ASYMPTOTIC BEHAVIOUR OF CORRELATION FUNCTIONS FOR ELECTRIC POTENTIAL AND FIELD FLUCTUATIONS IN A CLASSICAL ONE-COMPONENT PLASMA

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Abstract

The correlations of the electric potential fluctuations in a classical one-component plasma are studied for large distances between the observation points. The two-point correlation function for these fluctuations is known to decay slowly for large distances, even if exponential clustering holds for the charge correlation functions. In this paper the asymptotic behaviour of the general k-point electric potential correlation functions is analyzed. Each of these correlation functions can be split into a reducible part, which is given by a sum of products of lower-order correlation functions, and a remaining irreducible part. It is shown, on the basis of an exponential clustering hypothesis for the charge correlation functions, that for all $k \geq 3$ the irreducible parts of the electric potential correlation functions decay faster than any inverse power of the distance, if one or more of the observation points move far away from the others. Hence, the two-point electric potential correlation function is the only one with a slow algebraic decay. The same statement holds for the correlation functions of the electric field fluctuations.

1 Introduction

The electric potential in a system of charged point particles is a nonlocal quantity that is determined by the charge distribution at positions both near to and distant from the point of observation. As a consequence one may expect that correlations of fluctuations in the electric potential at different observation points will persist even when these points are far apart. Indeed, it has been proved[1] that the two-point correlation function $W^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ that describes correlations in the fluctuations of the electric potential at the points $\mathbf{r}_1$ and $\mathbf{r}_2$ is a slowly decaying function of the distance $|\mathbf{r}_1 - \mathbf{r}_2|$, with an asymptotic behaviour inversely proportional to the distance. Likewise, the correlation function for the fluctuations in the electric field possesses a slowly decaying tail inversely proportional to the third power of the distance.

A more complete picture of the behaviour of the correlations of the electric potential fluctuations is gained by studying the higher-order correlation functions $W^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_k)$ for $k \geq 3$, which describe correlations of the electric potential fluctuations at k different observation points $\mathbf{r}_1, \ldots \mathbf{r}_k$. In particular, one may wonder whether these higher-order correlation functions possess slowly decaying tails as well, if one or more of the observation points move towards infinity. It is the purpose of the present paper to determine the asymptotic behaviour of the electric potential correlation functions $W^{(k)}$ for arbitrary k. The asymptotic form of the correlation functions for the electric field fluctuations then follows by differentiation.

As a model for the Coulomb system we shall adopt the classical one-component plasma, in which a set of identical charged particles move in an inert neutralizing background of opposite charge. The equilibrium properties of this system have been studied extensively[2]. In particular, so-called multipole sum rules have been established under the assumption that the charge correlation functions decay exponentially fast. In the following this exponential clustering will be assumed throughout.

2 Correlation functions for potential fluctuations

The general k-point equilibrium correlation function describing potential fluctuations in a one-component plasma is defined as

$$W^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_k) = \langle \delta\varphi(\mathbf{r}_1) \ldots \delta\varphi(\mathbf{r}_k) \rangle \quad , \tag{2.1}$$

for integer $k \geq 2$. Here $\delta\varphi(\mathbf{r}) \equiv \varphi(\mathbf{r}) - \langle \varphi(\mathbf{r}) \rangle$ is the fluctuation in the electric potential at the position $\mathbf{r}$. This potential is generated by the plasma particles of charge e and by the uniform background with charge density $-ne$. The brackets indicate a canonical ensemble average at an inverse temperature β. The correlation function $W^{(k)}$ as defined in (2.1) is meant to be the thermodynamical limit, with the number of plasma particles N and the volume V both tending to ∞ at fixed particle density $n = N/V$, of the corresponding finite-system function. The existence of this limit, a prerequisite for which is the presence of a neutralizing background, is taken for granted in the following.

By writing the electric potential in (2.1) in terms of their sources we get

$$W^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_k) = e^k \int d\mathbf{r}'_1 \ldots d\mathbf{r}'_k \frac{1}{4\pi|\mathbf{r}_1 - \mathbf{r}'_1|} \cdots \frac{1}{4\pi|\mathbf{r}_k - \mathbf{r}'_k|} D^{(k)}(\mathbf{r}'_1, \ldots, \mathbf{r}'_k) \quad . \tag{2.2}$$

Here the sources are described by the k-point density correlation function

$$D^{(k)}(\mathbf{r}'_1, \ldots, \mathbf{r}'_k) = \left\langle \left[\sum_{\alpha_1=1}^{N} \delta(\mathbf{r}'_1 - \mathbf{q}_{\alpha_1}) - n \right] \ldots \left[\sum_{\alpha_k=1}^{N} \delta(\mathbf{r}'_k - \mathbf{q}_{\alpha_k}) - n \right] \right\rangle \quad , \tag{2.3}$$

with $\mathbf{q}_\alpha$ the position vectors of the plasma particles. It should be noted that in the thermodynamic limit the average local particle density at the position $\mathbf{r}'_i$ is given by n.

