Microscopic Calculation of the Dielectric Susceptibility Tensor for Coulomb Fluids II

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Abstract

For a Coulomb system contained in a domain \( \Lambda \), the dielectric susceptibility tensor \( \chi_\Lambda \) is defined as relating the average polarization in the system to a constant applied electric field, in the linear limit. According to the phenomenological laws of macroscopic electrostatics, \( \chi_\Lambda \) depends on the specific shape of the domain \( \Lambda \). In this paper we derive, using the methods of equilibrium statistical mechanics in both canonical and grand-canonical ensembles, the shape dependence of \( \chi_\Lambda \) and the corresponding finite-size corrections to the thermodynamic limit, for a class of general \( \nu \)-dimensional (\( \nu \geq 2 \)) Coulomb systems, of ellipsoidal shape, being in the conducting state. The microscopic derivation is based on a general principle: the total force acting on a system in thermal equilibrium is zero. The results are checked in the Debye-Hückel limit. The paper is a generalization of a previous one [L. Šamaj, J. Stat. Phys. 100:949 (2000)], dealing with the special case of a one-component plasma in two dimensions. In that case, the validity of the presented formalism has already been verified at the exactly solvable (dimensionless) coupling \( \Gamma = 2 \).

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1 INTRODUCTION

For systems with short-ranged pair interactions among constituents defined in a specifically shaped domain \( \Lambda \), the thermodynamic limit of an intensive quantity does not depend in general on the shape of the domain \( \Lambda \) and on the conditions at the boundary \( \partial \Lambda \) given by the surrounding medium. This is no longer true in the case of macroscopic systems with long-ranged pair interactions. A typical example is the domain-shape dependence of the dielectric susceptibility tensor for conductors predicted by the phenomenological laws of electrostatics \[1\]. The aim of this paper is to derive rigorously and precisely, using the methods of equilibrium statistical mechanics in both canonical and grand-canonical ensembles, the shape dependence of the dielectric susceptibility and the corresponding finite-size corrections to the thermodynamic limit, for a class of general classical \( \nu \)-dimensional microscopic Coulomb systems being in the conducting state. The case \( \nu = 1 \) has special features and will not be discussed here. The paper is a generalization of the previous one \[2\], referred to as I, which was devoted to the microscopic derivation of the dielectric susceptibility for the special case of a one-component plasma in two dimensions (2D).

In dimension \( \nu \), the Coulomb potential \( v \) at a spatial position \( \mathbf{r} = (r^1, r^2, \ldots, r^\nu) \), induced by a unit charge at the origin \( \mathbf{0} \), is the solution of the Poisson equation

\[
\Delta v(\mathbf{r}) = -s_\nu \delta(\mathbf{r}) \tag{1.1}
\]

where \( s_\nu = \frac{2\pi^{\nu/2}}{\Gamma(\nu/2)} \) is the surface area of the \( \nu \)-dimensional unit sphere. Explicitly,

\[
v(\mathbf{r}) = \begin{cases} 
-\ln(r/r_0) & \text{if } \nu = 2, \\
\frac{r^{2-\nu}}{\nu-2} & \text{otherwise}
\end{cases} \tag{1.2}
\]

Here, \( r = |\mathbf{r}| \) and \( r_0 \) is an arbitrary length scale. The corresponding force \( \mathbf{F}(\mathbf{r}) = -\nabla v(\mathbf{r}) \) reads

\[
\mathbf{F}(\mathbf{r}) = \frac{\mathbf{r}}{r^{\nu}} \tag{1.3}
\]

In a \( \nu \)-dimensional space, the definition of the Coulomb potential \( \Delta v(\mathbf{r}) \) implies in the Fourier space the characteristic small-\( k \) behavior \( \hat{v}(\mathbf{k}) \propto 1/k^2 \). This maintains many generic properties (like screening) of “real” 3D Coulomb systems.

We consider general Coulomb systems consisting of \( M \) mobile species \( \alpha = 1, \ldots, M \) with the corresponding charges \( q_\alpha \), embedded in a fixed uniform background of charge density \( \rho_b \). The most studied models are the one-component plasma (OCP) and the symmetric two-component plasma...
(TCP). The OCP corresponds to $M = 1$ with $q_1 = q$ and $\rho_b$ of opposite sign; it may be convenient to define a “background density” $n_b$ by $\rho_b = -qn_b$. The symmetric TCP corresponds to $M = 2$ with $q_1 = q, q_2 = -q$ and $\rho_b = 0$. The system is contained in a domain $\Lambda$ of specified shape with a smooth boundary $\partial \Lambda$. The surrounding medium is for simplicity a vacuum producing no image forces. The fixed background produces the one-particle potential $\rho_b \phi_b(\mathbf{r})$ where

$$\phi_b(\mathbf{r}) = \int_\Lambda d^v r' v(|\mathbf{r} - \mathbf{r}'|)$$

(1.4)

The corresponding electric field is $\rho_b E_b(\mathbf{r})$ where

$$E_b(\mathbf{r}) = -\nabla \phi_b(\mathbf{r}) = \int_\Lambda d^v r' \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^v}$$

(1.5)

The energy of a configuration $\{\mathbf{r}_i, q_{\alpha_i}\}$ of the charged particles plus the background is

$$E = \sum_{i<j} q_{\alpha_i} q_{\alpha_j} v(|\mathbf{r}_i - \mathbf{r}_j|) + \rho_b \sum_i q_{\alpha_i} \phi_b(\mathbf{r}_i) + E_{b-b}$$

(1.6)

Since the background-background interaction energy term $E_{b-b}$ does not depend on the particle coordinates, its particular value is irrelevant in the calculation of particle distribution functions. In the case of point particles, for many-component systems with at least two oppositely charged species, the singularity of $v(r)$ (1.2) at the origin prevents the thermodynamic stability against the collapse of positive-negative pairs of charges: in two dimensions for small enough temperatures, in three and higher dimensions for any temperature. However, in those cases, one can introduce short-range repulsive interactions which prevent the collapse. The derivations which follow allow for such interactions.

The Coulomb system in the domain $\Lambda$ at inverse temperature $\beta$ will be considered in both canonical (fixed particle numbers) and grand canonical (fixed species chemical potentials) ensembles. The thermal average will be denoted by $\langle \cdots \rangle$. In terms of the microscopic density of particles of species $\alpha$, $\hat{n}_\alpha(\mathbf{r}) = \sum_i \delta_{\alpha,\alpha_i} \delta(\mathbf{r} - \mathbf{r}_i)$, the microscopic densities of the total particle number and charge are defined respectively by

$$\hat{n}(\mathbf{r}) = \sum_\alpha \hat{n}_\alpha(\mathbf{r}), \quad \hat{\rho}(\mathbf{r}) = \sum_\alpha q_\alpha \hat{n}_\alpha(\mathbf{r})$$

(1.7)

At one-particle level, the total particle number and charge densities are given respectively by

$$n(\mathbf{r}) = \langle \hat{n}(\mathbf{r}) \rangle, \quad \rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle$$

(1.8)
At two-particle level, one introduces the two-body densities
\[ n_{\alpha\alpha'}^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \sum_{i \neq j} \delta_{\alpha_i, \alpha_{i'}} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \rangle = \langle \hat{n}_\alpha(\mathbf{r})\hat{n}_{\alpha'}(\mathbf{r}') \rangle - \langle \hat{n}_\alpha(\mathbf{r}) \rangle \delta_{\alpha, \alpha'} \delta(\mathbf{r} - \mathbf{r}') \] (1.9)

