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Classical Coulomb Systems: Screening and Correlations Revisited

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From the laws of macroscopic electrostatics of conductors (in particular, the existence of screening), taken as given, one can deduce universal properties for the thermal fluctuations in a classical Coulomb system at equilibrium. The universality is especially apparent in the long-range correlations of the electrical potentials and fields. The charge fluctuations are derived from the field fluctuations. This is a convenient way to study the surface charge fluctuations on a conductor with boundaries. Explicit results are given for simple geometries. The potentials and the fields have Gaussian fluctuations, except for a short-distance cutoff.

KEY WORDS: Coulomb systems; screening; fluctuations; correlations; surface correlations; universality.

1. INTRODUCTION

A salient property of matter is the screening effect: matter "in thermal equilibrium does not tolerate any charge inhomogeneity over more than a few intermolecular distances."(1) In the present paper, we consider those systems which can be described as made up of charged particles, interacting through Coulomb's law, to which equilibrium classical (i.e., non-quantum) statistical mechanics is applicable (for instance, electrolytes); then, screening has especially rich and simple consequences. From the existence of screening, taken as given, it is possible to deduce quantitative properties of the correlation functions. For instance, in the bulk, the charge–charge correlation function obeys the well-known Stillinger–Lovett sum rules;(2) other quantitative properties hold near walls or interfaces.(3) There is a

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delicate interplay between the statistical mechanics of correlations and the validity of macroscopic electrostatics.

In the standard approaches, the focus is on the charges. One assumes that an external charge is screened and, using linear response theory, one obtains information about the charge correlations. The purpose of the present paper is to revisit the subject with the focus put on the electric potential, the electric field, and their correlations. From this alternative point of view, it is possible to rederive known results in a way that we believe is often simpler and also to obtain new results. The present method, which relies on the validity of macroscopic electrostatics, is especially appropriate for studying surface properties such as surface charge correlations.

The Coulomb systems considered in the present paper form a large class of models. The one-component plasma is a model such that identical particles of one sign (say positive) are immersed in a neutralizing, inert, continuous background of the opposite sign. The two-component plasma is made up of two species of oppositely charged particles; a classical theory is possible only if some short-range interaction is also present, to prevent oppositely charged particles from collapsing on each other. One could also consider more complicated models, with more than two species of particles, a nonuniform one-particle potential added, etc. We shall only require that the model be a conductor, in that sense that the laws of macroscopic electrostatics are assumed to be obeyed for length scales large compared to the microscopic characteristic lengths of the model; for instance, an additional localized charge Q brought into the fluid should be perfectly screened, i.e., surround itself with a microscopic polarization cloud of charge $-Q$.

We shall also consider models with a two-dimensional Coulomb interaction: in two dimensions, the potential at a distance r from a unit point charge is $-\ln(r/L)$ (where L is some fixed length) instead of the familiar $1/r$ which holds in three dimensions. Two-dimensional Coulomb systems made up of oppositely charged particles exhibit the Kosterlitz–Thouless phase transition(4): while they are conductors above some transition temperature, they become dielectrics below that temperature. A similar transition occurs for one-dimensional systems with a logarithmic interaction.(5) The considerations of the present paper apply only to the conducting phase, i.e., above the transition temperature.

The present approach aims to provide an easy to visualize, physically reasonable picture of classical Coulomb fluids. No attempt is made at mathematical rigor. Since a basic ingredient is macroscopic electrostatics, a number of words will be used with a macroscopic meaning. "Inside" or "outside" a Coulomb fluid will mean "at a distance from the walls large compared to the microscopic scale." "Surface charge" will mean "charge in a layer of microscopic thickness under the surface." Etc.

The two-point correlations inside and outside a three-dimensional Coulomb system are discussed in Sections 2 and 3, respectively. In Section 4, we establish a general method for deriving the surface charge correlations. Examples are given in Section 5. Section 6 is about conducting surfaces. Section 7 is about systems with the two-dimensional logarithmic Coulomb interaction. In Section 8, it is shown that potential and field fluctuations are Gaussian (except for microscopic distances).

2. INSIDE A COULOMB SYSTEM

In this section, we consider some region inside a three-dimensional classical Coulomb fluid at equilibrium. This fluid is not necessarily homogeneous.

