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

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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 $\sigma = 1, \dots, s$, in a large volume V . The N_σ particles of species σ carry mass m_σ and positive charge e_σ . 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 ϕ depending on the distance $r = |\mathbf{r}|$ is proportional to $1/r^{d-2}$. It is the solution of the d -dimensional inhomogeneous Laplace equation $\Delta\phi(r) = -\delta(\mathbf{r})$, with Δ the d -dimensional Laplace operator and $\delta(\mathbf{r})$ 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

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

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 $d = 3$ 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 ϕ that solves the two-dimensional Laplace equation is logarithmic,

$$\phi(r) = -\frac{1}{2\pi} \log(r) + c, \quad (2.2)$$

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 $d \rightarrow 2$, if c_d is chosen as

$$c_d = -\frac{\Gamma(d/2 - 1)}{4\pi^{d/2}} + c. \quad (2.3)$$

Indeed, in the limit $d \rightarrow 2$ one finds

$$\lim_{d \rightarrow 2} \phi(r) = \lim_{d \rightarrow 2} \frac{\Gamma(d/2 - 1)}{4\pi^{d/2}} \left(\frac{1}{r^{d-2}} - 1 \right) + c = -\frac{1}{2\pi} \log(r) + c. \quad (2.4)$$

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 ,

$$\begin{aligned} H = T + U &= \sum_{\sigma\alpha} \frac{p_{\sigma\alpha}^2}{2m_\sigma} + \frac{1}{2} \sum'_{\sigma_1\alpha_1, \sigma_2\alpha_2} e_{\sigma_1} e_{\sigma_2} \phi(|\mathbf{r}_{\sigma_1\alpha_1} - \mathbf{r}_{\sigma_2\alpha_2}|) \\ &\quad - q_v \sum_{\sigma\alpha} e_\sigma \int^V d\mathbf{r} \phi(|\mathbf{r}_{\sigma\alpha} - \mathbf{r}|) + \frac{1}{2} q_v^2 \int^V d\mathbf{r} d\mathbf{r}' \phi(|\mathbf{r} - \mathbf{r}'|). \end{aligned} \quad (2.5)$$

The particle α of species σ has position $\mathbf{r}_{\sigma\alpha}$ and momentum $\mathbf{p}_{\sigma\alpha}$. The prime at the summation sign indicates the condition $\sigma_1\alpha_1 \neq \sigma_2\alpha_2$, 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 $g_{\sigma_1 \dots \sigma_k}^{(k)}$ satisfy the BGY hierarchy equations [2]

$$\begin{aligned} \frac{\partial}{\partial \mathbf{r}_1} g_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) &= -\beta e_{\sigma_1} g_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k) \sum_{j=2}^k e_{\sigma_j} \frac{\partial}{\partial \mathbf{r}_1} \phi(|\mathbf{r}_1 - \mathbf{r}_j|) \\ &\quad - \beta e_{\sigma_1} \sum_{\sigma_{k+1}} n_{\sigma_{k+1}} e_{\sigma_{k+1}} \int^V d\mathbf{r}_{k+1} [g_{\sigma_1 \dots \sigma_{k+1}}^{(k+1)}(\mathbf{r}_1, \dots, \mathbf{r}_{k+1}) - g_{\sigma_1 \dots \sigma_k}^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k)] \\ &\quad \times \frac{\partial}{\partial \mathbf{r}_1} \phi(|\mathbf{r}_1 - \mathbf{r}_{k+1}|), \end{aligned} \quad (3.1)$$

with $\beta = (k_B T)^{-1}$ the inverse temperature and $n_\sigma = \langle N_\sigma \rangle / V$ the average particle density of species σ . The correlation functions can be expanded in terms of Ursell functions $h_{\sigma_1 \dots \sigma_k}^{(k)}$ [18, 19]. In particular, the two-particle Ursell function $h_{\sigma_1 \sigma_2}^{(2)}$ is defined as $g_{\sigma_1 \sigma_2}^{(2)} - 1$. For large V the Ursell functions are translationally invariant, so that they depend on the difference between the positions only. In the following we shall assume that the Ursell functions satisfy the standard exponential clustering hypothesis, which implies that they tend to zero faster than any power if the separation between two positions goes to infinity.

