/2}}{r'} e_{\sigma} (\cos \theta) \left( \frac{r'}{r} \right)^{\ell}
\]
(3.3)

with \( d > 2 \). Here \( \theta \) is the angle between \( \mathbf{r} \) and \( \mathbf{r}' \). For \( r < r' \) a similar expansion holds, with \( \mathbf{r} \) and \( \mathbf{r}' \) interchanged. By expanding the potential in this way and using the orthogonality relation of the Gegenbauer polynomials one may establish the identity
\[
\frac{\partial}{\partial r_1} \int d\mathbf{r}_1 h^{(2)}_{\sigma_2\sigma_2}(\mathbf{r}_2, \mathbf{r}_3) \phi(r_{13}) = \frac{\partial \phi(r_{12})}{\partial r_1} \int_{r_2 < r_1} d\mathbf{r}_1 h^{(2)}_{\sigma_1\sigma_2}(\mathbf{r}_2, \mathbf{r}_3).
\]
(3.4)

Employing this equality in (3.2) and making use of the exponential clustering properties of the Ursell functions one proves the perfect-screening condition [9–11, 21, 22] for the two-particle mixture [7, 11, 23]. To derive the analogous identity for \( k = 3 \) the Pochhammer symbol.

Similarly, by using the Gegenbauer expansion and the exponential clustering property one derives from the hierarchy equations for \( k = 3 \) the perfect-screening rules,
\[
\sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int d\mathbf{r}_1 h^{(3)}_{\sigma_1\sigma_1\sigma_1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = -\left(e_{\sigma_1} + e_{\sigma_2}\right) h^{(2)}_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)
\]
(3.6)

\[
\sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int d\mathbf{r}_1 h^{(3)}_{\sigma_1\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \int_{r_2 < r_3} C_{\ell}(\cos \theta)
\]
(3.7)

with \( \theta \) the angle between \( \mathbf{r}_{12} \) and \( \mathbf{r}_{13} \), and with \( (x)_n = x(x+1) \cdots (x+n-1) \) the Pochhammer symbol.

For \( d = 3 \) the Gegenbauer polynomials in (3.7) reduce to Legendre polynomials, so that we recover one of the well-known perfect-screening rules for a three-dimensional ionic mixture [7, 11, 23]. To derive the analogous identity for \( d = 2 \) we use for \( \ell \geq 1 \) [20],
\[
\lim_{\lambda \to 0} \frac{1}{\lambda} C_{\ell}(x) = \frac{2}{\ell} T_{\ell}(x)
\]
(3.8)

with \( T_{\ell}(x) \) the Chebyshev polynomials of the first kind. With the help of this relation one finds from (3.3) in the limit \( d \to 2 \) the standard expansion of the logarithmic potential [20].

The perfect-screening rule (3.7) becomes upon taking the limit \( d \to 2 \),
\[
\sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int d\mathbf{r}_1 h^{(3)}_{\sigma_1\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) T_{\ell}(\cos \theta) = -e_{\sigma_2} T_{\ell}(\cos \theta) \quad (\ell = 1, 2, \ldots),
\]
(3.9)

which for the one-component case corroborates a previous result [24].
From the above results a consistency relation can be obtained. On the one hand, we can prove from (3.2) with (3.4) and (3.5), upon multiplying by \( r_{12} \) and integrating over \( r_2 \),

\[
\beta e_{\sigma_1} \sum_{\sigma_3} n_{\sigma_1} e_{\sigma_3} \int dr_2 \int dr_3 h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} (r_1, r_2, r_3) r_{12} \cdot \frac{\partial \phi (r_{12})}{\partial r_1} = -\frac{1}{2} \beta e_{\sigma_1} \sum_{\sigma_3} n_{\sigma_1} e_{\sigma_3} \int dr_3 h^{(2)}_{\sigma_2 \sigma_3} (r_2, r_3) r_{23}^2 \\
+ (d-2) \beta e_{\sigma_1} e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1 \sigma_2} (r_1, r_2) \phi (r_{12}) + [d-(d-2) c_d \beta e_{\sigma_1} e_{\sigma_2}] \int dr_2 h^{(2)}_{\sigma_1 \sigma_2} (r_1, r_2).
\]

(3.10)

On the other hand, from (3.7) for \( \ell = 1 \) one gets after multiplication by \( r_{12}^{-d} \) and integration over \( r_2 \),

\[
\sum_{\sigma_3} n_{\sigma_1} e_{\sigma_3} \int dr_2 \int dr_3 h^{(3)}_{\sigma_1 \sigma_2 \sigma_3} (r_1, r_2, r_3) r_{13} \cdot \frac{\partial \phi (r_{12})}{\partial r_1} = (d-2) e_{\sigma_1} \int dr_2 h^{(2)}_{\sigma_1 \sigma_2} (r_1, r_2) \phi (r_{12}) - (d-2) c_d e_{\sigma_1} \int dr_2 h^{(2)}_{\sigma_1 \sigma_2} (r_1, r_2).
\]

(3.11)

Comparison of (3.10) and (3.11) yields an identity, which by means of (3.5) gets the simple form

\[
\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1 \sigma_2} (r_1, r_2) r_{12}^2 \equiv -\frac{2d}{\beta}.
\]

(3.12)

For \( d = 3 \) this identity reduces to the well-known sum rule that was first obtained by Stillinger and Lovett [25] and discussed subsequently extensively [7, 19, 21, 26–28]. For the one-component case with \( d > 3 \) its form has been found before [13].

The sum rule (3.12) is independent of \( c_d \), as it should be, since the correlation functions cannot depend on the choice of an additive constant in the potential. For \( d > 2 \) the intermediate steps in deriving (3.12) simplify for the choice \( c_d = 0 \), but that is not essential for the proof. To treat the limit \( d \to 2 \) one has to choose the specific value (2.3) for \( c_d \), so that \( \phi (r) \) stays finite. With that particular choice the proof of (3.12) remains valid in the limit \( d \to 2 \). The form of (3.12) for \( d \to 2 \) is consistent with that found previously by taking \( d = 2 \) from the start [24, 28]. The above derivation shows how the general form of the Stillinger–Lovett relation for an ionic mixture reads for arbitrary \( d \geq 2 \).