The density function $D^{(k)}$ can be expanded in terms of Ursell functions $h^{(j)}$ of order $j \leq k$. A few examples are

$$D^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad = \quad n^2 h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + n\delta^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad , \tag{2.4}$$

$$
\begin{aligned}
D^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) &= n^3 h^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) + n^2 \Big[\delta^{(2)}(\mathbf{r}_1,\mathbf{r}_2)h^{(2)}(\mathbf{r}_1,\mathbf{r}_3) \\
&+ \delta^{(2)}(\mathbf{r}_1,\mathbf{r}_3)h^{(2)}(\mathbf{r}_1,\mathbf{r}_2) + \delta^{(2)}(\mathbf{r}_2,\mathbf{r}_3)h^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\Big] \\
&+ n\delta^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \quad , \qquad (2.5)
\end{aligned}
$$

where the generalized k-point delta function $\delta^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k)$ with $k \geq 2$ is defined as the (product of) delta function(s) $\delta(\mathbf{r}_1-\mathbf{r}_2)\ldots\delta(\mathbf{r}_1-\mathbf{r}_k)$. Incidentally, we remark that by definition $D^{(1)}(\mathbf{r}) = 0$.

The Ursell functions $h^{(k)}$ possess the cluster property: they are appreciably different from zero only if all their arguments are close together. As stated already in the introduction, we shall assume exponential clustering for the Ursell functions. Stated otherwise, they are supposed to decay faster than any inverse power of the distance, if one of the position variables is sent to infinity. Clearly, the density functions $D^{(k)}$ with $k = 2,3$, as given in (2.4)–(2.5), share this property. For higher k this is no longer true. In fact, $D^{(k)}$ for $k \geq 4$ contains contributions that are products of lower order $D^{(j)}$ functions with disjoint sets of position arguments. For general $k \geq 2$ we write $D^{(k)}$ as a sum of two terms:

$$
D^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k) = D^{(k)}_{\rm irr}(\mathbf{r}_1,\ldots,\mathbf{r}_k) + D^{(k)}_{\rm red}(\mathbf{r}_1,\ldots,\mathbf{r}_k) \quad . \qquad (2.6)
$$

The irreducible part $D^{(k)}_{\rm irr}$ has got the cluster property. It is a sum of terms of which the simplest are $n^k h^{(k)}$ and $n\delta^{(k)}$, as in (2.4)–(2.5). The remaining terms are products of one or more generalized delta function(s) and an Ursell function $h^{(p)}$ multiplied by n^p, with $2 \leq p \leq k-1$. These terms can be found by writing all partitions of the k labels of the position vectors occurring in $D^{(k)}_{\rm irr}$ in groups of arbitrary size. A generalized delta function is associated to each group of size two or higher, while a group of size 1 yields a factor 1. The arguments of the Ursell function are found by choosing one label from each group. With the formal definition $h^{(1)} \equiv 1$ all terms in $D^{(k)}_{\rm irr}$ follow in a unique way from the above recipe. Similar functions have been considered before[(3),(4)]. As an example we write the irreducible part of $D^{(4)}$:

$$
\begin{aligned}
D^{(4)}_{\rm irr}(\mathbf{r}_1,\ldots,\mathbf{r}_4) &= n^4 h^{(4)}(\mathbf{r}_1,\ldots,\mathbf{r}_4) \\
&+ n^3\Big[\delta^{(2)}(\mathbf{r}_1,\mathbf{r}_2)h^{(3)}(\mathbf{r}_1,\mathbf{r}_3,\mathbf{r}_4) + 5 \text{ terms}\Big] \\
&+ n^2\Big[\delta^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)h^{(2)}(\mathbf{r}_1,\mathbf{r}_4) + 3 \text{ terms}\Big] \\
&+ n^2\Big[\delta^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\,\delta^{(2)}(\mathbf{r}_3,\mathbf{r}_4)h^{(2)}(\mathbf{r}_1,\mathbf{r}_3) + 2 \text{ terms}\Big] \\
&+ n\delta^{(4)}(\mathbf{r}_1,\ldots,\mathbf{r}_4) \quad , \qquad (2.7)
\end{aligned}
$$

where the terms that are not written out explicitly follow by permutation of the indices.

Each partition of the labels $1,\ldots,k$ can be characterized by a set of non-negative integers $\{k_j\}$ such that k_j gives the number of groups of size j in the partition. Defining $S_p \equiv \sum_j k_j\, j^p$ for all non-negative integer p we have $S_1 = k$, while S_0 gives the number of groups in the partition. Hence, the irreducible part of $D^{(k)}$ can formally be written as

$$
D^{(k)}_{\rm irr} = \sum_{\{k_j\}}{}' \sum_{\rm perm} n^{S_0}\, h^{(S_0)} \prod_j \Big[\delta^{(j)}\Big]^{k_j} \quad , \qquad (2.8)
$$

where the prime at the summation symbol indicates the condition $S_1 = k$ and where we used the conventions $h^{(1)} \equiv 1$ and $\delta^{(1)} \equiv 1$. The symbol $\sum_{\rm perm}$ denotes a sum over the permutations that give rise to a reshuffling of the labels over the groups. Obviously, the number of these permutations for fixed values of $\{k_j\}$ is

$$\mathcal{N}_{\{k_j\}} = \frac{k!}{(1!)^{k_1}(2!)^{k_2}\ldots k_1!k_2!\ldots} \quad . \tag{2.9}$$

The reducible part $D^{(k)}_{\rm red}$ in (2.6) is a product of lower-order irreducible $D^{(k)}$ functions:

$$D^{(k)}_{\rm red}(\mathbf{r}_1,\ldots,\mathbf{r}_k) = \sum_{\rm part} D^{(p)}_{\rm irr}(\mathbf{r}_{i_1},\ldots,\mathbf{r}_{i_p}) D^{(q)}_{\rm irr}(\mathbf{r}_{i_{p+1}},\ldots,\mathbf{r}_{i_{p+q}})\ldots \quad . \tag{2.10}$$

The sum extends over all partitions $(i_1,\ldots i_p),(i_{p+1},\ldots i_{p+q}),\ldots$ of $1,\ldots k$ in groups that each contain at least two labels. Clearly, the reducible part of $D^{(k)}$ does not vanish if any group of two or more position vectors is far away from the other ones.