For $k = 2$, the hierarchy equation reads in terms of the Ursell functions

$$\begin{aligned} \beta e_{\sigma_1} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_1} &= - \frac{\partial h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} \\ &- \beta e_{\sigma_1} \frac{\partial}{\partial \mathbf{r}_1} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_2\sigma_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3) \phi(r_{13}) \\ &- \beta e_{\sigma_1} e_{\sigma_2} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} - \beta e_{\sigma_1} e_{\sigma_2} \frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} \end{aligned} \quad (3.2)$$

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]

$$\phi(|\mathbf{r} - \mathbf{r}'|) = \phi(r) + \frac{\Gamma(d/2 - 1)}{4\pi^{d/2} r^{d-2}} \sum_{\ell=1}^{\infty} C_{\ell}^{(d-2)/2}(\cos \theta) \left(\frac{r'}{r}\right)^{\ell} \quad (3.3)$$

with $d > 2$. Here θ 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

$$\frac{\partial}{\partial \mathbf{r}_1} \int d\mathbf{r}_3 h_{\sigma_2\sigma_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3) \phi(r_{13}) = \frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} \int_{r_{23} < r_{12}} d\mathbf{r}_3 h_{\sigma_2\sigma_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3). \quad (3.4)$$

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 Ursell function of a general d -dimensional ionic mixture,

$$\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -e_{\sigma_1}. \quad (3.5)$$

Similarly, by using the Gegenbauer expansion and the exponential clustering property one derives from the hierarchy equations for $k = 3$ the perfect-screening rules,

$$\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = -(e_{\sigma_1} + e_{\sigma_2}) h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (3.6)$$

$$\begin{aligned} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{13}^{\ell} C_{\ell}^{(d-2)/2}(\cos \theta) \\ = - \frac{(d-2)_{\ell}}{\ell!} e_{\sigma_2} r_{12}^{\ell} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (\ell = 1, 2, \dots), \end{aligned} \quad (3.7)$$

with θ 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],

$$\lim_{\lambda \rightarrow 0} \frac{1}{\lambda} C_{\ell}^{\lambda}(x) = \frac{2}{\ell} T_{\ell}(x) \quad (3.8)$$

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 $d \rightarrow 2$ the standard expansion of the logarithmic potential [20]. The perfect-screening rule (3.7) becomes upon taking the limit $d \rightarrow 2$,

$$\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{13}^{\ell} T_{\ell}(\cos \theta) = -e_{\sigma_2} r_{12}^{\ell} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (\ell = 1, 2, \dots), \quad (3.9)$$

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 \mathbf{r}_{12} and integrating over \mathbf{r}_2 ,

$$\begin{aligned} \beta e_{\sigma_1} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \mathbf{r}_{12} \cdot \frac{\partial \phi(r_{13})}{\partial \mathbf{r}_1} \\ = -\frac{1}{2} \beta e_{\sigma_1} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_2\sigma_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3) r_{23}^2 \\ + (d-2) \beta e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \phi(r_{12}) \\ + [d - (d-2)c_d \beta e_{\sigma_1} e_{\sigma_2}] \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (3.10)$$

On the other hand, from (3.7) for $\ell = 1$ one gets after multiplication by r_{12}^{-d} and integration over \mathbf{r}_2 ,

$$\begin{aligned} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \mathbf{r}_{13} \cdot \frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} \\ = (d-2) e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \phi(r_{12}) - (d-2) c_d e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (3.11)$$

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

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 = -\frac{2d}{\beta}. \quad (3.12)$$

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 $d \rightarrow 2$ 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 $d \rightarrow 2$. The form of (3.12) for $d \rightarrow 2$ 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 $\sum_{\sigma} e_{\sigma} N_{\sigma} = q_v V$. Its partition function Z depends on the volume V , the inverse temperature β , the background charge density q_v and $s - 1$ chemical potentials $\tilde{\mu}_{\sigma}$ ($\sigma \neq 1$). In the limit of an infinite system, the partition function leads to a thermodynamic function \tilde{p} that is defined by writing

$$\lim_{V \rightarrow \infty} \frac{1}{V} \log Z(\beta, \{\beta \tilde{\mu}_{\sigma}\}, q_v, V) = \beta \tilde{p}(\beta, \{\beta \tilde{\mu}_{\sigma}\}, q_v). \quad (4.1)$$

The energy density u_v and the particle densities n_σ for $\sigma \neq 1$ follow by taking derivatives

$$u_v = -\frac{\partial \beta \tilde{p}}{\partial \beta}, \quad n_\sigma = \frac{\partial \beta \tilde{p}}{\partial \beta \tilde{\mu}_\sigma} \quad (\sigma = 2, \dots, s). \quad (4.2)$$

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

$$p = \tilde{p} - q_v \frac{\partial \tilde{p}}{\partial q_v} \quad (4.3)$$

as is proved in appendix A.