4. Equilibrium ensemble and thermodynamics

To prepare the ground for the derivation of additional sum rules for the pair correlation functions of the ionic mixture we need to specify the equilibrium ensemble for the system. A convenient choice, which has been discussed before [7], is the restricted grand-canonical ensemble. It is a grand-canonical ensemble with particle numbers satisfying the constraint \( \sum_{\sigma} e_{\sigma} N_{\sigma} = q_0 V \). Its partition function \( Z \) depends on the volume \( V \), the inverse temperature \( \beta \), the background charge density \( q_0 \) and \( s - 1 \) chemical potentials \( \mu_\sigma (\sigma \neq 1) \). In the limit of an infinite system, the partition function leads to a thermodynamic function \( \tilde{p} \) that is defined by writing

\[
\lim_{V \to \infty} \frac{1}{V} \log Z (\beta, \{ \beta \mu_\sigma \}, q_0, V) = \beta \tilde{p} (\beta, \{ \beta \mu_\sigma \}, q_0).
\]

(4.1)
The energy density $u_v$ and the particle densities $n_{\sigma}$ for $\sigma \neq 1$ follow by taking derivatives

$$u_v = -\frac{\partial \beta \hat{p}}{\partial \beta}, \quad n_{\sigma} = \frac{\partial \beta \hat{p}}{\partial \beta \hat{\mu}_{\sigma}} \quad (\sigma = 2, \ldots, s).$$

(4.2)

In writing a partial derivative with respect to one of the variables $\beta$, $\{\beta \hat{\mu}_{\sigma}\}$, $q_v$, the other variables that are meant to remain constant are suppressed. The pressure follows from $\hat{p}$ through the relation

$$p = \hat{p} - q_v \frac{\partial \hat{p}}{\partial q_v}$$

(4.3)

as is proved in appendix A.

For $d > 2$ a scaling argument can be used to relate the partial derivatives of $\hat{p}$. In fact, the potential energy satisfies the identity

$$U(r_1, \ldots, r_N, V) = \lambda^{d-2} U(\lambda r_1, \ldots, \lambda r_N, \lambda^d V) + \frac{1}{2} \left( \lambda^{d-2} - 1 \right) c_d \sum_\sigma N_{\sigma} e_{\sigma}^2$$

(4.4)

for arbitrary positive $\lambda$. This property implies a specific scaling behaviour of the partition function $Z$ and the thermodynamic function $\hat{p}$. As a consequence, the pressure and the energy density of the ionic mixture are related as

$$p = \frac{d - 2}{d} u_v - \frac{1}{2} \left( d - 4 \right) n \frac{1}{\beta} + \frac{d - 2}{2d} c_d \sum_\sigma n_{\sigma} e_{\sigma}^2$$

(4.5)

with $n = \sum_\sigma n_{\sigma}$ the total particle density.

The partition function $Z$, and hence $\hat{p}$, depends on the additive constant $c_d$ via the Hamiltonian. However, the combination (4.3), which gives the pressure $p$, is invariant when $c_d$ is modified. On the other hand, the energy density $u_v$ as given by (4.2) does depend on $c_d$. Its dependence is such that $u_v + \frac{1}{2} c_d \sum_\sigma n_{\sigma} e_{\sigma}^2$ is invariant, so that (4.5) can be satisfied. The specific amount by which the Hamiltonian is shifted when a different choice for $c_d$ is made depends on the particle numbers $N_{\sigma}$, as (2.5) shows. Hence, the chemical potentials $\hat{\mu}_{\sigma}$ (with $\sigma \neq 1$) change as well when a different value for $c_d$ is chosen. However, the combination $\hat{\mu}_{\sigma} + \frac{1}{2} c_d e_{\sigma} (e_{\sigma} - e_1)$ is found to be invariant. Of course, the partial densities $n_{\sigma}$ do not depend on $c_d$.

It should be noted that both the pressure and the energy density can be written as a sum of a kinetic and a potential part,

$$p = \frac{n}{\beta} + p_{\text{pot}}, \quad u_v = \frac{dn}{\beta} + u_{v, \text{pot}}.$$

(4.6)

According to (4.5) the potential parts of the pressure and the energy density are related as $p_{\text{pot}} = \left( (d - 2)/d \right) \left( u_{v, \text{pot}} + \frac{1}{2} c_d \sum_\sigma n_{\sigma} e_{\sigma}^2 \right)$. In appendix A, it is shown how several auxiliary relations can be derived from (4.5).

For dimension $d > 2$ one may take $c_d = 0$, so that (4.5) gets a simpler form [12]. In contrast, for $d \to 2$ one should choose $c_d$ according to (2.3). With that choice the energy density $u_v$ stays finite for $d \to 2$. Hence, it drops out from (4.5) in the limit. As a consequence, we are left with the equation of state for the two-dimensional ionic mixture

$$p = \frac{n}{\beta} - \frac{1}{8\pi} \sum_\sigma n_{\sigma} e_{\sigma}^2,$$

(4.7)

which can also be obtained directly by applying a scaling argument to a system with a logarithmic potential [29, 30]. The present derivation shows how the second term at the right-hand side comes about as a consequence of the shift $c_d$ in the potential. Incidentally,
we remark that it is essential to choose the right value for $c_d$ before taking the limit $d \to 2$. For instance, choosing $c_d = 0$ in (4.5) and taking the limit naively, without realizing that $n_d$ diverges in that case, would have resulted in an incorrect equation of state.

In closing this section, we remark that alternatively one may choose to describe the equilibrium ionic mixture by means of a full grand-canonical ensemble with a background with fixed density [2, 12, 21, 31, 32].

5. Thermodynamic sum rules for pair correlation functions: zeroth- and second-moment rules

In the restricted grand-canonical ensemble the derivative of the partial density $n_{\sigma_1}$ with respect to the chemical potential combination $\beta \tilde{\mu}_{\sigma_2}$ is given by

$$\frac{Dn_{\sigma_1}}{D\beta \tilde{\mu}_{\sigma_2}} = \frac{1}{V} \langle N_{\sigma_1} N_{\sigma_2} \rangle - \frac{1}{V} \langle N_{\sigma_1} \rangle \langle N_{\sigma_2} \rangle,$$  

(5.1)

with the operator $D/D\beta \tilde{\mu}_{\sigma}$ defined as

$$\frac{D}{D\beta \tilde{\mu}_{\sigma}} = (1 - \delta_{\sigma_1}) \frac{\partial}{\partial \beta \tilde{\mu}_{\sigma}} - \delta_{\sigma_1} \sum_{\sigma' \neq \sigma} e_{\sigma'} \frac{\partial}{\partial \beta \tilde{\mu}_{\sigma'}}.$$  

(5.2)

The right-hand side of (5.1) can be expressed as an integral over the pair correlation function. As a result one finds

$$n_{\sigma_1} n_{\sigma_2} \int d\mathbf{r}_2 h^{(2)}_{\sigma_1 \sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{Dn_{\sigma_1}}{D\beta \tilde{\mu}_{\sigma_2}} - n_{\sigma_1} \delta_{\sigma_1 \sigma_2}.$$  

(5.3)

Upon summation over $\sigma_2$, with the weights $e_{\sigma_2}$, one recovers the perfect-screening rule (3.5). Taking an unweighted sum over $\sigma_2$ and using (A.8) to eliminate the derivative of the particle density $n$ we find the equality

$$\frac{1}{2} \frac{d(d - 4)}{d - 2} n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \int d\mathbf{r}_2 h^{(2)}_{\sigma_1 \sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = -(d - 2) \beta \frac{\partial n_{\sigma_1}}{\partial \beta} + dq_v \frac{\partial n_{\sigma_1}}{\partial q_v} - \frac{1}{2} \frac{d(d - 2)}{d - 2} n_{\sigma_1} \delta_{\sigma_1 \sigma_2}.$$  