The corresponding Ursell functions are defined by
\[ U_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') = n_{\alpha\alpha'}^{(2)}(\mathbf{r}, \mathbf{r}') - n_\alpha(\mathbf{r}) n_{\alpha'}(\mathbf{r}') \] (1.10)

and the truncated charge-charge structure function by
\[ S(\mathbf{r}, \mathbf{r}') = \langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle^T \equiv \langle \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') \rangle - \langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\rho}(\mathbf{r}') \rangle \] (1.11)

The small-\( k \) behavior of the Fourier transform of the Coulomb potential gives rise to exact moment constraints for the charge structure function \( S \) (see review [3]). In the bulk, \( \lim_{\Lambda \to \mathbb{R}} S_\Lambda(\mathbf{r}, \mathbf{r}') = S(|\mathbf{r} - \mathbf{r}'|) \) obeys the Stillinger-Lovett screening rules [4, 5] which imply the zeroth-moment (electroneutrality) condition
\[ \int d^\nu r S(\mathbf{r}) = 0 \] (1.12)

and the second-moment condition
\[ \beta \int d^\nu r |\mathbf{r}|^2 S(\mathbf{r}) = -\frac{2\nu}{s_\nu} \] (1.13)

For finite systems, the analog of the zeroth-moment sum rule
\[ \int_\Lambda d^\nu r S(\mathbf{r}, \mathbf{r}') = \int_\Lambda d^\nu r' S(\mathbf{r}, \mathbf{r}') = 0 \] (1.14)

holds only in the canonical ensemble where it reflects the trivial fact that the total charge in the domain \( \Lambda \) is fixed. In the grand canonical ensemble, the system is expected to exhibit charge fluctuations [6], in which case (1.14) does not hold. The information analogous to the bulk second-moment condition holds contained in the dielectric susceptibility tensor \( \chi_\Lambda \). Let us use the notation
\[ \hat{P}^i = \int_\Lambda d^\nu r r^i \hat{\rho}(\mathbf{r}) \quad i = 1, \ldots, \nu \] (1.15)

for the \( i \)th component of the total polarization in the system. The tensor \( \chi_\Lambda \) is defined as relating the average polarization to a constant applied field \( \mathbf{E}_0 \), in the linear limit:
\[ \frac{\langle \hat{P}^i \rangle_{\mathbf{E}_0}}{|\Lambda|} = \sum_{j=1}^\nu \chi^{ij}_\Lambda E^j_0 \] (1.16)
The linear response theory expresses the $\chi_\Lambda$-components as

$$
\chi^{ij}_\Lambda = \frac{\beta}{|\Lambda|} \left( \langle \hat{P}^i \hat{P}^j \rangle - \langle \hat{P}^i \rangle \langle \hat{P}^j \rangle \right)
= \frac{\beta}{|\Lambda|} \int _\Lambda d^\nu r_1 \int _\Lambda d^\nu r_2 r_1^i r_2^j S(r_1, r_2)
$$

where $\langle \cdots \rangle$ is an average defined for $E_0 = 0$. In the canonical ensemble where the sum rule (1.14) applies, the tensor components $\chi^{ij}_\Lambda$ are expressible in another equivalent way

$$
\chi^{ij}_\Lambda = -\frac{\beta}{2|\Lambda|} \int _\Lambda d^\nu r_1 \int _\Lambda d^\nu r_2 (r_1^i - r_2^j)^2 S(r_1, r_2)
$$

As $\Lambda \to \mathbb{R}^\nu$ one might naively expect that only the diagonal components $\chi^i = \lim _{\Lambda \to \mathbb{R}^\nu} \chi^{ii}_\Lambda$ ($i = 1, \ldots, \nu$) survive and, according to the bulk second-moment sum rule (1.13), that they tend to the uniform “Stillinger-Lovett” (SL) value

$$
\chi^i_{SL} = -\frac{\beta}{2} \int d^\nu r (r^i)^2 S(r) = \frac{1}{s_\nu}
$$

which does not depend on the shape of $\Lambda$. This is indeed true for a boundary-free domain like the surface of a sphere. As is explained below, relation (1.19) no longer holds in a geometry with a boundary.

According to phenomenological electrostatics, based on plausible but not rigorously justified arguments, the dielectric susceptibility $\chi$ of a macroscopic system is related to its dielectric constant $\epsilon$. For the considered Coulomb plasma in a conducting state, the equality $\epsilon^{-1} = 0$ implies

$$
\chi^{ij}_{\Lambda} = \frac{1}{s_\nu} (T^{-1}_{\Lambda})^{ij}
$$

where $T_{\Lambda}$ is the size-invariant but shape-dependent depolarization tensor with position-independent components

$$
T^{ij}_\Lambda = -\frac{1}{s_\nu} \int _\Lambda d^\nu r \frac{\partial^2 v(r)}{\partial r^i \partial r^j}
$$

Without any loss of generality one can choose a coordinate system in which $T_{\Lambda}$ is diagonal, $T^{ij}_\Lambda = T^i_\Lambda \delta_{ij}$, and consequently $\chi_{\Lambda}$ is also diagonal, $\chi^{ij}_\Lambda = \chi^i_\Lambda \delta_{ij}$. Then, Eq. (1.20) takes the form

$$
\chi^i_\Lambda = \frac{1}{s_\nu T^i_\Lambda}
$$

For $\nu$-dimensional ellipsoidal domains \[ which will be of interest in this work, the $T_{\Lambda}$-components (1.21) are expressible in an alternative form as

$$
T^{ij}_\Lambda = -\frac{1}{s_\nu} \frac{\partial^2}{\partial r^i \partial r^j} \phi_0(r)
$$
with \( \phi_b(r) \) defined by (1.4), where \( r \) is an arbitrary point in \( \Lambda \). With regard to the Poisson equation (1.1), the diagonal elements of \( T_\Lambda \) are constrained by \( \sum_{i=1}^\nu T_i^{\Lambda} = 1 \). In the special isotropic case of \( \nu \)-dimensional spheres, \( T_i^{\Lambda} = 1/\nu \) and the consequent \( \chi^{\Lambda}_\nu = \nu/s_\nu \) is \( \nu \) times \( \chi^{SL}_\nu \) of Eq. (1.19).

The discrepancy between the naive prediction of statistical mechanics (1.19) and phenomenological electrostatics (1.22) was explained in a nice series of papers [7]-[9] by Choquard et al. The point is that the susceptibility is made up of a bulk contribution, which saturates quickly to the SL value (1.19), and of a surface contribution. The surface contribution does not vanish in the thermodynamic limit due to the inverse-power-law behavior of the charge structure function at large distances along the boundary. Summing up both contributions one gets instead of (1.19) the shape-dependent result of macroscopic electrostatics (1.22). This fact was verified on the 2D disk geometry, in the high-temperature Debye-Hückel limit and at the exactly solvable coupling \( \Gamma = \beta q^2 = 2 \) of the OCP. A progress towards the microscopic verification of formula (1.22) was made in paper I. There, the mapping of the 2D OCP, when \( \Gamma \) is an even positive integer, onto a discrete 1D anticommuting-field theory [10] was used for generating a sum rule for the charge structure function. This sum rule comes from a specific unitary transformation of anticommuting variables keeping a “composite” form of the fermionic action. For \( \Lambda \) an elliptic domain, the sum rule confirms microscopically the asymptotic formula (1.22) and gives a finite-size correction term to \( \chi^{\Lambda}_\nu \) explicitly in terms of boundary contributions.

The underlying sum rule derived for the 2D OCP seemed to be closely related to the logarithmic nature of the 2D Coulomb potential. We show in this paper that actually the sum rule is nothing but a direct consequence of a general principle: the total force acting on a system in thermal equilibrium is zero. Using this principle, the sum rule is generalized to an arbitrary \( \nu \)-dimensional Coulomb plasma. As the result, for \( \Lambda \) a \( \nu \)-dimensional ellipsoidal domain, the asymptotic formula (1.22) for \( \chi^{\Lambda}_\nu \) is reproduced and its leading finite-size correction is obtained, in both canonical and grand canonical ensembles.