Having discussed the general form of the density functions $D^{(k)}$ we find upon substitution of (2.6) with (2.10) into (2.2) that the electric potential correlation functions can be written as:

$$W^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k) = W^{(k)}_{\rm irr}(\mathbf{r}_1,\ldots,\mathbf{r}_k) + \sum_{\rm part} W^{(p)}_{\rm irr}(\mathbf{r}_{i_1},\ldots,\mathbf{r}_{i_p}) W^{(q)}_{\rm irr}(\mathbf{r}_{i_{p+1}},\ldots,\mathbf{r}_{i_{p+q}})\ldots \quad , \tag{2.11}$$

with the irreducible correlation functions $W^{(k)}_{\rm irr}$ defined in a way analogous to (2.2), with $D^{(k)}$ replaced by $D^{(k)}_{\rm irr}$. The electric potential correlation functions are thus known once their irreducible parts for general k have been determined. From now on we shall concentrate on these irreducible parts.

The irreducible density function $D^{(k)}_{\rm irr}(\mathbf{r}_1,\ldots,\mathbf{r}_k)$ depends only on the differences of the position vectors, so that we may write it as $D^{(k)}_{\rm irr}(\mathbf{r}_{12},\ldots\mathbf{r}_{1k})$, with $\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j$. Shifting the integration variables in (2.2) we may write the irreducible correlation functions $W^{(k)}_{\rm irr}$ as

$$W^{(k)}_{\rm irr}(\mathbf{r}_1,\ldots,\mathbf{r}_k) = e^k \int d\mathbf{r}'_{12}\ldots d\mathbf{r}'_{1k}\; F^{(k)}(\mathbf{r}_{12}-\mathbf{r}'_{12},\ldots,\mathbf{r}_{1k}-\mathbf{r}'_{1k})\; D^{(k)}_{\rm irr}(\mathbf{r}'_{12},\ldots,\mathbf{r}'_{1k}) \quad , \tag{2.12}$$

with the function $F^{(k)}$ defined as

$$F^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_{k-1}) = \int d\mathbf{R}\, \frac{1}{4\pi R}\, \frac{1}{4\pi|\mathbf{r}_1-\mathbf{R}|}\cdots\frac{1}{4\pi|\mathbf{r}_{k-1}-\mathbf{R}|} \quad . \tag{2.13}$$

Since $D^{(k)}_{\rm irr}$ has got the cluster property the multiple integral in (2.12) is effectively extended only over values of the integration variables close to the origin, so that the convergence of the integral is warranted. The integral in (2.13) becomes singular if three or more arguments $\mathbf{r}_i$ coincide, and if two or more arguments are close to the origin. However, a simple power-counting argument shows that these singularities do not jeopardize the convergence of the integral in (2.12). The convergence of the integral in (2.13) for large $|\mathbf{R}|$ poses no problem either for $k \geq 4$. Convergence problems for (2.13) do arise, however, if k equals 2 or 3. For these values of k the shift of integration variables that has led to (2.12) is not allowed. We shall consider these cases separately.

The case $k = 2$ has been studied in detail previously[1]. By a careful analysis of the asymptotic properties of the integrand of (2.2) it has been shown that $W^{(2)}$ can be written in the form (2.12), with $F^{(2)}$ given as:

$$F^{(2)}(\mathbf{r}) = -\frac{|\mathbf{r}|}{8\pi} \quad . \tag{2.14}$$

An essential ingredient in proving (2.12) for $k = 2$ is the charge sum rule

$$n \int d\mathbf{r}\, h^{(2)}(\mathbf{r}) = -1 \quad , \tag{2.15}$$

which implies that the integral of the density function $D^{(2)}$ over the whole space vanishes:

$$\int d\mathbf{r}_{12}\, D^{(2)}(\mathbf{r}_{12}) = 0 \quad . \tag{2.16}$$

Next we consider the special case $k = 3$. By using the charge sum rule (2.15) and its counterpart for $h^{(3)}$:

$$n \int d\mathbf{r}_3\, h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = -2h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad , \tag{2.17}$$

one easily proves, on a par with (2.16):

$$\int d\mathbf{r}_{13}\, D^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13}) = 0 \quad . \tag{2.18}$$

As a consequence we may write (2.2) for $k = 3$ as

$$\begin{aligned} W^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= e^3 \int d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}'_3 \frac{1}{4\pi|\mathbf{r}_1 - \mathbf{r}'_1|} \frac{1}{4\pi|\mathbf{r}_2 - \mathbf{r}'_2|} \\ &\times \left[\frac{1}{4\pi|\mathbf{r}_3 - \mathbf{r}'_3|} - \frac{1}{4\pi|\mathbf{r}_3 - \mathbf{r}'_1|}\right] D^{(3)}(\mathbf{r}'_{12}, \mathbf{r}'_{13}) \quad . \end{aligned} \tag{2.19}$$

Upon shifting the integration variables we arrive at an expression of the form (2.12), with a function $F^{(3)}$ that depends not only on $\mathbf{r}_{12} - \mathbf{r}'_{12}$ and $\mathbf{r}_{13} - \mathbf{r}'_{13}$, but also on $\mathbf{r}_{13}$ separately:

$$\begin{aligned} F^{(3)}(\mathbf{r}_{12} - \mathbf{r}'_{12}, \mathbf{r}_{13} - \mathbf{r}'_{13}; \mathbf{r}_{13}) &= \int d\mathbf{R} \frac{1}{4\pi R} \frac{1}{4\pi|\mathbf{r}_{12} - \mathbf{r}'_{12} - \mathbf{R}|} \\ &\times \left[\frac{1}{4\pi|\mathbf{r}_{13} - \mathbf{r}'_{13} - \mathbf{R}|} - \frac{1}{4\pi|\mathbf{r}_{13} - \mathbf{R}|}\right] \quad . \end{aligned} \tag{2.20}$$

Clearly, this integral is convergent for large $|\mathbf{R}|$.