(5.4)

This zeroth-moment sum rule is independent of the perfect-screening sum rule. Like that rule it is valid for each species $\sigma_1$ separately. If an unweighted sum over $\sigma_1$ is carried out, one arrives at a less strong sum rule of the form

$$\frac{1}{2} \frac{d(d - 4)}{d - 2} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} \int d\mathbf{r}_2 h^{(2)}_{\sigma_1 \sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = -(d - 2) \beta \frac{\partial n}{\partial \beta} + dq_v \frac{\partial n}{\partial q_v} - \frac{1}{2} \frac{d(d - 2)}{d - 2} n + \frac{1}{2} \frac{d(d - 2)}{d - 2} c_d \beta \sum_{\sigma_1} e_{\sigma_1}^2 \frac{Dn}{D\beta \tilde{\mu}_{\sigma_1}}.$$  

(5.5)

For any $d > 2$ one may choose $c_d = 0$ in (5.4) and (5.5). For $d = 4$ the integrals in (5.4) and (5.5) drop out; the resulting equalities are trivial consequences of the relation (A.8). The case $d = 2$ deserves special attention, and will be discussed at the end of this section.

The derivative of the partial density $n_{\sigma}$ with respect to the inverse temperature $\beta$ reads

$$\frac{\partial n_{\sigma}}{\partial \beta} = -\frac{1}{V} \langle N_{\sigma} H \rangle + \frac{1}{V} \langle N_{\sigma} \rangle \langle H \rangle.$$  

(5.6)
Like the derivative with respect to the chemical potentials discussed above, it can be written in terms of integrals over Ursell functions, as shown in appendix B,

\[(d - 2)\beta \frac{\partial n_{\sigma_1}}{\partial \beta} = -\frac{1}{2} \beta q_v n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) r_{12}^2 - \frac{1}{2} d(d - 4) n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) - \frac{1}{2} d(d - 2) n_{\sigma_1}
+ \frac{1}{2} (d - 2) c_d \beta n_{\sigma_1} \left[ \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2}^2 \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) + e_{\sigma_1}^2 \right]. \tag{5.7} \]

An essential role in the proof of this identity is played by the symmetry properties of the Ursell functions, as is discussed in appendix C. Employing (5.3) and (5.4) for two of the integrals at the right-hand side, we find that many terms cancel. In this way, we obtain the second-moment sum rule

\[ n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) r_{12}^2 = -\frac{2d}{\beta} \frac{\partial n_{\sigma_1}}{\partial q_v}. \tag{5.8} \]

Summing over \(\sigma_1\) with the weights \(e_{\sigma_1}\) one recovers the Stillinger–Lovett rule (3.12). Taking the sum with equal weights we get the second-moment identity

\[ \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) r_{12}^2 = -\frac{2d}{\beta} \frac{\partial n}{\partial q_v}, \tag{5.9} \]

which is independent of the Stillinger–Lovett rule.

The above sum rules have been derived for all \(d > 2\). To obtain the corresponding rules for the case \(d = 2\) we choose \(c_d\) according to (2.3) and take the limit \(d \to 2\). The zeroth-order sum rule (5.3) retains the same form, whereas the sum rules (5.4) and (5.5) become

\[ n_{\sigma_1} \sum_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) = -q_v \frac{\partial n_{\sigma_1}}{\partial q_v} + \frac{\beta}{8\pi} \frac{D}{D\beta \mu_{\sigma_1}} \left( \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2}^2 \right) \tag{5.10} \]

and

\[ \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) = -q_v \frac{\partial n}{\partial q_v} + \frac{\beta}{8\pi} \sum_{\sigma_1} e_{\sigma_1}^2 \frac{Dn}{D\beta \mu_{\sigma_1}}. \tag{5.11} \]

As in the previous section, incorrect results would have been obtained from (5.4) and (5.5) when the choice \(c_d = 0\) had been made before evaluating the limit \(d \to 2\). In contrast, the sum rules (5.8) and (5.9) are independent of the choice of \(c_d\), so that the proof of their validity for \(d = 2\) is straightforward. It may be noted that in deriving the limiting form of the auxiliary relation (5.7) it is important once again to choose \(c_d\) correctly before taking the limit.

The above derivation of (5.8) for general \(d\) shows how one can combine perfect screening, symmetry and thermodynamics with the statistical relation (5.6) to establish a second-moment sum rule. For the special case \(d = 2\) the last-mentioned ingredient is not necessary, as is shown in detail in appendix C. This particular feature of the second-moment sum rule (5.8) for \(d = 2\) has been discovered recently [6].

### 6. Thermodynamic sum rules for pair correlation functions: fourth-moment rule

To derive an equality for the fourth moment of the two-particle Ursell function we start from an expression for its derivative with respect to the inverse temperature,
The first term at the right-hand side can be expressed in moments of the two-particle Ursell function, which follows from the symmetry properties of the three-particle Ursell function. Likewise, the second and the sixth terms can be rewritten by means of the symmetry relation (C.2). In the third term, we can carry out a partial integration and use the identity
\[ \frac{\partial \phi(r_{12})}{\partial r_{1}} = -(d - 2)\phi(r_{12}) + (d - 2)c_{d}. \] (6.3)
As a result we arrive at a relation involving the zeroth, the second and the fourth moments of the two-particle Ursell function,
\[
(d - 2)\beta \frac{\partial}{\partial \beta} \int d^{d-2}q_{1,2} n_{\sigma_{1}} n_{\sigma_{2}} \left( \sum_{\sigma_{3}} n_{\sigma_{3}} e_{\sigma_{3}} \right) \int dr_{3} h_{\sigma_{1}\sigma_{2}\sigma_{3}}^{(3)} (r_{1, 2, 3}) r_{3}^{2} 
- \frac{1}{2} d(d - 4) n_{\sigma_{1}} n_{\sigma_{2}} \sum_{\sigma_{3}} n_{\sigma_{3}} \int dr_{3} h_{\sigma_{1}\sigma_{2}\sigma_{3}}^{(3)} (r_{1, 2, 3}) - n_{\sigma_{1}} n_{\sigma_{2}} r_{12} \frac{\partial}{\partial r_{12}} h_{\sigma_{1}\sigma_{2}}^{(2)} (r_{1, 2}) 
- \frac{1}{2} \beta q_{v} n_{\sigma_{1}} n_{\sigma_{2}} e_{\sigma_{1}} e_{\sigma_{2}} \int dr_{2} r_{12}^{2} - d(d - 2) n_{\sigma_{1}} n_{\sigma_{2}} h_{\sigma_{1}\sigma_{2}}^{(2)} (r_{1, 2}) 
+ \frac{1}{2} (d - 2) c_{d} \beta n_{\sigma_{1}} n_{\sigma_{2}} \left( \sum_{\sigma_{3}} n_{\sigma_{3}} e_{\sigma_{3}}^{2} \right) \int dr_{3} h_{\sigma_{1}\sigma_{2}\sigma_{3}}^{(3)} (r_{1, 2, 3}) 
+ (e_{\sigma_{1}}^{2} + e_{\sigma_{2}}^{2}) h_{\sigma_{1}\sigma_{2}}^{(2)} (r_{1, 2}) \right].
\] (6.1)