The paper is organized as follows. Section 2 is devoted to the derivation of the crucial sum rule for an arbitrary \( \nu \)-dimensional Coulomb plasma. Based on this sum rule, the splitting of the susceptibility into its macroscopic part (1.22) plus a corresponding finite-size correction term is shown for \( \nu \)-dimensional domains of ellipsoidal shape in Section 3. Section 4 presents an analysis of the finite-size correction term, dependent on the particular ensemble. The formalism is documented in Section 5 on the Debye-Hückel limit. The check on the exactly solvable 2D OCP at coupling \( \Gamma = 2 \) has already been done in the previous paper I. Concluding remarks are given in Section 6.
2 SUM RULES

One of us has derived several sum rules for the 2D OCP in paper I, using a mapping on a fermionic field theory. Actually, these sum rules are much more general. In the present section, the generalization of some of these sum rules is obtained by simple arguments about the balance of forces or torques.

Writing that the total force acting on the particles is zero, at equilibrium, results into a sum rule relating their density \( n(r) \) and their charge density \( \rho(r) \):

\[
\rho_b \int_{\Lambda} d^\nu r \, E_b(r) \rho(r) - \frac{1}{\beta} \int_{\partial\Lambda} dS \, n(r) = 0 \quad (2.1)
\]

where the first term in the l.h.s. is the force exerted by the background, and the second term is the force exerted by the walls. \( dS \equiv dS_n \) where \( n \) is the unit vector normal to the surface element \( dS \) and directed towards the exterior of \( \Lambda \). This is the generalization of Eqs. (56) of paper I. For simplicity, we have assumed that the particle-wall interaction is a hard one, such that the center of each particle feels a hard wall on \( \partial\Lambda \).

A similar sum rule is obtained by assuming that a particle of species \( \alpha_1 \) is fixed at point \( r_1 \), and writing that the total force acting on the other particles vanishes. Now, the force that the fixed particle exerts on the other ones must also be included in the force balance, which reads

\[
\beta \rho_b \int_{\Lambda} d^\nu r_2 E_b(r_2) \sum_{\alpha_2} q_{\alpha_2} n^{(2)}_{\alpha_2\alpha_1}(r_2, r_1) - \int_{\partial\Lambda} dS_2 \sum_{\alpha_2} n^{(2)}_{\alpha_2\alpha_1}(r_2, r_1)
\]

\[
+ \beta \int_{\Lambda} d^\nu r_2 \sum_{\alpha_2} q_{\alpha_1} q_{\alpha_2} F(r_2 - r_1) n^{(2)}_{\alpha_2\alpha_1}(r_2, r_1) = 0 \quad (2.2)
\]

where we have used that the density of particles of species \( \alpha_2 \) at \( r_2 \), knowing that there is a particle of species \( \alpha_1 \) at \( r_1 \), is \( n^{(2)}_{\alpha_2\alpha_1}(r_2, r_1)/n_{\alpha_1}(r_1) \). If there are short-range interactions, they must be added to the definition \( (1.3) \) of the Coulomb force \( F \). Another form of Eq. (2.2) can be obtained by using the first BGY equation which can be written as

\[
\nabla n_{\alpha_1}(r_1) = \beta \rho_b E_b(r_1) q_{\alpha_1} n_{\alpha_1}(r_1)
\]

\[
+ \beta \int_{\Lambda} d^\nu r_2 \sum_{\alpha_2} q_{\alpha_1} q_{\alpha_2} F(r_1 - r_2) n^{(2)}_{\alpha_2\alpha_1}(r_2, r_1) \quad (2.3)
\]

With regard to the equality \( F(r_1 - r_2) = -F(r_2 - r_1) \), using Eq. (2.3) for the last term in the l.h.s of Eq. (2.2) gives

\[
\beta \rho_b \int_{\Lambda} d^\nu r_2 E_b(r_2) \left[ \sum_{\alpha_2} q_{\alpha_2} n^{(2)}_{\alpha_2\alpha_1}(r_2, r_1) + q_{\alpha_1} n_{\alpha_1}(r_1) \delta(r_2 - r_1) \right]
\]
Finally, we multiply Eq. (2.4) by $q_{\alpha_1}$ and sum on $\alpha_1$, we multiply Eq. (2.1) by $\beta \rho(r_1)$, and we subtract from each other the two resulting equations, with the result

$$
\beta \rho_b \int_{\Lambda} d^3r_2 r_2 \mathbb{E}_b(r_2) S(r_2, r_1) = \nabla \rho(r_1) + \int_{\partial \Lambda} dS_2 \sum_{\alpha_1, \alpha_2} q_{\alpha_1} U_{\alpha_2 \alpha_1}(r_2, r_1)
$$

(2.5)

This is the crucial sum rule which is the generalization of Eq. (60) of paper I.

Although we shall not need them in the following, let us mention that another class of sum rules can be obtained from the balance of torques. For instance, in three dimensions, writing that the total torque acting on the particles (due to both the background and the walls) vanishes at equilibrium gives the sum rule

$$
\beta \rho_b \int_{\Lambda} d^3r [r \times \mathbb{E}_b(r)] \rho(r) + \int_{\partial \Lambda} [dS \times \mathbb{r}] n(r) = 0
$$

(2.6)

This is the generalization of Eq. (41b) of paper I. If one particle is assumed to be fixed at some point, one obtains the torque analog of Eq. (2.5)

$$
\beta \rho_b \int_{\Lambda} d^3r_2 [r_2 \times \mathbb{E}_b(r_2)] S(r_2 | r_1) = [r_1 \times \nabla] \rho(r_1) - \int_{\partial \Lambda} [dS_2 \times \mathbb{r}_2] \sum_{\alpha_1, \alpha_2} q_{\alpha_1} U_{\alpha_2 \alpha_1}(r_2, r_1)
$$

(2.7)

This is the generalization of Eq. (45b) of paper I.

The sum rules (41a) and (45a) of paper I can also be generalized, following a method developed in refs. [11] and [12]. However, these generalizations will not be described here.

3 DERIVATION OF THE SUSCEPTIBILITY

Let $\Lambda$ be a $\nu$-dimensional ellipsoid in the reference frame defined by the axes of the ellipsoid,

$$
\Lambda : \sum_{i=1}^{\nu} \left( \frac{r_i}{R_i} \right)^2 \leq 1
$$

(3.1)

In this reference frame both tensors $\chi_\Lambda$ and $T_\Lambda$ are diagonal. For the domain shape under consideration, the depolarization tensor $T_\Lambda$ is expressible
as \(r \in \Lambda\), while \(\phi_b(r)\) is invariant under the transformations \(r^i \to -r^i\). This implies that
\[
\phi_b(r) = \text{const} - \frac{s_\nu}{2} \sum_{i=1}^{\nu} T^i_\Lambda (r^i)^2
\] (3.2)
The corresponding \(E_b(r) = -\nabla \phi(r)\) reads
\[
E_b(r) = s_\nu \sum_{i=1}^{\nu} T^i_\Lambda r^i e^i
\] (3.3)
where \(e^i\) is the unit vector along the \(i\)th axis. The components of \(T^i_\Lambda\) for a 2D ellipse read
\[
T^1_\Lambda = \frac{R^2}{R^1 + R^2}, \quad T^2_\Lambda = \frac{R^1}{R^1 + R^2}
\] (3.4)
The components of \(T^i_\Lambda\) are more complicated functions of \(R^1, R^2, R^3\) for a 3D ellipsoid \([1]\). In the isotropic case \(R^i = R\) of a \(\nu\)-dimensional sphere, \(T^i_\Lambda = 1/\nu\).