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

$$U(\mathbf{r}^{N_1}, \dots, \mathbf{r}^{N_s}, V) = \lambda^{d-2} U(\lambda \mathbf{r}^{N_1}, \dots, \lambda \mathbf{r}^{N_s}, \lambda^d V) + \frac{1}{2} (\lambda^{d-2} - 1) c_d \sum_{\sigma} N_{\sigma} e_{\sigma}^2 \quad (4.4)$$

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

$$p = \frac{d-2}{d} u_v - \frac{1}{2} (d-4) \frac{n}{\beta} + \frac{d-2}{2d} c_d \sum_{\sigma} n_{\sigma} e_{\sigma}^2 \quad (4.5)$$

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

The partition function Z , and hence \tilde{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_{σ} , as (2.5) shows. Hence, the chemical potentials $\tilde{\mu}_{\sigma}$ (with $\sigma \neq 1$) change as well when a different value for c_d is chosen. However, the combination $\tilde{\mu}_{\sigma} + \frac{1}{2} c_d e_{\sigma} (e_{\sigma} - e_1)$ is found to be invariant. Of course, the partial densities n_{σ} 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,

$$p = \frac{n}{\beta} + p^{\text{pot}}, \quad u_v = \frac{dn}{2\beta} + u_v^{\text{pot}}. \quad (4.6)$$

According to (4.5) the potential parts of the pressure and the energy density are related as $p^{\text{pot}} = [(d-2)/d](u_v^{\text{pot}} + \frac{1}{2} c_d \sum_{\sigma} n_{\sigma} e_{\sigma}^2)$. 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 $d \rightarrow 2$ one should choose c_d according to (2.3). With that choice the energy density u_v stays finite for $d \rightarrow 2$. 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

$$p = \frac{n}{\beta} - \frac{1}{8\pi} \sum_{\sigma} n_{\sigma} e_{\sigma}^2, \quad (4.7)$$

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 $d \rightarrow 2$. For instance, choosing $c_d = 0$ in (4.5) and taking the limit naively, without realizing that u_v 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_{σ_1} with respect to the chemical potential combination $\beta\tilde{\mu}_{\sigma_2}$ is given by

$$\frac{Dn_{\sigma_1}}{D\beta\tilde{\mu}_{\sigma_2}} = \frac{1}{V}\langle N_{\sigma_1}N_{\sigma_2} \rangle - \frac{1}{V}\langle N_{\sigma_1} \rangle \langle N_{\sigma_2} \rangle, \quad (5.1)$$

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

$$\frac{D}{D\beta\tilde{\mu}_{\sigma}} = (1 - \delta_{\sigma_1}) \frac{\partial}{\partial\beta\tilde{\mu}_{\sigma}} - \delta_{\sigma_1} \sum_{\sigma' \neq 1} \frac{e_{\sigma'}}{e_1} \frac{\partial}{\partial\beta\tilde{\mu}_{\sigma'}}. \quad (5.2)$$

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

$$n_{\sigma_1}n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{Dn_{\sigma_1}}{D\beta\tilde{\mu}_{\sigma_2}} - n_{\sigma_1}\delta_{\sigma_1\sigma_2}. \quad (5.3)$$

Upon summation over σ_2 , with the weights e_{σ_2} , one recovers the perfect-screening rule (3.5). Taking an unweighted sum over σ_2 and using (A.8) to eliminate the derivative of the particle density n we find the equality

$$\begin{aligned} \frac{1}{2}d(d-4)n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= -(d-2)\beta \frac{\partial n_{\sigma_1}}{\partial\beta} + dq_v \frac{\partial n_{\sigma_1}}{\partial q_v} \\ &- \frac{1}{2}d(d-2)n_{\sigma_1} + \frac{1}{2}(d-2)c_d\beta \frac{D}{D\beta\tilde{\mu}_{\sigma_1}} \left(\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2}^2 \right). \end{aligned} \quad (5.4)$$

This zeroth-moment sum rule is independent of the perfect-screening sum rule. Like that rule it is valid for each species σ_1 separately. If an unweighted sum over σ_1 is carried out, one arrives at a less strong sum rule of the form

$$\begin{aligned} \frac{1}{2}d(d-4) \sum_{\sigma_1, \sigma_2} n_{\sigma_1}n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= -(d-2)\beta \frac{\partial n}{\partial\beta} + dq_v \frac{\partial n}{\partial q_v} \\ &- \frac{1}{2}d(d-2)n + \frac{1}{2}(d-2)c_d\beta \sum_{\sigma_1} e_{\sigma_1}^2 \frac{Dn}{D\beta\tilde{\mu}_{\sigma_1}}. \end{aligned} \quad (5.5)$$