The proof of this identity is sketched in appendix B. Multiplying both sides with \( e_{\sigma_{1}} e_{\sigma_{2}} \phi(r_{12}) \), integrating over \( r_{2} \) and summing over \( \sigma_{1} \) and \( \sigma_{2} \), we get an expression for the derivative of the potential-energy density (B.1),
\[
2(d - 2)\beta \frac{\partial \mu_{\text{pot}}}{\partial \beta} = -\frac{1}{2} \beta q_{v} \sum_{\sigma_{1}, \sigma_{2}} n_{\sigma_{1}} n_{\sigma_{2}} \sum_{\sigma_{3}} n_{\sigma_{3}} e_{\sigma_{1}} e_{\sigma_{2}} e_{\sigma_{3}} \int dr_{2} dr_{3} h_{\sigma_{1}\sigma_{2}\sigma_{3}}^{(3)} (r_{1, 2, 3}) r_{3}^{2} \phi(r_{12}) 
- \frac{1}{2} d(d - 4) \sum_{\sigma_{1}, \sigma_{2}} n_{\sigma_{1}} n_{\sigma_{2}} \sum_{\sigma_{3}} n_{\sigma_{3}} e_{\sigma_{1}} e_{\sigma_{2}} e_{\sigma_{3}} \int dr_{2} dr_{3} h_{\sigma_{1}\sigma_{2}\sigma_{3}}^{(3)} (r_{1, 2, 3}) \phi(r_{12}) 
- \sum_{\sigma_{1}, \sigma_{2}} n_{\sigma_{1}} n_{\sigma_{2}} e_{\sigma_{1}} e_{\sigma_{2}} \int dr_{2} r_{12} \left( \frac{\partial}{\partial r_{1}} h_{\sigma_{1}\sigma_{2}}^{(2)} (r_{1, 2}) \right) \phi(r_{12}) 
- \frac{1}{2} \beta q_{v} \sum_{\sigma_{1}, \sigma_{2}} n_{\sigma_{1}} n_{\sigma_{2}} e_{\sigma_{1}} e_{\sigma_{2}} \int dr_{2} r_{12}^{2} \phi(r_{12}) - 2d(d - 2) \mu_{\text{pot}} 
+ \frac{1}{2} (d - 2) c_{d} \beta \sum_{\sigma_{1}, \sigma_{2}} n_{\sigma_{1}} n_{\sigma_{2}} e_{\sigma_{1}} e_{\sigma_{2}} \left( \sum_{\sigma_{3}} n_{\sigma_{3}} e_{\sigma_{3}}^{2} \right) \int dr_{2} dr_{3} h_{\sigma_{1}\sigma_{2}\sigma_{3}}^{(3)} (r_{1, 2, 3}) \phi(r_{12}) 
+ (e_{\sigma_{1}}^{2} + e_{\sigma_{2}}^{2}) \int dr_{2} r_{12}^{2} \phi(r_{12}) \right].
\] (6.2)
for the three-dimensional ionic mixture \([7, 21]\). Whereas the second moments, as given by the
established for the one-component plasma in two \([24]\) and three \([19, 33–35]\) dimensions and
sum rules \((3\, 10)\). Upon using \((A\, 8)\)–\((6\, 4)\), the zeroth and second moments at both sides of this relation can be replaced by the
thermodynamic expressions given in \((5\, 3)\) and \((5\, 8)\). The ensuing derivatives with respect to the
chemical potentials may be eliminated with the help of \((A\, 8)\). Furthermore, at the right-hand side the full energy density can be introduced with the help of \((4\, 6)\). These manipulations lead to an expression for the fourth moment of the Ursell function in terms of thermodynamic
derivatives only,
\[
\begin{align*}
    d^2 q_v^2 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \text{d} \mathbf{r}_2 h^{(2)}_{\sigma_1 \sigma_2}(\mathbf{r}_1, \mathbf{r}_2) r_{\sigma_1 \sigma_2}^2
    &= -8(d - 2)^2(d + 2)\beta^2 \frac{\partial u^\text{pot}}{\partial \beta}
    - 16(d - 1)(d - 2)(d + 2)\beta u_v
    + 4d(d - 2)(d - 4)(d + 2)\beta \frac{\partial n}{\partial \beta}
    + 4d^2(d - 4)(d + 2)q_v \frac{\partial n}{\partial q_v}
    - 4(d - 2)(d + 2)c_d \beta \left[ (d - 2)\beta \frac{\partial p}{\partial \beta} + d q_v \frac{\partial p}{\partial q_v} + d - 2 \left( \sum_{\sigma} n_{\sigma} e_{\sigma}^2 \right) \right].
\end{align*}
\]
\[\text{(6.5)}\]

Upon using \((A\, 9)\) we find that the right-hand side is proportional to the derivative of the
pressure \(p\) (in the form of \((4\, 5)\)) with respect to \(q_v\). In this way, we have found the rather
elegant fourth-moment sum rule
\[
\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int \text{d} \mathbf{r}_2 h^{(2)}_{\sigma_1 \sigma_2}(\mathbf{r}_1, \mathbf{r}_2) r_{\sigma_1 \sigma_2}^2 = -8d(d + 2) \frac{\partial p}{\beta q_v}.
\]
\[\text{(6.6)}\]

It is a generalization to arbitrary \(s\) and \(d\) of the well-known compressibility rule that has been
established for the one-component plasma in two \([24]\) and three \([19, 33–35]\) dimensions and
for the three-dimensional ionic mixture \([7, 21]\). Whereas the second moments, as given by the
sum rules \((3\, 12), (5\, 8)\) and \((5\, 9)\), are linear in \(d\), the fourth moment turns out to be quadratic
in \(d\).

For all \(d > 2\) we may put \(c_d = 0\), as before, so that the relations \((6\, 1)–(6\, 5)\) become somewhat simpler. To discuss the case \(d = 2\) we must choose \(c_d\) as in \((2\, 3)\). Upon taking
the limit \(d \to 2\) the terms in \((6\, 1)–(6\, 5)\) containing \(c_d\) remain finite, so that they cannot be
omitted. However, the final result \((6\, 6)\) does not depend on \(c_d\) explicitly, so that it remains
valid as such in the limit \(d \to 2\). Hence, we have established the fourth-moment rule \((6\, 6)\) for
all \(d \geq 2\).