Inserting (3.3) into the sum rule (2.5), and defining the components \(dS^i_2 = dS_2 \cdot e^i\), one gets for each component the equality
\[
\beta \rho_b s_\nu T^i_\Lambda \int_{\Lambda} d\nu r^i \rho(r) + \int_{\partial\Lambda} dS^i_2 \sum_{\alpha_1,\alpha_2} q_{\alpha_1} U_{\alpha_2,\alpha_1}(r_2, r_1)
\] (3.5)
We multiply both sides of (3.5) by \(r^1\), then integrate \(\int_{\Lambda} d\nu r^1\) and use the definition (1.17) of the dielectric susceptibility, for obtaining
\[
\rho_b s_\nu T^i_\Lambda \chi^i_\Lambda |\Lambda| = \int_{\Lambda} d\nu r^i \frac{\partial}{\partial r^1} \rho(r) + \int_{\Lambda} d\nu r^i \int_{\partial\Lambda} dS^i_2 \sum_{\alpha_1,\alpha_2} q_{\alpha_1} U_{\alpha_2,\alpha_1}(r_2, r_1)
\] (3.6)
Simple algebra gives
\[
\int_{\Lambda} d\nu r^i \frac{\partial}{\partial r^1} \rho(r) = \int_{\Lambda} d\nu r \frac{\partial}{\partial r^i} [r^i \rho(r)] - \int_{\Lambda} d\nu r [\rho(r) + \rho_b - \rho_b]
\]
\[
= \int_{\partial\Lambda} dS^i r^i \rho(r) - \langle \hat{Q} \rangle + \rho_b |\Lambda|
\] (3.7)
where
\[
\hat{Q} = \int_{\Lambda} d\nu r [\hat{\rho}(r) + \rho_b]
\] (3.8)
is the microscopic total charge (including the fixed background charge) in the domain. Provided that \(\rho_b \neq 0\), Eq. (3.6) can be thus rewritten in the
This is the desired splitting of the susceptibility onto its macroscopic part (1.22) plus a finite-size correction term.

The formula (3.9) can be further simplified in the isotropic case of a \(\nu\)-dimensional spherical domain \(\Lambda\) with a radius \(R\) and a volume \(|\Lambda| = s_\nu R^{\nu}/\nu\). Since now the components \(\chi_i^{\Lambda}\) do not depend on \(i\), we can consider their common value \(\bar{\chi}_\Lambda = \sum_{i=1}^{\nu} \chi_i^{\Lambda}/\nu\). For the \(\nu\)-dimensional sphere it holds

\[
dS_i = \frac{r_i^2}{R} dS_2, \quad \sum_{i=1}^{\nu} r_i^1 dS_i^2 = r_1 \cos \theta dS_2
\]

where \(\theta\) is the angle between \(\mathbf{r}_1\) and \(\mathbf{r}_2\). Since \(\langle \hat{\rho}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2) \rangle^T\) depends on the orientations of \(\mathbf{r}_1\) and \(\mathbf{r}_2\) only through their angle \(\theta\), we can choose \(\mathbf{r}_2\) along the 1-axis and replace \(\int_{\partial \Lambda} dS_2\) by \(s_\nu R^{\nu-1}\). Eq. (3.9) takes the form

\[
\bar{\chi}_\Lambda = \frac{\nu}{s_\nu} - \frac{\nu}{\rho_b s_\nu} \left[ \frac{\langle \hat{Q} \rangle}{|\Lambda|} - \frac{1}{R} \int_{\Lambda} d^\nu r \langle \hat{\rho}(\mathbf{r})\hat{n}(\mathbf{R}) \rangle^T \right]
\]

(3.11)

where \(\mathbf{R} = (R, 0, \ldots, 0)\). It is sometimes convenient to express \(r^1\) in the integral on the r.h.s. of (3.11) as \(r^1 = R - (R - r^1)\) and in this way to obtain an alternative “boundary” form of Eq. (3.11),

\[
\bar{\chi}_\Lambda = \frac{\nu}{s_\nu} - \frac{\nu}{\rho_b s_\nu} \left[ \frac{\langle \hat{Q} \rangle}{|\Lambda|} - \langle \hat{Q}\hat{n}(\mathbf{R}) \rangle^T + \frac{1}{R} \int_{\Lambda} d^\nu r (R - r^1) \langle \hat{\rho}(\mathbf{r})\hat{n}(\mathbf{R}) \rangle^T \right]
\]

(3.12)

The above formalism applies to the case \(\rho_b \neq 0\), with no restriction on the use of canonical or grand-canonical ensembles. When \(\rho_b \to 0\), for the sake of simplicity we shall restrict ourselves to the symmetric TCP in a \(\nu\)-dimensional sphere and to only microscopic states such that the total charge of the system is equal to zero, \(\hat{Q} = 0\). This is either the case of the canonical ensemble with imposed charge neutrality, or the case of a restricted grand-canonical ensemble when the fixed background of charge \(-Nq\) is first neutralized by \(N\) opposite charges +\(q\) and then ±\(q\) charges are added to the system in a variable number of neutral pairs [13]. Under these conditions, relation (3.12) reduces to

\[
\bar{\chi}_\Lambda = \frac{\nu}{s_\nu} - \frac{\nu}{\rho_b s_\nu} \frac{1}{R} \int_{\Lambda} d^\nu r (R - r^1) \langle \hat{\rho}(\mathbf{r})\hat{n}(\mathbf{R}) \rangle^T_{\rho_b}
\]

(3.13)
where the notation $\langle \cdots \rangle_{\rho_b}$ is used to emphasize that the average is taken in presence of the background. The background-charge density $\rho_b$ couples to particle coordinates in the Boltzmann factor $\exp[-\beta \rho_b \int_{\Lambda} d^nr' \phi_b(r') \hat{\rho}(r')]$, where $\phi_b$ is given in (3.2). In the limit $\rho_b \to 0$, the thermal average $\langle \cdots \rangle_{\rho_b}$ of a microscopic quantity can be expanded around $\rho_b = 0$, denoted simply as $\langle \cdots \rangle$, using the linear response theory:

$$\langle \cdots \rangle_{\rho_b} = \langle \cdots \rangle - \beta \rho_b \int_{\Lambda} d^nr' \phi_b(r') \langle \cdots \hat{\rho}(r') \rangle^T + O(\rho_b^2) \quad (3.14)$$

Since, due to the $+ \leftrightarrow -$ charge symmetry of the TCP, $\langle \hat{\rho}(r) \rangle = 0$ and $\langle \hat{\rho}(r) \hat{n}(R) \rangle = 0$ at any point $r \in \Lambda$, relation (3.13) can be rewritten in the $\rho_b \to 0$ limit as follows

$$\bar{\chi}_\Lambda = \frac{\nu}{s_{\nu}} - \beta \frac{1}{2 R} \int_{\Lambda} d^nr (R - r^3) \int_{\Lambda} d^nr' (r')^2 \times [\langle \hat{\rho}(r) \hat{\rho}(r') \hat{n}(R) \rangle - \langle \hat{\rho}(r) \hat{\rho}(r') \rangle \langle \hat{n}(R) \rangle] \quad (3.15)$$

We see that for the TCP with no background, three-body densities enter the finite-size contribution.

4 NON-EQUIVALENCE OF ENSEMBLES

Although the macroscopic result for the $\nu$-dimensional sphere $\bar{\chi}_\Lambda \sim \nu/s_{\nu}$ is the same in both the canonical and grand-canonical ensembles, the finite-size correction term in (3.12) is ensemble-dependent.