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_{σ} with respect to the inverse temperature β reads

$$\frac{\partial n_{\sigma}}{\partial\beta} = -\frac{1}{V}\langle N_{\sigma}H \rangle + \frac{1}{V}\langle N_{\sigma} \rangle \langle H \rangle. \quad (5.6)$$

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,

$$\begin{aligned}
(d-2)\beta \frac{\partial n_{\sigma_1}}{\partial \beta} &= -\frac{1}{2}\beta q_v n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 \\
&\quad - \frac{1}{2}d(d-4)n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2}d(d-2)n_{\sigma_1} \\
&\quad + \frac{1}{2}(d-2)c_d \beta n_{\sigma_1} \left[\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2}^2 \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + e_{\sigma_1}^2 \right]. \tag{5.7}
\end{aligned}$$

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

$$n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 = -\frac{2d}{\beta} \frac{\partial n_{\sigma_1}}{\partial q_v}. \tag{5.8}$$

Summing over σ_1 with the weights e_{σ_1} one recovers the Stillinger–Lovett rule (3.12). Taking the sum with equal weights we get the second-moment identity

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 = -\frac{2d}{\beta} \frac{\partial n}{\partial q_v}, \tag{5.9}$$

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 $d \rightarrow 2$. The zeroth-order sum rule (5.3) retains the same form, whereas the sum rules (5.4) and (5.5) become

$$n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -q_v \frac{\partial n_{\sigma_1}}{\partial q_v} + \frac{\beta}{8\pi} \frac{D}{D\beta \tilde{\mu}_{\sigma_1}} \left(\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2}^2 \right) \tag{5.10}$$

and

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -q_v \frac{\partial n}{\partial q_v} + \frac{\beta}{8\pi} \sum_{\sigma_1} e_{\sigma_1}^2 \frac{Dn}{D\beta \tilde{\mu}_{\sigma_1}}. \tag{5.11}$$

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 $d \rightarrow 2$. 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,

$$\begin{aligned}
(d-2)\beta \frac{\partial}{\partial \beta} [n_{\sigma_1} n_{\sigma_2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)] &= -\frac{1}{2} \beta q_v n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{23}^2 \\
&\quad - \frac{1}{2} d(d-4) n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - n_{\sigma_1} n_{\sigma_2} \mathbf{r}_{12} \cdot \frac{\partial}{\partial \mathbf{r}_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\
&\quad - \frac{1}{2} \beta q_v n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 - d(d-2) n_{\sigma_1} n_{\sigma_2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\
&\quad + \frac{1}{2} (d-2) c_d \beta n_{\sigma_1} n_{\sigma_2} \left[\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3}^2 \int d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right. \\
&\quad \left. + (e_{\sigma_1}^2 + e_{\sigma_2}^2) h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \right]. \tag{6.1}
\end{aligned}$$

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 \mathbf{r}_2 and summing over σ_1 and σ_2 , we get an expression for the derivative of the potential-energy density (B.1),

$$\begin{aligned}
2(d-2)\beta \frac{\partial u_v^{\text{pot}}}{\partial \beta} &= -\frac{1}{2} \beta q_v \sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{23}^2 \phi(r_{12}) \\
&\quad - \frac{1}{2} d(d-4) \sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \phi(r_{12}) \\
&\quad - \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 \mathbf{r}_{12} \cdot \left[\frac{\partial}{\partial \mathbf{r}_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \right] \phi(r_{12}) \\
&\quad - \frac{1}{2} \beta q_v \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 \phi(r_{12}) - 2d(d-2) u_v^{\text{pot}} \\
&\quad + \frac{1}{2} (d-2) c_d \beta \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \left[\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3}^2 \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \phi(r_{12}) \right. \\
&\quad \left. + (e_{\sigma_1}^2 + e_{\sigma_2}^2) \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \phi(r_{12}) \right]. \tag{6.2}
\end{aligned}$$

The first term at the right-hand side can be expressed in moments of the two-particle Ursell functions by using the relation (C.4), 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

$$\mathbf{r}_{12} \cdot \frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} = -(d-2)\phi(r_{12}) + (d-2)c_d. \tag{6.3}$$