As a final remark we point out that a shorter proof of the fourth-moment rule for the
special case \(d = 2\) can be found from a particular symmetry relation connecting second and
fourth moments, as discussed in appendix C. The derivative \(\partial h^{(2)}_{\sigma_1 \sigma_2}/\partial \beta\) is not needed in that
line of reasoning.
7. Concluding remarks

By making a systematic use of the properties of the restricted grand-canonical ensemble and the hierarchy equations for the correlation functions we have been able to derive the sum rules that govern the first few moments of the two-particle Ursell functions for a multi-component ionic mixture with an arbitrary spatial dimension \( d \geq 2 \). The dependence on \( d \) of the various moments has been determined in detail. While most discussions in the literature had to treat two-dimensional mixtures with a logarithmic potential as a separate case, we have shown that a unified description of mixtures for all \( d \geq 2 \) is indeed possible by making a careful choice of additive constants in the potential.

Our main results for the moments of the two-particle Ursell function are presented in (3.5), (3.12), (5.3)–(5.5), (5.8)–(5.9) and (6.6). The ensuing results for the moments of the two-particle correlation function follow by replacing \( h^{(2)}_{\sigma_1,\sigma_2}(r_1, r_2) \) with \( g^{(2)}_{\sigma_1,\sigma_2} = 1 \). Whereas the zeroth-moment perfect-screening rules (3.5) and the second-moment rule (3.12) could be derived without invoking thermodynamical properties, the proof of the other sum rules had to be based on statistical ensemble theory. Accordingly, the ensuing rules in sections 5 and 6 depend on thermodynamical derivatives with respect to the basic variables describing ionic mixtures in a restricted grand-canonical ensemble, namely \( \beta, \{\beta\tilde{\mu}_\sigma\} \) (for \( \sigma = 2, \ldots, s \)) and \( q_v \).

If one wishes, one may express the sum rules in terms of derivatives with respect to a different set of independent variables involving—apart from \( \beta \)—the chemical potentials \( \{\mu_\sigma\} \) with \( \sigma = 1, \ldots, s \), in a way described previously [7]. For completeness we give the sum rules (5.3), (5.8) and (6.6) in terms of derivatives with respect to these alternative variables,

\[
n_{\sigma_1} n_{\sigma_2} \int dr_1 h^{(2)}_{\sigma_1,\sigma_2}(r_1, r_2) = \frac{1}{\beta} \left( \frac{\partial n_{\sigma_1}}{\partial \mu_{\sigma_2}} - \frac{1}{S} \frac{\partial q_v}{\partial \mu_{\sigma_2}} \right) n_{\sigma_1} \delta_{\sigma_1,\sigma_2} \tag{7.1}
\]

\[
n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int dr_1 h^{(2)}_{\sigma_1,\sigma_2}(r_1, r_2)^2 = -\frac{2d}{\beta S} \frac{\partial q_v}{\partial \mu_{\sigma_1}} \tag{7.2}
\]

\[
\sum_{\sigma_1,\sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_1 h^{(2)}_{\sigma_1,\sigma_2}(r_1, r_2)^4 = -\frac{8d(d + 2)}{\beta S} \tag{7.3}
\]

with the abbreviation \( S = \sum_{\sigma} e_\sigma \partial q_v / \partial \mu_\sigma \). As before, in writing the partial derivatives at the right-hand sides the independent variables that are kept constant are suppressed.

The sum rules discussed in this paper are essential in understanding the equilibrium fluctuations in an ionic mixture. In particular, the fluctuations in the partial densities, the pressure and the energy density are governed by these rules, as has been shown in [36] for the three-dimensional case. The fluctuation formulae in turn are necessary in order to determine specific dynamical properties of the ionic mixture, such as the time evolution of the collective modes [37, 38].

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Appendix A. Stability, thermodynamic pressure and some auxiliary relations

In this appendix, we shall first discuss the stability of ionic mixtures in arbitrary dimension. Furthermore, we shall establish the relation between the thermodynamic pressure and the partition function in the restricted grand-canonical ensemble. Finally, a few thermodynamic auxiliary relations will be derived.

By generalizing the argument given in [17] so as to be applicable to a mixture in arbitrary dimension $d > 2$ one finds the bound

$$U \geq -\frac{d}{2\pi(d+2)(d-2)} q e^{(d-2)/d} \left[ \Gamma\left(\frac{1}{2}d + 1\right) \right]^{2/d} \sum_{\sigma} N_{\sigma} e_{\sigma}^{1+2/d} - \frac{1}{2} c_d \sum_{\sigma} N_{\sigma} e_{\sigma}^2,$$

(A.1)

which for the one-component case (and $c_d = 0$) agrees with the bound presented by Sari et al [39, 40]. Taking moreover $d = 3$ one recovers the result in [17]. For $d \rightarrow 2$ and $c_d = 0$ the bound in (A.1) goes to $-\infty$, so that it becomes useless. However, upon choosing $c_d$ as in (2.3) the inequality (A.1) becomes in the limit $d \rightarrow 2$,

$$U \geq -\frac{1}{8\pi} \sum_{\sigma} N_{\sigma} e_{\sigma}^2 \log \left(\frac{\pi q_v e_{\sigma}}{e_{\sigma}}\right) - \frac{1}{2} \left( c + \frac{3}{8\pi} \right) \sum_{\sigma} N_{\sigma} e_{\sigma}^2.$$

(A.2)

For the one-component case (and the choice $c = 0$) this inequality has been derived previously [39]. It should be remarked that different bounds have been obtained in the past [41]–[44]. For our present discussion these are not relevant, since we only wish to confirm here that the multi-component ionic mixture is stable for arbitrary $d > 2$.

Furthermore, we want to derive the relation (4.3) between the pressure $p$ and the thermodynamic function $\tilde{p}$, which follows from the partition function according to (4.1). Generalizing the definition of the (thermal) pressure in a one-component plasma by Choquard et al [45] to an ionic mixture, we write it as the derivative of the free energy $F$ with respect to the volume $V$ at constant temperature $T$, constant (average) particle numbers $n_{\sigma} V$ (for $\sigma = 2, \ldots, s$) and constant total background charge $q_v V$,

$$p = -\left( \frac{\partial F(T, \{n_{\sigma}\}, q_v V)}{\partial V} \right)_{T, \{n_{\sigma}\}, q_v V},$$

(A.3)

Taking account of the implicit dependence on $V$ we get

$$p = -f_v + \sum_{\sigma (\neq 1)} n_{\sigma} \left( \frac{\partial f_v}{\partial n_{\sigma}} \right)_{T, \{n_{\sigma}\}, q_v} + q_v \left( \frac{\partial f_v}{\partial q_v} \right)_{T, \{n_{\sigma}\}},$$

(A.4)

with $f_v(T, \{n_{\sigma}\}, q_v) = F/V$ the free energy density. The construction of the restricted grand-canonical ensemble implies the relations [7]

$$df_v = -s_v dT + \sum_{\sigma (\neq 1)} \bar{\mu}_{\sigma} n_{\sigma} + \bar{\mu}_q dq_v,$$