The integral over $\mathbf{R}$ in (2.20) can be carried out by employing the Legendre expansion for the Coulomb factors depending on $\boldsymbol{\rho}_{1i} \equiv \mathbf{r}_{1i} - \mathbf{r}'_{1i}$ and $\mathbf{r}_{13}$. In this way we get by performing the integration over the spherical angles that determine $\mathbf{R}$:

$$\begin{aligned} F^{(3)}(\boldsymbol{\rho}_{12}, \boldsymbol{\rho}_{13}; \mathbf{r}_{13}) &= \frac{1}{4\pi} \int_0^\infty dR\, R \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{(-1)^m}{(2\ell+1)^2} Y_{\ell,m}(\hat{\boldsymbol{\rho}}_{12})\, f_\ell(\rho_{12}, R) \\ &\times \left[Y_{\ell,-m}(\hat{\boldsymbol{\rho}}_{13})\, f_\ell(\rho_{13}, R) - Y_{\ell,-m}(\hat{\mathbf{r}}_{13})\, f_\ell(r_{13}, R)\right] \quad , \end{aligned} \tag{2.21}$$

with the abbreviation

$$f_\ell(x,y) = \theta(x-y)\frac{y^\ell}{x^{\ell+1}} + \theta(y-x)\frac{x^\ell}{y^{\ell+1}} \quad . \tag{2.22}$$

Upon performing the integral over R we obtain the expression:

$$F^{(3)}(\boldsymbol{\rho}_{12},\boldsymbol{\rho}_{13};\mathbf{r}_{13}) = \bar{F}^{(3)}(\boldsymbol{\rho}_{12},\boldsymbol{\rho}_{13}) - \bar{F}^{(3)}(\boldsymbol{\rho}_{12},\mathbf{r}_{13}) \quad , \tag{2.23}$$

with

$$\bar{F}^{(3)}(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\frac{(-1)^m}{2\ell+1}c_\ell(r,r')\; Y_{\ell,m}(\hat{\mathbf{r}})Y_{\ell,-m}(\hat{\mathbf{r}}') \quad . \tag{2.24}$$

The coefficients c_ℓ are defined as:

$$c_\ell(r,r') = \frac{1}{2}\theta(r-r')\left(\frac{r'}{r}\right)^\ell\left[\frac{1}{\ell} - \frac{r'}{(\ell+1)r}\right] + \frac{1}{2}\theta(r'-r)\left(\frac{r}{r'}\right)^\ell\left[\frac{1}{\ell} - \frac{r}{(\ell+1)r'}\right] \quad , \tag{2.25}$$

for $\ell > 0$, whereas for $\ell = 0$ one has:

$$c_0(r,r') = -\frac{1}{2}\theta(r-r')\left(\frac{r'}{r} + 2\log r\right) - \frac{1}{2}\theta(r'-r)\left(\frac{r}{r'} + 2\log r'\right) \quad . \tag{2.26}$$

As (2.23) with (2.24) shows, the three-point function $F^{(3)}$ can be expanded in terms of spherical harmonics that depend on the orientation of the vectors $\boldsymbol{\rho}_{1i}$ for $i = 2,3$, and of $\mathbf{r}_{13}$. The higher-order functions $F^{(k)}$ with $k \geq 4$, as defined in (2.13), can likewise be expanded in spherical harmonics:

$$F^{(k)}(\mathbf{r}_1,\cdots,\mathbf{r}_{k-1}) = \sum_{\{\ell_i\},\{m_i\}} c_{\{\ell_i\},\{m_i\}}(r_1,\cdots,r_{k-1})\prod_{i=1}^{k-1} Y_{\ell_i,m_i}(\hat{\mathbf{r}}_i) \quad . \tag{2.27}$$

It follows from (2.13) that $F^{(k)}$ is invariant under simultaneous rotation of all variables $\mathbf{r}_i$. Hence, the coefficients c transform as invariant direct products of $k-1$ spherical tensors of rank ℓ_i.

In the following we shall need a differential property of the functions $F^{(k)}$ and $\bar{F}^{(3)}$. For $k \geq 4$ we obtain by differentiation of the integrand of (2.13):

$$\Delta_{\mathbf{r}_i}\,\Delta_{\mathbf{r}_j}\,F^{(k)}(\mathbf{r}_1,\cdots,\mathbf{r}_{k-1}) = 0 \quad , \tag{2.28}$$

for all $\mathbf{r}_i \neq \mathbf{r}_j$. By inserting (2.27) and employing the identity:

$$\Delta_{\mathbf{r}}\,f(r)Y_{\ell,m}(\hat{\mathbf{r}}) = [\Delta_{r,\ell}f(r)]\;Y_{\ell,m}(\hat{\mathbf{r}}) \quad , \tag{2.29}$$

with

$$\Delta_{r,\ell} \equiv \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{\ell(\ell+1)}{r^2} \quad , \tag{2.30}$$