As a result we arrive at a relation involving the zeroth, the second and the fourth moments of the two-particle Ursell function,

$$\begin{aligned}
d\beta^2 q_v^2 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^4 \\
+ 2d(d-6)(d+2)\beta q_v \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 \\
- 4d^2(d-4)(d+2) \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)
\end{aligned}$$

$$\begin{aligned}
 &= -8(d-2)^2(d+2)\beta^2 \frac{\partial u_v^{\text{pot}}}{\partial \beta} - 16(d-1)(d-2)(d+2)\beta u_v^{\text{pot}} \\
 &+ 2(d-2)(d+2)c_d\beta \left[2\beta q_v \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 \right. \\
 &+ d(d-6) \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + (d^2 - 6d + 4) \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1}^2 \left. \right] \\
 &- 2(d-2)^2(d+2)c_d^2\beta^2 \left[\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 e_{\sigma_2}^2 \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \sum_{\sigma_1} n_{\sigma_1} e_{\sigma_1}^4 \right].
 \end{aligned} \tag{6.4}$$

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,

$$\begin{aligned}
 &d\beta^2 q_v^2 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^4 \\
 &= -8(d-2)^2(d+2)\beta^2 \frac{\partial u_v}{\partial \beta} - 16(d-1)(d-2)(d+2)\beta u_v \\
 &+ 4d(d-2)(d-4)(d+2)\beta \frac{\partial n}{\partial \beta} + 4d^2(d-4)(d+2)q_v \frac{\partial n}{\partial q_v} \\
 &- 4(d-2)(d+2)c_d\beta \left[(d-2)\beta \frac{\partial}{\partial \beta} + dq_v \frac{\partial}{\partial q_v} + d - 2 \right] \left(\sum_{\sigma} n_{\sigma} e_{\sigma}^2 \right).
 \end{aligned} \tag{6.5}$$

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

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^4 = -\frac{8d(d+2)}{\beta q_v} \frac{\partial p}{\partial q_v}. \tag{6.6}$$

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 $d \rightarrow 2$ 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 $d \rightarrow 2$. 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 $\partial h_{\sigma_1 \sigma_2}^{(2)} / \partial \beta$ 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 $h_{\sigma_1\sigma_2}^{(2)}$ with $g_{\sigma_1\sigma_2}^{(2)} - 1$. 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 $\sigma = 2, \dots, s$) 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 β —the chemical potentials $\{\mu_\sigma\}$ with $\sigma = 1, \dots, s$, 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,

$$n_{\sigma_1}n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\beta} \left(\frac{\partial n_{\sigma_1}}{\partial \mu_{\sigma_2}} - \frac{1}{S} \frac{\partial q_v}{\partial \mu_{\sigma_1}} \frac{\partial q_v}{\partial \mu_{\sigma_2}} \right) - n_{\sigma_1} \delta_{\sigma_1\sigma_2} \tag{7.1}$$

$$n_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 = -\frac{2d}{\beta S} \frac{\partial q_v}{\partial \mu_{\sigma_1}} \tag{7.2}$$

$$\sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^4 = -\frac{8d(d+2)}{\beta S}, \tag{7.3}$$

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

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

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 $d \rightarrow 2$,

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

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 $d \geq 2$.

Furthermore, we want to derive the relation (4.3) between the 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 $\sigma = 2, \dots, s$) and constant total background charge $q_v V$,

$$p = -\left(\frac{\partial F(T, \{n_{\sigma}\}, q_v, V)}{\partial V}\right)_{T, \{n_{\sigma} V\}, q_v V}. \quad (\text{A.3})$$

Taking account of the implicit dependence on V we get

$$p = -f_v + \sum_{\sigma(\neq 1)} n_{\sigma} \left(\frac{\partial f_v}{\partial n_{\sigma}}\right)_{T, \{n_{\sigma'}\}, q_v} + q_v \left(\frac{\partial f_v}{\partial q_v}\right)_{T, \{n_{\sigma}\}}, \quad (\text{A.4})$$

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]

$$df_v = -s_v dT + \sum_{\sigma(\neq 1)} \tilde{\mu}_{\sigma} dn_{\sigma} + \tilde{\mu}_q dq_v \quad (\text{A.5})$$

$$\tilde{p} = -f_v + \sum_{\sigma(\neq 1)} \tilde{\mu}_{\sigma} n_{\sigma}, \quad (\text{A.6})$$

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

$$p = -f_v + \sum_{\sigma(\neq 1)} \tilde{\mu}_{\sigma} n_{\sigma} + \tilde{\mu}_q q_v. \quad (\text{A.7})$$