(A.5)

$$\bar{p} = -f_v + \sum_{\sigma (\neq 1)} \bar{\mu}_{\sigma} n_{\sigma},$$

(A.6)

with $s_v$ the entropy density and $\bar{\mu}_q = -\partial \bar{p}/\partial q_v$. Hence, (A.4) can be written as

$$p = -f_v + \sum_{\sigma (\neq 1)} \bar{\mu}_{\sigma} n_{\sigma} + \bar{\mu}_q q_v.$$  

(A.7)

Comparison of (A.6) and (A.7) yields the relation between $\bar{p}$ and the pressure $p$ that we wished to prove.
Finally, in the main text we need several equalities involving partial derivatives of thermodynamic quantities. Upon differentiating the relation (4.5) with respect to $\beta \tilde{\mu}_\sigma$, at constant $\beta$ and $q_v$, we get

\[
(d - 2)\beta \frac{\partial n_\sigma}{\partial \beta} = d q_v \frac{\partial n_\sigma}{\partial q_v} - \frac{1}{2} d(d - 4) \frac{D n_\sigma}{D \beta \tilde{\mu}_\sigma} + \frac{1}{2} (d - 2) c_d \beta \frac{D}{D \beta \tilde{\mu}_\sigma} \left( \sum_{\sigma'} n_{\sigma'} e_{\sigma'}^2 \right),
\]

(A.8)

with the operator $D/D \beta \tilde{\mu}_\sigma$ defined in (5.2). Likewise, differentiation of (4.5) with respect to $\beta$ yields

\[
(d - 2)\beta \frac{\partial u_v}{\partial \beta} = d q_v \frac{\partial u_v}{\partial q_v} - 2(d - 1) u_v + \frac{1}{2} d(d - 4) \frac{\partial n}{\partial \beta} + \frac{1}{2} (d - 2) c_d \left( 1 + \beta \frac{\partial}{\partial \beta} \right) \left( \sum_{\sigma} n_{\sigma} e_{\sigma}^2 \right).
\]

(A.9)

For $d > 2$ we may choose $c_d = 0$, so that the last terms at the right-hand sides of (A.8) and (A.9) drop out. For $d \to 2$ we choose $c_d$ as in (2.3). When the limit is taken, the left-hand sides of (A.8) and (A.9) disappear, while the last terms at the right-hand sides yield a finite contribution. As a result we get for $d = 2$,

\[
q_v \frac{\partial n_\sigma}{\partial q_v} - n_\sigma + \frac{D}{D \beta \tilde{\mu}_\sigma} \left( n - \frac{\beta}{8\pi} \sum_{\sigma'} n_{\sigma'} e_{\sigma'}^2 \right) = 0
\]

(A.10)

and

\[
q_v \frac{\partial u_v}{\partial q_v} - u_v - \frac{\partial n}{\partial \beta} + \frac{1}{8\pi} \left( 1 + \beta \frac{\partial}{\partial \beta} \right) \left( \sum_{\sigma} n_{\sigma} e_{\sigma}^2 \right) = 0.
\]

(A.11)

The auxiliary relations (A.8) and (A.9) have been used in the main text.

Appendix B. Derivatives of densities and Ursell functions with respect to the inverse temperature

In deriving the second- and fourth-moment sum rules we need expressions for the derivatives of the partial densities and the two-particle Ursell functions with respect to $\beta$. The derivative of $n_\sigma$ with respect to $\beta$ follows by evaluating its formal expression:

\[
\beta \frac{\partial n_\sigma}{\partial \beta} = -n_\sigma \frac{\partial}{\partial \beta} \left( \sum_{\sigma'} n_{\sigma'} e_{\sigma'}^2 \right) + \frac{1}{2} \frac{d n_\sigma}{d \beta} \sum_{\sigma'} n_{\sigma'} e_{\sigma'}^2 \int dr_2 h_{\sigma_1 \sigma_2}^{(2)}(r_1, r_2, r_3) \phi(r_12). \quad (B.1)
\]

The average $\langle N_{\sigma} H \rangle$ can likewise be expressed in terms of integrals over Ursell functions. As a result we find

\[
\beta \frac{\partial n_{\sigma_1}}{\partial \beta} = -\beta n_{\sigma_1} \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int dr_2 dr_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(r_1, r_2, r_3) \phi(r_123) - \beta n_{\sigma_1} e_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int dr_2 h_{\sigma_1 \sigma_2}^{(2)}(r_1, r_2) \phi(r_12) - \frac{1}{2} \frac{d n_{\sigma_1}}{d \beta} \sum_{\sigma_2} n_{\sigma_2} \int dr_2 h_{\sigma_1 \sigma_2}^{(2)}(r_1, r_2) - \frac{1}{2} \frac{d n_{\sigma_1}}{d \beta}.
\]

(B.2)
Employing the symmetry relation (C.2) to eliminate the integral with the three-particle Ursell function, we arrive at (5.7).

Furthermore, we need an expression for the derivative of the two-particle Ursell function with respect to $\beta$. In the restricted grand-canonical ensemble one has quite generally $\frac{\partial(f)}{\partial\beta} = -\langle f H \rangle + \langle f \rangle \langle H \rangle$ for an arbitrary phase function $f$. Taking $f = \sum_{\alpha_i\alpha_j} \delta(\mathbf{r}_1 - \mathbf{r}_{\alpha_i}) \delta(\mathbf{r}_2 - \mathbf{r}_{\alpha_j})$ and using (2.5) one derives

$$\frac{\beta}{\partial\beta} [n_{\alpha_1} n_{\alpha_2} h^{(2)}_{\alpha_1\alpha_2}(\mathbf{r}_1, \mathbf{r}_2)] = -\frac{1}{2} \beta n_{\alpha_1} n_{\alpha_2} \sum_{\sigma_1, \sigma_4} n_{\alpha_1} n_{\alpha_2} e_{\sigma_1} e_{\sigma_4}$$

$$\times \int d\mathbf{r}_3 d\mathbf{r}_4 h^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \phi(r_{14})$$

$$- \frac{1}{2} d\mathbf{n}_{\alpha_1} n_{\alpha_2} \sum_{\sigma_3} n_{\alpha_3} e_{\sigma_3} \int d\mathbf{r}_3 h^{(3)}_{\alpha_1\alpha_2\sigma_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

$$- \beta n_{\alpha_1} n_{\alpha_2} \sum_{\sigma_1} n_{\alpha_1} e_{\sigma_1} \int d\mathbf{r}_3 h^{(3)}_{\alpha_2\sigma_1\sigma_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \phi(r_{13}) + e_{\sigma_2} \phi(r_{23})$$

$$- d\mathbf{n}_{\alpha_1} n_{\alpha_2} h^{(2)}_{\alpha_1\alpha_2}(\mathbf{r}_1, \mathbf{r}_2) - \beta n_{\alpha_1} n_{\alpha_2} e_{\sigma_1} e_{\sigma_2} h^{(2)}_{\alpha_1\alpha_2}(\mathbf{r}_1, \mathbf{r}_2) \phi(r_{12})$$