4.1 Canonical Ensemble

In the canonical ensemble, the microscopic total charge is fixed, $\hat{Q} = Q$. Let us analyze term by term the finite-size corrections appearing on the r.h.s. of Eq. (3.12).

If there is some excess charge in the domain $\Lambda$, due to the electrostatic repulsion it has tendency to move to the domain boundary $\partial \Lambda$ and to create there a macroscopic surface charge density $\sigma = Q/|\partial \Lambda|$. We note that, as a consequence, $\langle \hat{Q} \rangle/|\Lambda| = \nu \sigma/R$, and it is reasonable to assume that $\sigma$ is finite. The other thermal averages in (3.12) are assumed to be taken for a fixed $\sigma$.

Since the microscopic total charge does not fluctuate, $\langle \hat{Q} \hat{n}(R) \rangle^T = 0$.

One has to be cautious when identifying the $R \to \infty$ limit of the dipole moment in the last term with its flat hard-wall counterpart: owing to a slow power-law decay of the correlations along a plain hard wall\cite{14-17}, the limit cannot be freely interchanged with the integration. In particular, let
us consider in \( \nu \)-dimensions a semi-infinite Coulomb plasma which occupies the half-space \( x > 0 \); we denote by \( y \) the set of remaining \((\nu-1)\) coordinates normal to \( x \). The plane at \( x = 0 \) is charged with the uniform surface charge density \( \sigma \). It is shown in Appendix that in dimensions \( \nu = 2, 3 \) the \( R \to \infty \) limit of the considered sphere dipole moment is related to the corresponding flat dipole moment as follows:

\[
\lim_{R \to \infty} \int \Lambda d\nu r(R - r)(\hat{\rho}(r)\hat{n}(R))^T = 2 \int_0^\infty dx x \int dy (\hat{\rho}(x, y)\hat{n}(0, 0))^T
\]

The factor 2 in this equation was first observed in paper I for the case of the 2D OCP at coupling \( \Gamma = 2 \). Its temperature-independence is also checked in the Debye-Hückel limit (see the next section).

We conclude that in \( \nu = 2, 3 \) dimensions the formula for the dielectric susceptibility tensor of the Coulomb conductor, evaluated in the canonical ensemble up to the leading \( 1/R \) finite-size correction term, reads

\[
\chi_\Lambda \sim \frac{\nu}{s_\nu} - \frac{\nu}{\rho_b s_\nu} \frac{1}{R} \left[ \nu\sigma + 2 \int_0^\infty dx x \int dy (\hat{\rho}(x, y)\hat{n}(0, 0))^T \right]
\]

This result can be readily extended to the \( \rho_b \to 0 \) limit of the symmetric TCF with \( Q = 0 \) (and, consequently, \( \sigma = 0 \)), discussed at the end of the previous section. Using for the truncated correlation in (3.14) the linear response (3.14), now in the half-space geometry with \( \phi_b(r') = -s_\nu (x')^2/2 \), one arrives at

\[
\chi_\Lambda \sim \frac{\nu}{s_\nu} - \nu \beta \frac{1}{R} \int_0^\infty dx x \int dy \int_0^\infty dx' (x')^2 \int dy' \left[ \langle \hat{\rho}(x, y)\hat{\rho}(x', y')\hat{n}(0, 0) \rangle - \langle \hat{\rho}(x, y)\hat{\rho}(x', y') \rangle \langle \hat{n}(0, 0) \rangle \right]
\]

Although the finite-size analysis was made for the \( \nu = 2, 3 \) spherical geometries, it can be simply generalized via Eq. (4.1) to an arbitrary \( \nu \)-dimensional ellipsoid: the leading correction term is still of the order of 1 over the characteristic length of the domain.

### 4.2 Grand Canonical Ensemble

The grand-canonical analysis of the finite-size corrections in (3.12) fundamentally depends on the dimension.

**Two Dimensions.** In the grand canonical ensemble, necessarily the total charge \( \hat{Q} \) vanishes and does not fluctuate \( \hat{\rho}_b \) (except in a very special case not discussed here). This is because bringing a charged particle into the system from a reservoir at infinity, with a hole left in the reservoir,
would cost an infinite energy, and this cannot be achieved with finite fugacities. Thus, the terms \( \langle \hat{Q} \rangle \) and \( \langle \hat{Q} \hat{n}(\mathbf{R}) \rangle^T \) vanish in (3.11) and (3.12). Furthermore, (4.1) and (4.3) are still valid.

**Three Dimensions.** In the grand canonical ensemble, for a finite system, \( \langle \hat{Q} \rangle \) is determined by the fugacities and does not vanish, except for special adjustments of these fugacities. However, \( \langle \hat{Q} \rangle \) is at most of order \( R \). Indeed, when the sphere already carries a charge \( Q \), the work required from bringing one more particle of charge \( q \) into the system from the reservoir has an electric part \( qQ/R \). Therefore, with finite chemical potentials, \( qQ/R \) has to be finite.

The total charge does fluctuate, with a variance such that \( \beta \langle \hat{Q}^2 \rangle^T = R \) in the large-\( R \) limit, and the term \( \langle \hat{Q} \hat{n}(\mathbf{R}) \rangle^T \) in (3.12) does not vanish, and is of order \( 1/R \) as shown below.

Indeed, considering for simplicity the case of the OCP in a 3D sphere of radius \( R \), \( \langle \hat{Q} \hat{n}(\mathbf{R}) \rangle^T \) is proportional to the total charge on the sphere when one of the particles of charge \( q \) is fixed on the surface. Macroscopic electrostatics says that, when a point charge \( q \) is at distance \( r \geq R \) from the center of a grounded sphere, it induces on it a surface charge \( q' = -(R/r)q \). Thus, the total charge \( q + q' \) vanishes if \( r = R \). However, actually, the “surface” charge has some microscopic thickness \( \lambda \) of the order of the charge correlation length, and it is better to describe approximately the configuration of a particle fixed on the surface as a particle at distance \( R \) from the center of a sphere of radius \( R - \lambda \). Thus \( q' = -[(R - \lambda)/R]q \), the total charge \( q + q' \) is of order \( q\lambda/R \), and \( \langle \hat{Q} \hat{n}(\mathbf{R}) \rangle^T \) is expected to be of order \( \rho\lambda/R \).

Finally, in (3.11) and (3.12), in the large-\( R \) limit, the term \( \langle \hat{Q} \rangle/|\Lambda| \) is at most of order \( 1/R^2 \) and can be discarded. But the term \( \langle \hat{Q} \hat{n}(\mathbf{R}) \rangle^T \) gives to (3.12) a contribution of order \( 1/R \), like the dipole integral, and both should be kept in the leading finite-size correction. As to (4.1) and (4.3), they are still valid.

## 5 DEBYE-HÜCKEL THEORY

The formulas (3.11) and (4.1) will now be tested in the weak-coupling limit, which is described by the Debye-Hückel theory, for the general system of \( M \) species of point particles plus a background, in two or three dimensions.