Comparison of (A.6) and (A.7) yields the relation between \tilde{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 β and q_v , we get

$$(d-2)\beta\frac{\partial n_\sigma}{\partial\beta} = dq_v\frac{\partial n_\sigma}{\partial q_v} - dn_\sigma - \frac{1}{2}d(d-4)\frac{Dn}{D\beta\tilde{\mu}_\sigma} + \frac{1}{2}(d-2)c_d\beta\frac{D}{D\beta\tilde{\mu}_\sigma}\left(\sum_{\sigma'}n_{\sigma'}e_{\sigma'}^2\right), \quad (\text{A.8})$$

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

$$(d-2)\beta\frac{\partial u_v}{\partial\beta} = dq_v\frac{\partial u_v}{\partial q_v} - 2(d-1)u_v + \frac{1}{2}d(d-4)\frac{\partial n}{\partial\beta} - \frac{1}{2}(d-2)c_d\left(1+\beta\frac{\partial}{\partial\beta}\right)\left(\sum_{\sigma}n_{\sigma}e_{\sigma}^2\right). \quad (\text{A.9})$$

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 $d \rightarrow 2$ 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 $d = 2$,

$$q_v\frac{\partial n_\sigma}{\partial q_v} - n_\sigma + \frac{D}{D\beta\tilde{\mu}_\sigma}\left(n - \frac{\beta}{8\pi}\sum_{\sigma'}n_{\sigma'}e_{\sigma'}^2\right) = 0 \quad (\text{A.10})$$

and

$$q_v\frac{\partial u_v}{\partial q_v} - u_v - \frac{\partial n}{\partial\beta} + \frac{1}{8\pi}\left(1+\beta\frac{\partial}{\partial\beta}\right)\left(\sum_{\sigma}n_{\sigma}e_{\sigma}^2\right) = 0. \quad (\text{A.11})$$

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 β . The derivative of n_σ with respect to β follows by evaluating its formal expression: $\partial n_\sigma/\partial\beta = -\langle N_\sigma H \rangle/V + \langle N_\sigma \rangle \langle H \rangle/V$. The average $\langle H \rangle$ of the Hamiltonian is proportional to the internal energy u_v , which is the sum of a kinetic and a potential part of the form (4.6). The latter can be written as an integral over the two-particle Ursell function

$$u_v^{\text{pot}} = \frac{1}{2}\sum_{\sigma_1, \sigma_2}n_{\sigma_1}n_{\sigma_2}e_{\sigma_1}e_{\sigma_2}\int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\phi(r_{12}). \quad (\text{B.1})$$

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

$$\begin{aligned} \beta\frac{\partial n_{\sigma_1}}{\partial\beta} &= -\frac{1}{2}\beta n_{\sigma_1}\sum_{\sigma_2, \sigma_3}n_{\sigma_2}n_{\sigma_3}e_{\sigma_2}e_{\sigma_3}\int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\phi(r_{23}) \\ &\quad - \beta n_{\sigma_1}e_{\sigma_1}\sum_{\sigma_2}n_{\sigma_2}e_{\sigma_2}\int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\phi(r_{12}) \\ &\quad - \frac{1}{2}dn_{\sigma_1}\sum_{\sigma_2}n_{\sigma_2}\int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2}dn_{\sigma_1}. \end{aligned} \quad (\text{B.2})$$

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 β . In the restricted grand-canonical ensemble one has quite generally $\partial\langle f \rangle/\partial\beta = -\langle fH \rangle + \langle f \rangle\langle H \rangle$ for an arbitrary phase function f . Taking $f = \sum_{\alpha_1, \alpha_2} \delta(\mathbf{r}_1 - \mathbf{r}_{\sigma_1\alpha_1})\delta(\mathbf{r}_2 - \mathbf{r}_{\sigma_2\alpha_2})$ and using (2.5) one derives