$$- \frac{1}{2} \beta n_{\alpha_1} n_{\alpha_2} \sum_{\sigma_1, \sigma_4} n_{\alpha_3} n_{\sigma_4} e_{\sigma_1} e_{\sigma_4} \int d\mathbf{r}_3 d\mathbf{r}_4 \left[ h^{(2)}_{\alpha_1\sigma_3}(\mathbf{r}_1, \mathbf{r}_3) h^{(2)}_{\alpha_2\sigma_4}(\mathbf{r}_2, \mathbf{r}_4) \right] \phi(r_{14})$$

$$- \beta n_{\alpha_1} n_{\alpha_2} \sum_{\sigma_1} n_{\alpha_3} e_{\sigma_3} \int d\mathbf{r}_3 \left[ e_{\sigma_2} h^{(2)}_{\alpha_1\alpha_2}(\mathbf{r}_2, \mathbf{r}_3) \phi(r_{13}) + e_{\sigma_2} h^{(2)}_{\sigma_1\alpha_1}(\mathbf{r}_1, \mathbf{r}_3) \phi(r_{23}) \right]$$

$$- \beta n_{\alpha_1} n_{\alpha_2} e_{\sigma_1} e_{\sigma_2} \phi(r_{12}). \quad (B.3)$$

For large separation of the position arguments the left-hand side vanishes faster than any inverse power of $r_{12}$. At the right-hand side, the first three integrals and the two terms proportional to $h^{(2)}_{\alpha_1\alpha_2}$ share this feature. However, the property of being of short range is not obviously true for the last two integral terms, while it is certainly false for the final term, which is proportional to $\phi(r_{12})$ and hence of long range. Nevertheless, by employing (3.4) and (3.5) one may rewrite the sum of these terms in a form that shows their short-range character as a function of $r_{12}$ explicitly,

$$-\frac{\beta}{d} n_{\alpha_1} n_{\alpha_2} \sum_{\sigma_1, \sigma_4} n_{\alpha_3} n_{\sigma_4} e_{\sigma_1} e_{\sigma_4} \int d\mathbf{r}_3 h^{(2)}_{\alpha_1\sigma_3}(\mathbf{r}_1, \mathbf{r}_3) \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_3} \int d\mathbf{r}_4 h^{(2)}_{\sigma_4\alpha_2}(\mathbf{r}_2, \mathbf{r}_4)$$

$$+ \beta n_{\alpha_1} n_{\alpha_2} \sum_{\sigma_1, \sigma_4} n_{\alpha_3} n_{\sigma_4} e_{\sigma_1} e_{\sigma_4} \int d\mathbf{r}_3 h^{(2)}_{\alpha_1\sigma_3}(\mathbf{r}_2, \mathbf{r}_3) \left[ \phi(r_{13}) - c_d \right] \int d\mathbf{r}_4 h^{(2)}_{\sigma_4\alpha_2}(\mathbf{r}_1, \mathbf{r}_4)$$

$$+ \beta n_{\alpha_1} n_{\alpha_2} e_{\sigma_1} \left[ \phi(r_{12}) - c_d \right] \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 h^{(2)}_{\alpha_1\sigma_3}(\mathbf{r}_1, \mathbf{r}_3). \quad (B.4)$$

Substituting these terms and using moreover the symmetry relation (C.6) in the first term at the right-hand side of (B.3), we arrive at the somewhat simpler expression (6.1) given in the main text. It should be noted that at the right-hand side of (6.1) the potential does not occur explicitly any more.
Appendix C. Symmetry relations

The Ursell functions are symmetric under a permutation of both their position arguments \( r_i \) and their component labels \( \sigma_i \). From that symmetry one proves

\[
(d - 2) \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int dr_2 dr_3 h^{(3)}_{\sigma_1\sigma_2\sigma_3}(r_1, r_2, r_3) [\phi(r_{23}) - c_d] = 2 \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int dr_2 dr_3 h^{(3)}_{\sigma_1\sigma_2\sigma_3}(r_1, r_2, r_3) r_{12} \cdot \frac{\partial \phi(r_{23})}{\partial r_2}.
\]

(C.1)

At the right-hand side we use (3.10). Employing moreover the perfect-screening relations (3.5) and (3.6) we get the identity

\[
(d - 2) \beta \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int dr_2 dr_3 h^{(3)}_{\sigma_1\sigma_2\sigma_3}(r_1, r_2, r_3) \phi(r_{23}) \]

\[
+ 2(d - 2) \beta e_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) \phi(r_{12})
\]

\[
= \beta q_v \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2)^2 r_{12}^2 - 2 d \sum_{\sigma_2} n_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2)
\]

\[
- (d - 2) c_d \beta \left[ \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2}^2 \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) + e_{\sigma_1}^2 \right],
\]

(C.2)

which is used in section 6 and appendix B.

A second identity is obtained by starting from an equality that is analogous to (C.1) and follows likewise from the symmetry of the three-particle Ursell function

\[
(d - 2) \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int dr_2 dr_3 h^{(3)}_{\sigma_1\sigma_2\sigma_3}(r_1, r_2, r_3) [\phi(r_{23}) - c_d] \times \left[ r_{12}^2 + r_{23}^2 + 2 r_{12}^2 (r_{12} \cdot r_{23})^2 \right]
\]

\[
= 2 \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int dr_2 dr_3 h^{(3)}_{\sigma_1\sigma_2\sigma_3}(r_1, r_2, r_3) r_{12}^2 r_{12}^2 \cdot \frac{\partial \phi(r_{23})}{\partial r_2}.
\]

(C.3)

The right-hand side can be expressed in terms of two-particle Ursell functions by employing the hierarchy equation (3.2). At the left-hand side we may invoke the perfect-screening rule (3.7) for \( \ell = 1, 2 \), when the sum over \( \sigma_1 \) with weights \( n_{\sigma_1} e_{\sigma_1} \) is carried out as well. In this way, we arrive at the identity

\[
(d - 2) \beta \sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int dr_2 dr_3 h^{(3)}_{\sigma_1\sigma_2\sigma_3}(r_1, r_2, r_3) r_{12}^2 \phi(r_{12})
\]

\[
+ (d - 2) \beta \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) r_{12}^4 \phi(r_{12})
\]

\[
= \frac{d}{2(d + 2)} \beta q_v \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) r_{12}^4
\]

\[
- 2 d \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) r_{12}^2
\]

\[
- (d - 2) c_d \beta \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 e_{\sigma_2} \int dr_2 h^{(2)}_{\sigma_1\sigma_2}(r_1, r_2) r_{12}^2
\]

(C.4)

which is needed in section 6 of the main text.
Finally, we want to establish an equality for the four-particle Ursell function. It follows by starting from an equality for \( h^{(4)} \) of a similar form as (C.1),
\[
(d - 2) \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_3 \, dr_4 \, h^{(4)}_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}(r_1, r_2, r_3, r_4) \left[ \phi(r_{34}) - c_d \right] = 2 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_3 \, dr_4 \, h^{(4)}_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}(r_1, r_2, r_3, r_4) r_{13} \cdot \frac{\partial \phi(r_{34})}{\partial r_1}.
\]
(C.5)