### 5.1 General Formalism

A consistent way of deriving the Debye-Hückel theory for a finite system is to start with the renormalized Mayer diagrammatic expansion (which is reviewed, for instance, in refs. [18] and [19]), in the grand canonical ensem-
ble, and to make a topological reduction, replacing the fugacities by the densities. The weak-coupling limit for the correlation functions is obtained by resumming the chain diagrams with the densities taken as constants \( n_\alpha \) (taking into account their position-dependence near the boundary \( \partial \Lambda \) would give corrections of higher order). This is equivalent to writing the Ornstein-Zernicke equations with the direct correlation functions replaced by \(-\beta \) times the corresponding interaction potential:

\[
h_{\alpha_1 \alpha_2}(\mathbf{r}_1, \mathbf{r}_2) = -\beta q_{\alpha_1} q_{\alpha_2} v(|\mathbf{r}_1 - \mathbf{r}_2|) + \sum_{\alpha_3} \int_\Lambda d^\nu r_3 [-\beta q_{\alpha_1} q_{\alpha_3} v(|\mathbf{r}_1 - \mathbf{r}_3|)] n_{\alpha_3} h_{\alpha_3 \alpha_2}(\mathbf{r}_3, \mathbf{r}_2)
\]

where the correlation functions \( h \) are related to the Ursell functions by

\[
U_{\alpha_1 \alpha_2}(\mathbf{r}_1, \mathbf{r}_2) = n_{\alpha_1} n_{\alpha_2} h_{\alpha_1 \alpha_2}(\mathbf{r}_1, \mathbf{r}_2).
\]

The set (5.1) of \( M^2 \) coupled equations can be transformed into one equation. Indeed, let us make the ansatz

\[
h_{\alpha_1 \alpha_2}(\mathbf{r}_1, \mathbf{r}_2) = -\beta q_{\alpha_1} q_{\alpha_2} G(\mathbf{r}_1, \mathbf{r}_2)
\]

Using (5.2) in (5.1) one does check that these Ornstein-Zernicke equations are satisfied provided that

\[
\frac{\kappa^2}{s_\nu} = s_\nu \beta \sum_\alpha n_\alpha q_\alpha^2; \text{ the Debye length is } 1/\kappa.
\]

Using (5.2) one finds

\[
\langle \hat{\rho}(\mathbf{r}_1) \hat{n}(\mathbf{r}_2) \rangle_T = -\frac{\rho \kappa^2}{s_\nu} G(\mathbf{r}_1, \mathbf{r}_2) + \rho \delta(\mathbf{r}_1 - \mathbf{r}_2)
\]

and

\[
S(\mathbf{r}_1, \mathbf{r}_2) \equiv \langle \hat{\rho}(\mathbf{r}_1) \hat{\rho}(\mathbf{r}_2) \rangle_T = -\frac{1}{\beta} \left( \frac{\kappa^2}{s_\nu} \right)^2 G(\mathbf{r}_1, \mathbf{r}_2) + \frac{\kappa^2}{\beta s_\nu} \delta(\mathbf{r}_1 - \mathbf{r}_2)
\]

The integral equation (5.3) for \( G \) can be transformed into a differential equation by taking the Laplacian with respect to \( \mathbf{r}_1 \). One obtains the usual Debye-Hückel equation for the screened Coulomb potential \( G \)

\[
[\Delta_1 - \kappa^2] G(\mathbf{r}_1, \mathbf{r}_2) = -s_\nu \delta(\mathbf{r}_1 - \mathbf{r}_2)
\]

However, in a finite system, the differential equation (5.6) must be supplemented by boundary conditions. In the present approach, these boundary conditions are provided by the integral equation (5.3).

It has been seen in Section 3 that, in general, when there is a background, the finite-size correction to the susceptibility can be expressed in
terms of the two-body correlation appearing in (3.11), while, in the limit of no background, one obtains the more complicated expression (3.15) in terms of a three-body correlation. The Debye-Hückel theory has the very special feature that this complication does not arise. Indeed, since \( \rho = -\rho_b \), one sees in (5.4) that \( \langle \hat{\rho}(r_1) \hat{n}(r_2) \rangle^T / \rho_b \) is expressed in terms of the two-body function \( G \) even in the limit \( \rho_b \to 0 \). Furthermore \( \langle \hat{Q} \rangle = 0 \). Therefore (3.11) still involves only a two-body correlation in this limit \( \rho_b \to 0 \).

5.2 2D Disk

In an infinite plane, (5.6) gives \( G(r_1, r_2) = K_0(\kappa |r_1 - r_2|) \), where \( K_0 \) is a modified Bessel function. In a finite disk of radius \( R \), the solution is of the form

\[
G(r_1, r_2) = \sum_{\ell=0}^{\infty} [I_\ell(s_<)K_\ell(s_>) + a_\ell I_\ell(s_1)I_\ell(s_2)] \mu_\ell \cos \ell \theta
\]

where \( s_{1,2} = \kappa r_{1,2} \), \( s_< \) and \( s_> \) are the smallest and the largest, respectively, of \( s_1 \) and \( s_2 \), \( I_\ell \) and \( K_\ell \) are modified Bessel functions, and \( a_\ell \) a coefficient to be determined; \( \mu_\ell \) is the Neumann factor \( \mu_0 = 1, \mu_\ell = 2 \) for \( \ell \geq 1 \). In the square bracket of (5.7) the first term corresponds to an expansion of \( K_0(\kappa |r_1 - r_2|) \), while the second term corresponds to the general symmetric solution of (5.6) without the r.h.s. \( \delta \) term.

The determination of \( a_0 \) from the integral equation (5.3) has been discussed in ref. \[20\], where it has been argued that the length scale \( r_0 \) in the 2D Coulomb potential \( v \) must be made infinite at the end of the calculation. The result is \( a_0 = K_1(Z)/I_1(Z) \), where \( Z = \kappa R \).

For determining \( a_\ell \) when \( \ell \geq 1 \), we consider the integral equation (5.3), and use for \( G \) the expansion (5.7) and for \( v \) the expansion

\[
v(|r_1 - r_2|) = -\ln \frac{|r_1 - r_2|}{r_0} = -\ln \frac{r_>}{r_0} + \sum_{\ell=1}^{\infty} \frac{1}{\ell} \left( \frac{r_<}{r_>} \right) \ell \cos \ell (\theta_2 - \theta_1)
\]

In the angular integral on \( \theta_3 \), only the terms involving the same \( \ell \) in the two expansions (5.7) and (5.8) survive. In terms of the square bracket in (5.7), i.e.

\[
G_\ell(r_1, r_2) \equiv I_\ell(s_<)K_\ell(s_>) + a_\ell I_\ell(s_1)I_\ell(s_2)
\]

one obtains, when \( r_1 > r_2 \),

\[
2G_\ell(r_1, r_2) = \frac{1}{\ell} \left( \frac{r_2}{r_1} \right) \ell - \kappa^2 \int_0^{r_1} dr_3 r_3 \frac{1}{\ell} \left( \frac{r_3}{r_1} \right) G_\ell(r_3, r_2) - \kappa^2 \int_{r_1}^R dr_3 r_3 \frac{1}{\ell} \left( \frac{r_1}{r_3} \right) G_\ell(r_3, r_2), \quad \ell \geq 1
\]

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One could solve (5.10). However, it is simpler to remark that it implies
\[ \frac{\partial G_\ell(r_1,r_2)}{\partial r_1}|_{r_1=R} = -\left(\ell/R\right)G_\ell(R,r_2) \]
Therefore, using the definition (5.9) for \( G_\ell(R,r_2) \) gives
\[ K'_\ell(Z) + a_\ell I'_\ell(Z) = -\frac{\ell}{Z} [K_\ell(Z) + a_\ell I_\ell(Z)], \quad \ell \geq 1 \quad (5.11) \]
a relation that Choquard et al.\[9\] have obtained by another method, involving a continuation of (5.6) outside the disk; that method led to some ambiguity for determining \( a_0 \). From (5.11), using simple relations obeyed by the Bessel functions, one obtains
\[ a_\ell = \frac{K_{\ell-1}(Z)}{I_{\ell-1}(Z)} \quad (5.12) \]
This final equation turns out to be valid for all \( \ell \), including \( \ell = 0 \).