one finds that this implies the identity

$$\Delta_{r_i,\ell_i}\,\Delta_{r_j,\ell_j}c_{\{\ell_i\},\{m_i\}}(r_1,\cdots,r_{k-1}) = 0 \quad , \tag{2.31}$$

for all $r_i \neq r_j$ and all $\{\ell_i\}, \{m_i\}$. Likewise, one proves from (2.25)–(2.26):

$$\Delta_{r,\ell}\Delta_{r',\ell}\, c_\ell(r,r') = \frac{2\ell+1}{r^3}\delta(r-r') \quad , \tag{2.32}$$

which yields in view of (2.24):

$$\Delta_{\mathbf{r}}\, \Delta_{\mathbf{r}'}\, \bar{F}^{(3)}(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi r}\, \delta(\mathbf{r}-\mathbf{r}') \quad . \tag{2.33}$$

Finally, for $k=2$ it follows from (2.14) that

$$\Delta_{\mathbf{r}}\, \Delta_{\mathbf{r}}\, F^{(2)}(\mathbf{r}) = \delta(\mathbf{r}) \quad . \tag{2.34}$$

3 Asymptotic behaviour of the two-point and three-point correlation functions

The asymptotic behaviour of the two-point correlation function $W^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ for large values of r_{12} is obtained by starting from (2.12) with (2.14) and expanding the function $F^{(2)}(\mathbf{r}_{12}-\mathbf{r}'_{12})$ around $\mathbf{r}_{12}$:

$$F^{(2)}(\mathbf{r}_{12}-\mathbf{r}'_{12}) = -\frac{1}{8\pi}\exp\left(-\mathbf{r}'_{12}\cdot\nabla_{\mathbf{r}_{12}}\right) r_{12} \quad . \tag{3.1}$$

Let us now use the expansion formula[5],[6] :

$$\begin{aligned}\exp\left(\mathbf{r}'\cdot\nabla_{\mathbf{r}}\right) f(r) &= 4\pi\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}(-1)^m Y_{\ell,m}(\hat{\mathbf{r}}')Y_{\ell,-m}(\hat{\mathbf{r}})\sum_{s=0}^{\infty}\frac{1}{(2s)!!(2\ell+2s+1)!!}(r')^{\ell+2s} \\ &\times\ r^\ell\left(\frac{1}{r}\frac{d}{dr}\right)^\ell\frac{1}{r}\left(\frac{d}{dr}\right)^{2s} r f(r) \quad ,\end{aligned} \tag{3.2}$$

which is valid for any spherically symmetric function $f(r)$ for which a convergent Taylor expansion can be made. Upon applying this expansion to $F^{(2)}$ it is seen that only the terms with $s=0$ and 1 contribute. Furthermore, it should be kept in mind that upon substitution of the expansion in (2.12) all terms with $\ell \neq 0$ drop out, since $D^{(2)}(\mathbf{r}'_{12})$ is isotropic. As a result we are left with the fairly simple asymptotic formula:

$$W^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \sim -\frac{e^2}{8\pi}\left[r_{12}\int d\mathbf{r}'_{12}\, D^{(2)}(\mathbf{r}'_{12}) + \frac{1}{3r_{12}}\int d\mathbf{r}'_{12}\,(r'_{12})^2\, D^{(2)}(\mathbf{r}'_{12})\right] \quad . \tag{3.3}$$

All higher-order terms have disappeared from the expression at the right-hand side. Hence, this result gives the asymptotic expansion of $W^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ for large values of r_{12}, apart from terms that decay faster than any inverse power of r_{12}. This result can be checked by inserting instead of (3.2) a finite Taylor expansion in (2.12) and making an estimate of the remainder in a similar way as in refs. 7 and 8.

The first term in (3.3) vanishes on account of (2.16). Furthermore, the Stillinger-Lovett sum rule[9]

$$n\int d\mathbf{r}\, r^2\, h^{(2)}(r) = -\frac{6}{k_D^2} \quad , \tag{3.4}$$

with $k_D^2 = \beta n e^2$ the squared Debye wave number, yields a simple form for the coefficient of r_{12}^{-1} in (3.3), so that we finally get the asymptotic expression:

$$W^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \sim \frac{1}{4\pi\beta r_{12}} + o\left(\frac{1}{r_{12}^n}\right) \quad , \tag{3.5}$$

for large r_{12} and for any positive integer n. We have thus found that the asymptotic expansion for the two-point electric potential correlation function $W^{(2)}$ is given by a single algebraic term proportional to the inverse of the distance. The remainder decays faster than any inverse power of the distance. This result for the two-particle correlation function is in accordance with earlier findings[(1),(10)].

Let us now consider the asymptotic behaviour of the three-point correlation function $W^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ for large separations r_{12} and r_{13}. It is obtained by inserting the expanded form of (2.23):

$$F^{(3)}(\boldsymbol{\rho}_{12}, \boldsymbol{\rho}_{13}; \mathbf{r}_{13}) = \exp\left(-\mathbf{r}'_{12} \cdot \nabla_{\mathbf{r}_{12}}\right) \left[\exp\left(-\mathbf{r}'_{13} \cdot \nabla_{\mathbf{r}_{13}}\right) - 1\right] \bar{F}^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13}) \tag{3.6}$$

in the integrand of (2.12). According to (2.24) the function $\bar{F}^{(3)}$ is a sum of products of spherical harmonics and radial functions. The expansion of such a function follows by employing the general formula[(5),(6)]