Upon using the hierarchy equation (3.1) for \( k = 3 \), the expansion (3.3), the identity (3.4) and the perfect-screening rules (3.5)–(3.6) we get, by taking steps analogous to those of appendix B of [7],
\[
\frac{1}{2} (d - 2) \beta \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_3 \, dr_4 \, h^{(4)}_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}(r_1, r_2, r_3, r_4) \phi(r_{34}) = - (d - 2) \beta \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int dr_3 \, h^{(3)}_{\sigma_1 \sigma_2 \sigma_3}(r_1, r_2, r_3) \left[ e_{\sigma_1} \phi(r_{13}) + e_{\sigma_2} \phi(r_{23}) \right] + \frac{1}{2} \beta q_3 \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int dr_3 \, h^{(3)}_{\sigma_1 \sigma_2 \sigma_3}(r_1, r_2, r_3) r_{13}^2 \\
- d \sum_{\sigma_1} n_{\sigma_1} \int dr_3 \, h^{(3)}_{\sigma_1 \sigma_2 \sigma_3}(r_1, r_2, r_3) + r_{12} \cdot \frac{\partial}{\partial r_1} h^{(2)}_{\sigma_1 \sigma_2}(r_1, r_2) \\
- \beta \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_3 \, h^{(2)}_{\sigma_1 \sigma_2}(r_1, r_3) r_{13} \cdot \frac{\partial \phi(r_{23})}{\partial r_2} \int_{r_{23} > r_{12}} dr_4 \, h^{(2)}_{\sigma_1 \sigma_3}(r_2, r_4) \\
+ (d - 2) \beta \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int dr_3 \, h^{(2)}_{\sigma_1 \sigma_3}(r_2, r_3) \left[ \phi(r_{13}) - c_d \right] \\
\times \int_{r_{13} > r_{12}} dr_4 \, h^{(2)}_{\sigma_1 \sigma_4}(r_1, r_4) + (d - 2) \beta e_{\sigma_2} \left[ \phi(r_{12}) - c_d \right] \\
\times \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int_{r_{13} > r_{12}} dr_3 \, h^{(2)}_{\sigma_1 \sigma_3}(r_1, r_3) - (d - 2) \beta e_{\sigma_1} e_{\sigma_2} h^{(2)}_{\sigma_1 \sigma_2}(r_1, r_2) \phi(r_{12}) \\
+ \frac{1}{2} \beta q_3 e_{\sigma_1} h^{(2)}_{\sigma_1 \sigma_2}(r_1, r_2) r_{12}^2 - \frac{1}{2} (d - 2) c_d \beta \\
\times \left[ \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1} \int dr_3 \, h^{(3)}_{\sigma_1 \sigma_2 \sigma_3}(r_1, r_2, r_3) + \left( e_{\sigma_1}^2 + e_{\sigma_2}^2 \right) h^{(2)}_{\sigma_1 \sigma_2}(r_1, r_2) \right].
\]
(C.6)

This rather complicated identity has been used in appendix B. Inspection of the terms at the right-hand side shows that for large \( r_{12} \) each of these vanishes faster than any inverse power of \( r_{12} \), as it should be in view of the short-range character of the four-point Ursell function at the left-hand side.

For \( d > 2 \) the above identities may be simplified by putting \( c_d = 0 \). That choice is not allowed when one is interested in the limit \( d \to 2 \). In that case one takes \( c_d \) according to (2.3). In the limit \( d \to 2 \) the left-hand side of the identity (C.2) vanishes, so that we get an identity that connects the zeroth and second moments of the two-particle Ursell
function,
\[
\beta q_0 \sum_{\sigma_2} n_{\sigma_1} e_{\sigma_2} \int \mathrm{d}r_2 h_{\sigma_1\sigma_2}^{(2)}(r_1, r_2) r_2^2 = 4 \sum_{\sigma_2} n_{\sigma_1} e_{\sigma_2} \int \mathrm{d}r_2 h_{\sigma_1\sigma_2}^{(2)}(r_1, r_2)
\]
\[
- \frac{\beta}{2\pi} \left\{ \sum_{\sigma_2} n_{\sigma_1} e_{\sigma_2}^2 \int \mathrm{d}r_2 h_{\sigma_1\sigma_2}^{(2)}(r_1, r_2) + e_{\sigma_1}^2 \right\}.
\]

(C.7)

It should be noted that the last two terms would have been missed when in (C.2) the limit \( d \to 2 \) had been taken naively after putting \( c_d = 0 \). The identity (C.7), which is valid for the special case \( d = 2 \) only, has been obtained recently [6]. Upon substituting (5.3) into the right-hand side and using (A.10) we recover (5.8) for \( d = 2 \). In fact, this shows that for \( d = 2 \) the second-moment sum rule (5.8) can be derived from perfect screening, symmetry and thermodynamics alone, without having recourse to the rather complicated expression for the derivative \( \partial n_{\sigma}/\partial \beta \) of the partial density with respect to the inverse temperature. The latter expression is essential in deriving the second-moment sum rule for arbitrary \( d > 2 \).

Similarly, for \( d \to 2 \) the symmetry relation (C.4) reduces to an identity connecting the second and fourth moments of the two-particle Ursell function,
\[
\beta q_0 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} e_{\sigma_2} \int \mathrm{d}r_2 h_{\sigma_1\sigma_2}^{(2)}(r_1, r_2) r_2^2 = 16 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} e_{\sigma_2} e_{\sigma_1} \int \mathrm{d}r_2 h_{\sigma_1\sigma_2}^{(2)}(r_1, r_2) r_2^2
\]
\[
- \frac{2\beta}{\pi} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} e_{\sigma_2}^2 e_{\sigma_1} \int \mathrm{d}r_2 h_{\sigma_1\sigma_2}^{(2)}(r_1, r_2) r_2^2.
\]

(C.8)

The last term is missed when one puts \( c_d = 0 \) in (C.4) before taking the limit \( d \to 2 \). Substituting (5.8) and using the equation of state (4.7) we are led to (6.6) for \( d = 2 \). Hence, in a similar way as discussed above for the second-moment sum rule, the derivation of the fourth-moment sum rule can be simplified for the special case \( d = 2 \). For that case it is enough to make use of the perfect-screening and second-moment rules, symmetry properties and thermodynamical relations in the proof, whereas for general \( d \) the derivative \( \partial h_{\sigma_1\sigma_2}^{(2)}/\partial \beta \) of the two-particle Ursell function with respect to the inverse temperature needs to be determined.

Incidentally, we remark that for the one-component case the identity (C.8) has been obtained before [24].

We are left with (C.6) in the limit \( d \to 2 \). The resulting identity is rather complicated and is not needed in the main text, so that we refrain from writing it down.

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