Using (5.11) and (5.12) in (5.2), one can easily check the perfect screening expected in two dimensions, even in the grand canonical ensemble: the charge in the cloud around a particle of charge \( q_{\alpha_2} \) is \(-q_{\alpha_2}\).
\[ \int_A d^2r_1 \sum_{\alpha_1} q_{\alpha_1} n_{\alpha_1} h_{\alpha_1\alpha_2}(r_1,r_2) = -q_{\alpha_2} \quad (5.13) \]

We now turn to the dielectric susceptibility. From its definition (1.17), using the present \( S(r_1,r_2) \), one obtains \[9\]
\[ \bar{\chi}_A = \frac{1}{\pi} \left[ 1 - \frac{2I_1(\kappa R)}{\kappa R I_0(\kappa R)} \right] \quad (5.14) \]
Alternatively, one can use the general method of the present paper and check the expression (3.11). Here \( \langle \hat{Q} \rangle = 0 \), and \( \rho_b = -\rho \). Let \(-D_{\text{disk}}\) be the dipole moment defined as the integral in (3.11) (we call this dipole moment \(-D\) rather than \(D\) for using the same notation as in the Appendix). Only the part \( \ell = 1 \) of \( G \) contributes to this integral. Using \( \langle \hat{\rho}(r)\hat{n}(R) \rangle^T \) from (5.4) and \( G_1 \) from (5.9) with \( a_1 \) from (5.11) gives, after simple manipulations on the Bessel functions,
\[ D_{\text{disk}} = -\frac{2\rho I_1(\kappa R)}{I_0(\kappa R)} \quad (5.15) \]
It should be remarked that, since in 2D \( \langle \hat{Q}\hat{n}(R) \rangle^T = 0 \), \( D_{\text{disk}} \) is also the integral in (3.12). Using (5.15) in (3.11) or (3.12), one retrieves the same \( \bar{\chi}_A \) as in (5.14). In the large-\( R \) limit, in (5.14) \( I_1(\kappa R)/I_0(\kappa R) \to 1 \) and one sees that the correction term is indeed of order \( 1/R \):
\[ \bar{\chi}_A \sim \frac{1}{\pi} - \frac{2}{\pi \kappa R} \quad (5.16) \]
The dipole moment $D_{\text{flat}}$ for a flat wall, in the 2D Debye-Hückel theory, has been computed in [16]. It can be checked that, in the limit $R \to \infty$, $D_{\text{disk}}$ does have twice the value found for $D_{\text{flat}}$.

### 5.3 3D Sphere

In infinite space, (5.6) gives $G(r_1, r_2) = \exp(-\kappa|r_1 - r_2|)/|r_1 - r_2|$. In a finite sphere of radius $R$, the same considerations as in 2D now give [9]

$$G(r_1, r_2) = \sum_{\ell=0}^{\infty} \frac{2\ell + 1}{\sqrt{r_1 r_2}} \left[ I_{\ell + \frac{1}{2}}(s_<)K_{\ell + \frac{1}{2}}(s_>) + b_\ell I_{\ell + \frac{1}{2}}(s_1)I_{\ell + \frac{1}{2}}(s_2) \right] P_\ell(\cos \theta)$$

(5.17)

where $P_\ell$ is a Legendre polynomial. As in 2D, the coefficients $b_\ell$ can be determined by using the integral equation (5.3), with the same result as in ref. [9]:

$$b_\ell = \frac{K_{\ell - \frac{1}{2}}(Z)}{I_{\ell - \frac{1}{2}}(Z)}$$

(5.18)

With our method, there is no special problem or ambiguity with the case $\ell = 0$.

As expected, there is no perfect screening, since the starting point was the grand canonical ensemble. Using (5.17) and (5.18) in (5.2) gives

$$\int \Lambda d^3 r_1 \sum_{\alpha_1, n_{\alpha_1}} h_{\alpha_1, \alpha_2}(r_1, r_2) = -q_{\alpha_2} \left[ 1 - \frac{\sinh \kappa R_2}{\kappa R_2 \cosh \kappa R} \right]$$

(5.19)

rather than $-q_{\alpha_2}$.

The dielectric susceptibility, computed from its definition (1.17) is found to be [11]

$$\chi_\Lambda = \frac{3}{4\pi} \left[ 1 - \frac{3I_\frac{1}{2}(\kappa R)}{\kappa R I_{-\frac{1}{2}}(\kappa R)} \right] \sim \frac{3}{4\pi} \left[ 1 - \frac{3}{\kappa R} \right]$$

(5.20)

Alternatively, one can use the general method of the present paper. Again $\langle \hat{Q} \rangle = 0$, $\rho_b = -\rho$, and only the part $\ell = 1$ of $G$ contributes to the integral in (3.11). One retrieves for the susceptibility the result (5.20).

It should be noted that, in 3D, $\hat{Q}$ fluctuates and $\langle \hat{Q}_\Lambda(\mathbf{R}) \rangle^T \neq 0$. One finds

$$\langle \hat{Q}_\Lambda(\mathbf{R}) \rangle^T = \rho \frac{I_\frac{1}{2}(\kappa R)}{\kappa R I_{-\frac{1}{2}}(\kappa R)} \sim \frac{\rho}{\kappa R}$$

(5.21)

in agreement with the qualitative estimate of Section 4.2. Therefore, with $D_{\text{sph}}$ defined as the integral in (3.12), the equivalence of (3.11) and (3.12) gives

$$D_{\text{sph}} \sim \frac{2\rho}{\kappa}$$

(5.22)
and the finite-size correction to $\bar{\chi}_\Lambda$ can be decomposed as

$$\bar{\chi}_\Lambda \sim \frac{3}{4\pi} \left[ \frac{1}{\kappa R} - \frac{2}{\kappa R} \right]$$

(5.23)

where the term $1/\kappa R$ is the contribution from $\langle \hat{Q} \hat{n}(R) \rangle^T$ and the term $2/\kappa R$ is the contribution from the dipole moment $D_{sph}$ seen from the boundary. Again, in the limit $R \to \infty$, $D_{sph}$ does have twice the value found for a flat wall [16] in the Debye-Hückel theory.

6 CONCLUSION

Macroscopic electrostatics predicts a shape-dependent value for the dielectric susceptibility of a conductor (the response, sometimes called polarizability, to a uniform applied electric field). In the present paper, it has been shown that classical (i.e. non-quantum) equilibrium statistical mechanics of a large class of microscopic models results into a dielectric susceptibility which is the sum of the macroscopic value plus an explicit finite-size correction. Thus, the limits of validity of macroscopic electrostatics are clearly exhibited.

The basis for the microscopic derivation only is that the total force acting on a system vanishes at equilibrium. It is quite surprising that such a simple statement is sufficient, and the reason for that still is an open problem.

Our approach deals with models of Coulomb systems made of charged particles embedded in a uniformly charged background. The case of no background is dealt with as a limiting case. It seems that our method cannot be used for directly starting with a system without a background.

Classical statistical mechanics has been used. It gives an acceptable phenomenological description of some systems such as electrolytes or molten salts. We have not attempted to deal with a more fundamental description of real matter based on quantum statistical mechanics of point charges.