$$\begin{aligned}
\beta \frac{\partial}{\partial\beta} [n_{\sigma_1} n_{\sigma_2} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2)] &= -\frac{1}{2} \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} e_{\sigma_3} e_{\sigma_4} \\
&\times \int d\mathbf{r}_3 d\mathbf{r}_4 h_{\sigma_1\sigma_2\sigma_3\sigma_4}^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \phi(r_{34}) \\
&- \frac{1}{2} dn_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\
&- \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 h_{\sigma_1\sigma_2\sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) [e_{\sigma_1} \phi(r_{13}) + e_{\sigma_2} \phi(r_{23})] \\
&- dn_{\sigma_1} n_{\sigma_2} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \beta n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \phi(r_{12}) \\
&- \frac{1}{2} \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} e_{\sigma_3} e_{\sigma_4} \int d\mathbf{r}_3 d\mathbf{r}_4 [h_{\sigma_1\sigma_3}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) h_{\sigma_2\sigma_4}^{(2)}(\mathbf{r}_2, \mathbf{r}_4) \\
&+ h_{\sigma_1\sigma_4}^{(2)}(\mathbf{r}_1, \mathbf{r}_4) h_{\sigma_2\sigma_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3)] \phi(r_{34}) \\
&- \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int d\mathbf{r}_3 [e_{\sigma_1} h_{\sigma_2\sigma_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3) \phi(r_{13}) + e_{\sigma_2} h_{\sigma_1\sigma_3}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) \phi(r_{23})] \\
&- \beta n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \phi(r_{12}). \tag{B.3}
\end{aligned}$$

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 $h_{\sigma_1\sigma_2}^{(2)}$ 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,

$$\begin{aligned}
&-\frac{\beta}{d-2} n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} e_{\sigma_3} e_{\sigma_4} \int d\mathbf{r}_3 h_{\sigma_1\sigma_3}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) \mathbf{r}_{13} \cdot \frac{\partial\phi(r_{23})}{\partial\mathbf{r}_2} \int_{r_{24}>r_{23}} d\mathbf{r}_4 h_{\sigma_2\sigma_4}^{(2)}(\mathbf{r}_2, \mathbf{r}_4) \\
&+ \beta n_{\sigma_1} n_{\sigma_2} \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} e_{\sigma_3} e_{\sigma_4} \int d\mathbf{r}_3 h_{\sigma_2\sigma_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3) [\phi(r_{13}) - c_d] \int_{r_{14}>r_{13}} d\mathbf{r}_4 h_{\sigma_1\sigma_4}^{(2)}(\mathbf{r}_1, \mathbf{r}_4) \\
&+ \beta n_{\sigma_1} n_{\sigma_2} e_{\sigma_2} [\phi(r_{12}) - c_d] \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int_{r_{13}>r_{12}} d\mathbf{r}_3 h_{\sigma_1\sigma_3}^{(2)}(\mathbf{r}_1, \mathbf{r}_3). \tag{B.4}
\end{aligned}$$

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 \mathbf{r}_i and their component labels σ_i . From that symmetry one proves

$$\begin{aligned} (d-2) \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) [\phi(r_{23}) - c_d] \\ = 2 \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \mathbf{r}_{12} \cdot \frac{\partial \phi(r_{23})}{\partial \mathbf{r}_2}. \end{aligned} \quad (\text{C.1})$$

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

$$\begin{aligned} (d-2)\beta \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \phi(r_{23}) \\ + 2(d-2)\beta e_{\sigma_1} \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \phi(r_{12}) \\ = \beta q_v \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 - 2d \sum_{\sigma_2} n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\ - (d-2)c_d \beta \left[\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2}^2 \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + e_{\sigma_1}^2 \right], \end{aligned} \quad (\text{C.2})$$

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

$$\begin{aligned} (d-2) \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) [\phi(r_{23}) - c_d] \\ \times [r_{12}^2 + \mathbf{r}_{12} \cdot \mathbf{r}_{23} + 2r_{23}^{-2}(\mathbf{r}_{12} \cdot \mathbf{r}_{23})^2] \\ = 2 \sum_{\sigma_2, \sigma_3} n_{\sigma_2} n_{\sigma_3} e_{\sigma_2} e_{\sigma_3} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{12}^2 \mathbf{r}_{12} \cdot \frac{\partial \phi(r_{23})}{\partial \mathbf{r}_2}. \end{aligned} \quad (\text{C.3})$$

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 σ_1 with weights $n_{\sigma_1} e_{\sigma_1}$ is carried out as well. In this way, we arrive at the identity

$$\begin{aligned} (d-2)\beta \sum_{\sigma_1, \sigma_2, \sigma_3} n_{\sigma_1} n_{\sigma_2} n_{\sigma_3} e_{\sigma_1} e_{\sigma_2} e_{\sigma_3} \int d\mathbf{r}_2 d\mathbf{r}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{23}^2 \phi(r_{12}) \\ + (d-2)\beta \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 \phi(r_{12}) \\ = \frac{d}{2(d+2)} \beta q_v \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^4 \\ - 2d \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 \\ - (d-2)c_d \beta \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 \end{aligned} \quad (\text{C.4})$$