$$\begin{aligned}
&\exp\left(\mathbf{r}' \cdot \nabla_{\mathbf{r}}\right) f(r) Y_{\ell,m}(\hat{\mathbf{r}}) \\
&= \sum_{\ell'=0}^{\infty} \sum_{\ell''=0}^{\infty} \sum_{m'=-\ell'}^{\ell'} \sum_{m''=-\ell''}^{\ell''} (-1)^{m'+m''} \left[4\pi(2\ell+1)(2\ell'+1)(2\ell''+1)\right]^{1/2} \\
&\times \begin{pmatrix} \ell & \ell' & \ell'' \\ m & -m' & -m'' \end{pmatrix} \begin{pmatrix} \ell & \ell' & \ell'' \\ 0 & 0 & 0 \end{pmatrix} Y_{\ell',m'}(\hat{\mathbf{r}}') Y_{\ell'',m''}(\hat{\mathbf{r}}) \\
&\times \sum_{s=0}^{\infty} \frac{1}{(2s)!!(2\ell'+2s+1)!!} (r')^{\ell'+2s} D(\ell'', \ell, \ell'+2s) f(r) \quad ,
\end{aligned} \tag{3.7}$$

which is a generalization of (3.2) to functions with an angular dependence. The product of two 3-j symbols is sometimes called a Gaunt coefficient[(6)]. It is proportional to the integral of a product of three spherical harmonics. Furthermore, D is a differential symbol that is defined as:

$$D(\ell'', \ell, N) = \frac{1}{r^{\ell''+1}} \left(\frac{1}{r}\frac{d}{dr}\right)^{|\ell-\ell''|} r^{\ell+1} (\Delta_{r,\ell})^{(N-|\ell-\ell''|)/2} \quad , \quad \ell \geq \ell'' \quad , \tag{3.8}$$

$$D(\ell'', \ell, N) = r^{\ell''} \left(\frac{1}{r}\frac{d}{dr}\right)^{|\ell-\ell''|} \frac{1}{r^{\ell}} (\Delta_{r,\ell})^{(N-|\ell-\ell''|)/2} \quad , \quad \ell \leq \ell'' \quad , \tag{3.9}$$

with the operator $\Delta_{r,\ell}$ as defined in (2.30). From the 3-j symbols it follows that $N - |\ell - \ell''|$ is an even non-negative integer. It is positive for $s > 0$.

When the expansion formula (3.7) is applied to (3.6), with (2.24) inserted, the resulting expression for $F^{(3)}$ depends on $\mathbf{r}'_{12}$ and $\mathbf{r}'_{13}$ through functions of the form

$$\prod_{i=2,3} (r'_{1i})^{\ell_{1i}+2s_{1i}} \, Y_{\ell_{1i},m_{1i}}(\hat{\mathbf{r}}'_{1i}) \quad , \tag{3.10}$$

with non-negative integers $\ell_{12}, \ell_{13}, s_{12}$ and s_{13}. Owing to the form of (3.6) terms that are independent of $\mathbf{r}'_{13}$ drop out, so that one has $\ell_{13} + 2s_{13} > 0$. Furthermore, the property (2.32) of the coefficients c_ℓ implies that at most one of the labels s_{12} and s_{13} can differ from 0.

In view of the above the asymptotic expansion of $W^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ for large r_{12} and r_{13} is given by a series of inverse powers of $R = \min(r_{12}, r_{13})$. The coefficients in this series are (sums of) products of bounded functions of the ratio r_{12}/r_{13}, of bounded functions of the angles determining the orientation of the vectors $\mathbf{r}_{12}, \mathbf{r}_{13}$, and of the basic integrals

$$C^{(3)}_{\{\ell_{1i}\},\{m_{1i}\},\{s_{1i}\}} \equiv \int d\mathbf{r}'_{12} d\mathbf{r}'_{13}\; D^{(3)}(\mathbf{r}'_{12}, \mathbf{r}'_{13}) \prod_{i=2,3} (r'_{1i})^{\ell_{1i}+2s_{1i}}\; Y_{\ell_{1i},m_{1i}}(\hat{\mathbf{r}}'_{1i}) \quad , \tag{3.11}$$

for $\ell_{13} + 2s_{13} > 0$ and $s_{12}s_{13} = 0$.

Since at least one of the parameters s_{1i} in (3.11) vanishes and $D^{(3)}$ is symmetric, it is enough to consider integrals of the type

$$\int d\mathbf{r}_{13}\; D^{(3)}(\mathbf{r}_{12}, \mathbf{r}_{13})\, (r_{13})^\ell\, Y_{\ell,m}(\hat{\mathbf{r}}_{13}) \quad , \tag{3.12}$$

for arbitrary integer ℓ and m, with $\ell \geq 0$ and $|m| \leq \ell$. To evaluate these one inserts (2.5) and uses the general multipole sume rule for the three-point Ursell function

$$n \int d\mathbf{r}_{13} h^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) r_{13}^\ell Y_{\ell,m}(\hat{\mathbf{r}}_{13}) = -h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \left[r_{12}^\ell Y_{\ell,m}(\hat{\mathbf{r}}_{12}) + \delta_{\ell,0}(4\pi)^{-1/2} \right] \quad , \tag{3.13}$$

which reduces to the charge sum rule (2.17) for $\ell = 0$. This sum rule generally holds if the equilibrium state has good cluster properties[(7),(11)]. In this way one readily finds that the integrals (3.12) vanish for all ℓ and m. As a consequence we have derived

$$C^{(3)}_{\{\ell_{1i}\},\{m_{1i}\},\{s_{1i}\}} = 0 \quad , \tag{3.14}$$

for all allowed values of the parameters. In the next section we shall see that a similar result holds for the higher order irreducible density functions as well and that it could have been expected on general grounds.