APPENDIX: DIPOLE MOMENTS

We briefly summarize known facts about the large-distance behavior of particle correlations along a plain, possibly homogeneously charged, hard-wall in $\nu = 2, 3$ dimensions. Let us first review the case of a semi-infinite Coulomb plasma which occupies the half-space $x > 0$; $y$ denotes the set of $(\nu - 1)$ coordinates normal to the $x$-axis. According to ref. [16], for the charge-density correlator one expects an asymptotic power-law behavior
along the boundary of type
\[ \langle \hat{\rho}(x, y)\hat{n}(x', 0) \rangle^T \sim \frac{g_\nu(x, x')}{|y|^{\nu}}, \quad |y| \to \infty \] (A.1)

where \( g_\nu(x, x') \), which as a function of \( x \) and \( x' \) has a fast decay away from the wall, obeys the relation
\[ \frac{s_\nu}{2} \int_0^\infty dx g_\nu(x, x') = \int_0^\infty dx x \int dy \langle \hat{\rho}(x, y)\hat{n}(x', 0) \rangle^T, \quad \nu = 2, 3 \] (A.2)

valid for any \( x' \geq 0 \). A behavior of type (A.1) at large distances was observed also in the large-\( R \)-limit of the \( \nu \)-dimensional sphere \([8, 17]\). For two points \( r \) and \( r' \) inside the sphere, it is only necessary to identify \( x \) and \( x' \) with the corresponding point distances from the sphere surface and \( |y| \) with the Euclidean distance (chord) of the point projections onto the sphere surface:
\[ x = R - r, \quad x' = R - r' \quad |y| = 2R \sin(\theta/2) \] (A.3)

where \( \theta \) is the angle between \( r \) and \( r' \). At small distances, an infinitesimal deformation of a flat boundary towards the sphere has a negligible effect on the correlations. We can therefore write, on both microscopic and macroscopic scales, that, as the radius of the sphere \( R \to \infty \),
\[ \langle \hat{\rho}(r)\hat{n}(r') \rangle^T\big|_{\text{sphere}} \sim \langle \hat{\rho}(x, y)\hat{n}(x', 0) \rangle^T\big|_{\text{flat}} \] (A.4)

In the dipole integral on the r.h.s. of (3.12), the correlator of interest is taken at the point \( r' = R \) fixed at the boundary, which corresponds to \( x' = 0 \) in (A.3). To simplify the notation, we define
\[ \psi_{\text{sph}}(x, \theta) = \langle \hat{\rho}(r)\hat{n}(r') \rangle^T\big|_{\text{sphere}}, \quad \psi_{\text{flat}}(x, |y|) = \langle \hat{\rho}(x, y)\hat{n}(0, 0) \rangle^T\big|_{\text{flat}} \] (A.5)

Within the identification (A.3) with \( x' = 0 \), the asymptotic \( R \to \infty \) equivalence (A.4) now takes the form
\[ \psi_{\text{sph}}(x, \theta) \sim \psi_{\text{flat}}(x, |y|): \quad |y| = 2R \sin(\theta/2) \] (A.6)

Our task is to relate the \( R \to \infty \) limit of the sphere dipole moment \( D_{\text{sph}} \) seen from the boundary and the flat dipole moment \( D_{\text{flat}} \), defined as follows
\[ D_{\text{sph}} = \int_A d^\nu r (R - r^1) \psi_{\text{sph}}(R - r, \theta) \] (A.7)
\[ D_{\text{flat}} = \int_0^\infty dx \int dy \psi_{\text{flat}}(x, |y|) \] (A.8)

Because of slight differences, the derivations of the relation are made separately for 2D (with notation “disk” instead of “sph”) and 3D.
2D Disk

Using the substitution $x = R - r$ and writing $r^1 = (R - x)[1 - 2\sin^2(\theta/2)]$, the disk dipole moment is expressible as

$$D_{\text{disk}} = \int_0^R dx \, x (R - x) \int_{-\pi}^{\pi} \sin^2(\theta/2) \psi_{\text{disk}}(x, \theta)$$

(A.9)

In the large-$R$ limit, we make use of the transformation (A.6) to get

$$D_{\text{disk}} = I_1 + I_2,$$

where

$$I_1 = \int_0^R dx \, x \left(1 - \frac{x}{R}\right) \int_{-2R}^{2R} dy \frac{\psi_{\text{flat}}(x, y)}{\sqrt{1 - \frac{y^2}{4R^2}}}$$

(A.10)

$$I_2 = 2 \int_0^R dx \, R \left(1 - \frac{x}{R}\right)^2 \int_{-2R}^{2R} dy \frac{y^2}{4R^2} \psi_{\text{flat}}(x, y)$$

(A.11)

Since $\psi_{\text{flat}}(x, y)$ as a function of $x$ has a fast decay away from the wall, the $x/R$ terms in $I_1$ and $I_2$ can be neglected in comparison with the unity when $R \to \infty$. After simple algebra, one finds for $I_1$

$$\lim_{R \to \infty} I_1 = D_{\text{flat}} + \int_0^\infty dx \, \lim_{R \to \infty} 2R \int_{-1}^{1} dt \left(\frac{1}{\sqrt{1 - t^2}} - 1\right) \psi_{\text{flat}}(x, 2tR)$$

(A.12)

Considering $\psi_{\text{flat}}(x, 2tR) \sim g_2(x, 0)/(2tR)^2$ implies a converging integral over $t$, so that $\lim_{R \to \infty} I_1 = D_{\text{flat}}$. As concerns the second integral $I_2$, it can be analogously written as

$$\lim_{R \to \infty} I_2 = \int_0^\infty dx \, \lim_{R \to \infty} (2R)^2 \int_{-1}^{1} \frac{dt}{\sqrt{1 - t^2}} t^2 \psi_{\text{flat}}(x, 2tR)$$

(A.13)

As above, we consider the leading asymptotic behavior of $\psi_{\text{flat}}(x, 2tR)$, with the result

$$\lim_{R \to \infty} I_2 = \int_0^\infty dx \, g_2(x, 0) \int_{-1}^{1} \frac{dt}{\sqrt{1 - t^2}} = D_{\text{flat}}$$

(A.14)

Here, relation with $s_2 = 2\pi$ was applied at $x' = 0$. We conclude that

$$\lim_{R \to \infty} D_{\text{disk}} = 2D_{\text{flat}}, \quad \nu = 2$$

(A.15)
3D Sphere

In 3D, the volume element $d^3r = r^2 dr d\Omega$, where the angular part $d\Omega = \sin \theta d\theta d\varphi$ with $\theta \in (0, \pi)$ and $\varphi \in (0, 2\pi)$. Using the substitution $x = R-r$, the sphere dipole moment (A.7) reads

$$D_{\text{sph}} = \int_0^R dx \left( R - x \right) (2\pi) \int_0^{2R} dy y \psi_{\text{flat}}(x, y)$$

In the large-$R$ limit, the transformation (A.6) implies $D_{\text{sph}} = I_1 + I_2$, where

$$I_1 = \int_0^R dx \left( 1 - \frac{x}{R} \right)^2 \int_0^{2R} dy y \psi_{\text{flat}}(x, y)$$

$$I_2 = 2 \int_0^R dx R \left( 1 - \frac{x}{R} \right)^3 \int_0^{2R} dy y^2 \psi_{\text{flat}}(x, y)$$

Here, we have used $\int d\Omega = (2\pi/R^2) \int_0^R dy y$. As in 2D, the $x/R$ terms are neglected as $R \to \infty$. Thus, $\lim_{R \to \infty} I_1 = D_{\text{flat}}$ and

$$\lim_{R \to \infty} I_2 = 2\pi \int_0^\infty dx \lim_{R \to \infty} (2R)^3 \int_0^1 dt t^3 \psi_{\text{flat}}(x, 2tR)$$

The leading asymptotic behavior $\psi_{\text{flat}}(x, 2tR) \sim g_3(x, 0)/(2tR)^3$ as $R \to \infty$ gives

$$\lim_{R \to \infty} I_2 = 2\pi \int_0^\infty dx g_3(x, 0) = D_{\text{flat}}$$

where the relation (A.2) with $s_3 = 4\pi$ was applied at $x' = 0$. Finally,

$$\lim_{R \to \infty} D_{\text{sph}} = 2D_{\text{flat}}, \quad \nu = 3$$

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