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),

$$(d-2) \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} e_{\sigma_3} e_{\sigma_4} \int \mathbf{dr}_3 \mathbf{dr}_4 h_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) [\phi(r_{34}) - c_d] \\ = 2 \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} e_{\sigma_3} e_{\sigma_4} \int \mathbf{dr}_3 \mathbf{dr}_4 h_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \mathbf{r}_{13} \cdot \frac{\partial \phi(r_{34})}{\partial \mathbf{r}_3}. \quad (\text{C.5})$$

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_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} e_{\sigma_3} e_{\sigma_4} \int \mathbf{dr}_3 \mathbf{dr}_4 h_{\sigma_1 \sigma_2 \sigma_3 \sigma_4}^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \phi(r_{34}) \\ = -(d-2)\beta \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int \mathbf{dr}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) [e_{\sigma_1} \phi(r_{13}) + e_{\sigma_2} \phi(r_{23})] \\ + \frac{1}{2} \beta q_v \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int \mathbf{dr}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{23}^2 \\ - d \sum_{\sigma_3} n_{\sigma_3} \int \mathbf{dr}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + \mathbf{r}_{12} \cdot \frac{\partial}{\partial \mathbf{r}_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\ - \beta \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} e_{\sigma_3} e_{\sigma_4} \int \mathbf{dr}_3 h_{\sigma_1 \sigma_3}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) \mathbf{r}_{13} \cdot \frac{\partial \phi(r_{23})}{\partial \mathbf{r}_2} \int_{r_{24} > r_{23}} \mathbf{dr}_4 h_{\sigma_2 \sigma_4}^{(2)}(\mathbf{r}_2, \mathbf{r}_4) \\ + (d-2)\beta \sum_{\sigma_3, \sigma_4} n_{\sigma_3} n_{\sigma_4} e_{\sigma_3} e_{\sigma_4} \int \mathbf{dr}_3 h_{\sigma_2 \sigma_3}^{(2)}(\mathbf{r}_2, \mathbf{r}_3) [\phi(r_{13}) - c_d] \\ \times \int_{r_{14} > r_{13}} \mathbf{dr}_4 h_{\sigma_1 \sigma_4}^{(2)}(\mathbf{r}_1, \mathbf{r}_4) + (d-2)\beta e_{\sigma_2} [\phi(r_{12}) - c_d] \\ \times \sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3} \int_{r_{13} > r_{12}} \mathbf{dr}_3 h_{\sigma_1 \sigma_3}^{(2)}(\mathbf{r}_1, \mathbf{r}_3) - (d-2)\beta e_{\sigma_1} e_{\sigma_2} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \phi(r_{12}) \\ + \frac{1}{2} \beta q_v e_{\sigma_1} h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 - \frac{1}{2} (d-2) c_d \beta \\ \times \left[\sum_{\sigma_3} n_{\sigma_3} e_{\sigma_3}^2 \int \mathbf{dr}_3 h_{\sigma_1 \sigma_2 \sigma_3}^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + (e_{\sigma_1}^2 + e_{\sigma_2}^2) h_{\sigma_1 \sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \right]. \quad (\text{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 equal to 0. That choice is not allowed when one is interested in the limit $d \rightarrow 2$. In that case one takes c_d according to (2.3). In the limit $d \rightarrow 2$ 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,

$$\beta q_v \sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 = 4 \sum_{\sigma_2} n_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \frac{\beta}{2\pi} \left[\sum_{\sigma_2} n_{\sigma_2} e_{\sigma_2}^2 \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + e_{\sigma_1}^2 \right]. \quad (\text{C.7})$$

It should be noted that the last two terms would have been missed when in (C.2) the limit $d \rightarrow 2$ 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 $d \rightarrow 2$ the symmetry relation (C.4) reduces to an identity connecting the second and fourth moments of the two-particle Ursell function,

$$\beta q_v \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^4 = 16 \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2 - \frac{2\beta}{\pi} \sum_{\sigma_1, \sigma_2} n_{\sigma_1} n_{\sigma_2} e_{\sigma_1}^2 e_{\sigma_2} \int d\mathbf{r}_2 h_{\sigma_1\sigma_2}^{(2)}(\mathbf{r}_1, \mathbf{r}_2) r_{12}^2. \quad (\text{C.8})$$

The last term is missed when one puts $c_d = 0$ in (C.4) before taking the limit $d \rightarrow 2$. 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 $d \rightarrow 2$. 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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