The coefficients of all inverse powers of $R = \min(r_{12}, r_{13})$ in the asymptotic expansion of $W^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ have now been shown to vanish. Hence, we have reached the asymptotic result:

$$W^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \sim o(R^{-n}) \quad , \tag{3.15}$$

for large distances $R = \min(r_{12}, r_{13})$ between one of the position vectors ($\mathbf{r}_1$) and the other two ($\mathbf{r}_2, \mathbf{r}_3$), and for all positive integer n. In other words, the three-point correlation function for the electric potential fluctuations has got the exponential clustering property.

4 Asymptotic behaviour of the general k-point correlation function

We now turn to the asymptotic behaviour of the irreducible correlation function $W^{(k)}_{\text{irr}}$ of arbitrary order $k \geq 4$. To derive its asymptotic form we make a Taylor expansion of the

function $F^{(k)}$, as before. Inserting (2.27) we get:

$$F^{(k)}(\boldsymbol{\rho}_{12},\ldots,\boldsymbol{\rho}_{1k}) = \exp\left(-\mathbf{r}'_{12}\cdot\nabla_{\mathbf{r}_{12}}\ldots-\mathbf{r}'_{1k}\cdot\nabla_{\mathbf{r}_{1k}}\right) \times \sum_{\{\ell_{1i}\},\{m_{1i}\}} c_{\{\ell_{1i}\},\{m_{1i}\}}(r_{12},\ldots,r_{1k})\prod_{i=2}^{k} Y_{\ell_{1i},m_{1i}}(\hat{\mathbf{r}}_{1i}) \quad , \tag{4.1}$$

for $\boldsymbol{\rho}_{1i} = \mathbf{r}_{1i} - \mathbf{r}'_{1i}$. Using the expansion formula (3.7) we find that the general term of the asymptotic expansion of the k-point irreducible correlation function $W^{(k)}_{\rm irr}(\mathbf{r}_1,\ldots,\mathbf{r}_k)$ for large separations between $\mathbf{r}_1$ and $\mathbf{r}_2,\ldots,\mathbf{r}_k$ is given by a series of inverse powers of $R = \min(r_{12},\ldots,r_{1k})$, with coefficients that are determined by the integrals:

$$C^{(k)}_{\{\ell_{1i}\},\{m_{1i}\},\{s_{1i}\}} \equiv \int d\mathbf{r}'_{12}\ldots d\mathbf{r}'_{1k}\, D^{(k)}_{\rm irr}(\mathbf{r}'_{12},\ldots,\mathbf{r}'_{1k})\prod_{i=2}^{k}(r'_{1i})^{\ell_{1i}+2s_{1i}}\, Y_{\ell_{1i},m_{1i}}(\hat{\mathbf{r}}'_{1i}) \quad . \tag{4.2}$$

Owing to the property (2.31) at most one of the labels s_{1i} differs from 0. In view of the symmetry of $D^{(k)}$ we assume $s_{1k} = 0$ and consider the integrals

$$\int d\mathbf{r}_{1k}\, D^{(k)}_{\rm irr}(\mathbf{r}_{12},\ldots,\mathbf{r}_{1k})\,(r_{1k})^{\ell} Y_{\ell,m}(\hat{\mathbf{r}}_{1k}) \quad , \tag{4.3}$$

which are in fact the multipole moments carried by the irreducible density functions $D^{(k)}_{\rm irr}$.

A linear response theory argument can be used to prove that none of the density functions $D^{(k)}$ can carry multipoles of any order[2]. The same must then be true for the irreducible density functions, so that all integrals (4.3) vanish.

For $\ell = m = 0$ a more rigorous proof of this statement has been given with the help of the hierarchy equations for the Ursell functions[4]. In fact, it has been shown that the general charge sum rules for an Ursell function of arbitrary order[12]

$$n\int d\mathbf{r}_{1k}\, h^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k) = -kh^{(k-1)}(\mathbf{r}_1,\ldots,\mathbf{r}_{k-1}) \quad , \tag{4.4}$$

which hold for any $k > 1$ provided the Ursell functions possess the exponential clustering property, are equivalent to the vanishing of the integrals (4.3) for $\ell = m = 0$.

For higher values of ℓ and m one can likewise prove the vanishing of (4.3) by starting from the complete set of multipole sume rules for the Ursell functions[7],[11]

$$n\int d\mathbf{r}_{1k}\, h^{(k)}(\mathbf{r}_1,\ldots,\mathbf{r}_k) r^{\ell}_{1k}\, Y_{\ell,m}(\hat{\mathbf{r}}_{1k}) = = -h^{(k-1)}(\mathbf{r}_1,\ldots,\mathbf{r}_{k-1})\left[\sum_{i=2}^{k-1} r^{\ell}_{1i}\, Y_{\ell,m}(\hat{\mathbf{r}}_{1i}) + \delta_{\ell,0}(4\pi)^{-1/2}\right] \quad , \tag{4.5}$$

valid for $k > 2$ and $\ell \geq 0$. For $k = 3$ this sum rule has been written already in (3.13), while for $\ell = 0$ it reduces to (4.4). To show the vanishing of (4.3) we make use of the fact that all terms of $D^{(k)}_{\rm irr}$ can be associated to partitions of the labels $1,\ldots,k$, as stated in (2.8). Let us consider in particular the partition $(1)(2)\ldots(k)$, in which all labels form a group on their own. In the corresponding contribution to (4.3) the integral can be carried out with the help of (4.5). As a result we generate the terms that are associated with the

partitions $(1)\dots(j-1)(j,k)(j+1)\dots(k-1)$, for $1 \le j \le k-1$, but with an additional minus sign. (The term that corresponds to the partition $(1,k)(2)\dots(k-1)$ is present only for $\ell = 0$.) Hence, all terms that correspond to partitions with one group of two labels and $k-2$ single labels (in other words, with $k_1 = k-2, k_2 = 1$ and $k_j = 0$ for $j > 2$) drop out, if the label k is contained in the group of two. In the remaining partitions with the same $\{k_j\}$ the label k is again standing apart in a group of its own. As a consequence we may once more employ the multipole sum rule (4.5) to perform the integral in all terms corresponding to the partitions with $k_1 = k-2, k_2 = 1$ and $k_j = 0$ for $j > 2$ that are left over. It is an easy matter to check that this procedure can be repeated. All partitions gradually come into play. It turns out that the final result for (4.3) is precisely 0, since the contributions from all partitions are successively cancelling.

From the vanishing of (4.3) one concludes that the coefficients $C^{(k)}_{\{\ell_{1i}\},\{m_{1i}\},\{s_{1i}\}}$, as defined in (4.2), are all equal to 0. Hence, the asymptotic expansion for the irreducible part $W^{(k)}_{\rm irr}(\mathbf{r}_1,\dots,\mathbf{r}_k)$ of the k-point correlation function for electric potential fluctuations does not contain any algebraic terms for $k \ge 4$, so that we can write on a par with (3.15):

$$W^{(k)}_{\rm irr}(\mathbf{r}_1,\dots,\mathbf{r}_k) \sim o(R^{-n}) \quad , \tag{4.6}$$

for large $r_{12},\dots,r_{1k}$, with $R = \min(r_{12},\dots,r_{1k})$, and for all positive integer n.

The reasoning followed to prove the above result can easily be generalized so as to establish a more general asymptotic formula for $W^{(k)}_{\rm irr}$, with $k \ge 4$, that applies if its arguments fall apart in two groups with a large separation between the groups. In fact, one may show for any m satisfying $1 \le m \le k-1$:

$$W^{(k)}_{\rm irr}(\mathbf{r}_1,\dots,\mathbf{r}_k) \sim o(R^{-n}) \quad , \tag{4.7}$$

which is valid for large $R = \min(r_{ij})$, with $1 \le i \le m$ and $m+1 \le j \le k$, and for all positive integer n. In other words, $W^{(k)}_{\rm irr}$ has got the exponential clustering property for all $k \ge 4$.

5 Concluding remarks

In the previous section we have shown that the irreducible part $W^{(k)}_{\rm irr}(\mathbf{r}_1,\dots,\mathbf{r}_k)$ of the k-point electric potential correlation function, with $k \ge 4$, decays faster than any inverse power of the distance if one of its position arguments gets infinitely far removed from the others. The three-point electric potential correlation function $W^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ shares this property, as we have seen in section 3. The only exception to the general rule is thus the two-point function $W^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$, which decays proportional to $|\mathbf{r}_1-\mathbf{r}_2|^{-1}$ for large separations of its arguments.

We have determined the asymptotic behaviour of $W^{(k)}_{\rm irr}$ by analyzing the expression (2.12), in which use has been made of the translation invariance of the system. An alternative way[13] to establish the results proceeds by starting directly from (2.2) with (2.11) and showing (again with the help of the vanishing of (4.3)) that the integral over $\mathbf{r}'_2,\dots,\mathbf{r}'_k$ of the product of $D^{(k)}_{\rm irr}$ and the Coulomb factors depending on $\mathbf{r}_2,\dots,\mathbf{r}_k$ is a short-ranged function of the differences $\mathbf{r}_2-\mathbf{r}'_1,\dots\mathbf{r}_k-\mathbf{r}'_1$. As a consequence one may conclude that $W^{(k)}_{\rm irr}$ is of short range in the position differences $\mathbf{r}_{ij}$ for $1 < i < j \le k$.

In view of (2.11) we conclude that the asymptotic form of the full electric potential correlation function $W^{(k)}(\mathbf{r}_1, \ldots \mathbf{r}_k)$ for observation points $\mathbf{r}_i$ that are all far apart is given by a sum of products of slowly decaying two-point correlation functions $W^{(2)}$ for even k, whereas it goes to 0 exponentially fast for odd k. A different way to express this property follows by introducing the generating functional $\mathcal{F}[f(\mathbf{r})]$ for the electric potential correlation functions:

$$W^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_k) = \frac{\delta^k}{\delta f(\mathbf{r}_1) \ldots \delta f(\mathbf{r}_k)} \mathcal{F}[f(\mathbf{r})] \Big|_{f(\mathbf{r})=0} \quad . \tag{5.1}$$

In terms of this generating functional the statement made above can be rephrased by saying that the asymptotics of the correlation functions is given by a generating functional $\mathcal{F}_{\text{asympt}}$ that has a simple Gaussian form:

$$\mathcal{F}_{\text{asympt}}[f(\mathbf{r})] = \exp\left[\frac{1}{8\pi\beta} \int d\mathbf{r} d\mathbf{r}' f(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} f(\mathbf{r}')\right] \quad . \tag{5.2}$$

In the above we have concentrated on the asymptotic properties of the correlation functions for the fluctuations in the electric potential. It is a trivial matter to deduce similar results for the asymptotic behaviour of the electric field correlation functions, as these follow directly by differentiation.

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