2.1. Potential and Field Correlations

Let $\phi(\mathbf{r})$ be the microscopic electrical potential at point $\mathbf{r}$. We wish to rederive the asymptotic formula for the potential–potential correlation function(6)

$$\beta\langle\phi(\mathbf{r})\,\phi(\mathbf{r}')\rangle^T \sim \frac{1}{|\mathbf{r}-\mathbf{r}'|}, \qquad |\mathbf{r}-\mathbf{r}'| \to \infty \tag{2.1}$$

where β is the inverse temperature $\langle\cdots\rangle^T$ means a truncated equilibrium statistical average: $\langle AB\rangle^T = \langle AB\rangle - \langle A\rangle\langle B\rangle$.

For deriving (2.1), we use screening and linear response. Let us put into the fluid an infinitesimal test charge q at $\mathbf{r}$. The Hamiltonian H_0 of the fluid must now be supplemented with the fluid–test charge interaction term, which can be written as $H' = q\phi(\mathbf{r})$, where ϕ is the potential due to the fluid; it sould be noted that ϕ is defined as *not* including the potential due to q. By linear response theory, the average of this potential at some point $\mathbf{r}'$ is changed by

$$\langle\phi(\mathbf{r}')\rangle_q - \langle\phi(\mathbf{r}')\rangle = -\beta q\langle\phi(\mathbf{r})\,\phi(\mathbf{r}')\rangle^T \tag{2.2}$$

where $\langle\cdots\rangle_q$ means a statistical average computed with the full Hamiltonian $H_0 + H'$, while $\langle\cdots\rangle$ is an average computed with H_0 only. Our assumption about screening is that q surrounds itself with a polarization cloud of microscopic size, of charge $-q$; the rest of the system is unchanged, except that, in the case of an insulated conductor, charge conservation requires that a charge $+q$ spreads on the walls. Therefore, for $|\mathbf{r}'-\mathbf{r}|$ large compared to the microscopic scale, the l.h.s. of (2.2) is the potential due to a pointlike charge $-q$ at $\mathbf{r}$ and a surface charge $+q$; at $\mathbf{r}'$ inside the conductor, that surface charge creates a constant potential q/C, where C is the capacitance. Altogether, for an insulated conductor,

$$\langle\phi(\mathbf{r}')\rangle_q - \langle\phi(\mathbf{r}')\rangle = -\frac{q}{|\mathbf{r}-\mathbf{r}'|} + \frac{q}{C} \tag{2.3}$$

From (2.2) and (2.3), one obtains

$$\beta\langle\phi(\mathbf{r})\,\phi(\mathbf{r}')\rangle^T = \frac{1}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{C} \tag{2.4}$$

For a grounded conductor, no surface charge appears, and the last term in (2.3) and (2.4) must be omitted. If the system becomes infinitely large, $1/C$ goes to zero. Thus, for infinite systems, one recovers (2.1) in all cases.

From our derivation, the "asymptotic" validity of (2.1) (for an infinite system) now has a more explicit meaning: (2.1) can be considered as an equality provided $|\mathbf{r}-\mathbf{r}'|$ is large compared to the microscopic scale (the screening length). From now on, we shall write (2.1) and similar equations as equalities, with the understanding that there is some microscoic short-distance cutoff. This point of view, commonly used in field theory or in the theory of critical phenomena, is convenient for studying those properties which are independent of the microscopic detail, i.e., universal.

Since the electrical field is $E_\mu(\mathbf{r}) = -\partial_\mu\phi(\mathbf{r})$, the field–field correlation function is easily obtained from (2.4) (with or without the last term) as

$$\begin{aligned}\beta\langle E_\mu(\mathbf{r})\,E_\nu(\mathbf{r}')\rangle^T &= \frac{\partial^2}{\partial r_\mu\,\partial r'_\nu}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\\ &= -\frac{3(\mathbf{r}-\mathbf{r}')_\mu(\mathbf{r}-\mathbf{r}')_\nu - \delta_{\mu\nu}(\mathbf{r}-\mathbf{r}')^2}{|\mathbf{r}-\mathbf{r}'|^5}\end{aligned} \tag{2.5}$$

while $\langle\mathbf{E}(\mathbf{r})\rangle = 0$, since $\langle\phi(\mathbf{r})\rangle$ is a constant inside a conductor.

2.2. Charge Correlations

The charge density $\rho(\mathbf{r})$ is related to the potential $\phi(\mathbf{r})$ by Poisson's equation $\Delta\phi = -4\pi\rho$. Thus, by taking the Laplacian on $\mathbf{r}$ in both sides of (2.4), one obtains

$$\beta\langle\rho(\mathbf{r})\,\phi(\mathbf{r}')\rangle^T = \delta(\mathbf{r}-\mathbf{r}') \tag{2.6}$$

Of course, writing the r.h.s. of (2.6) as a delta function disregards some spreading and microscopic structure for small distances. But the simplified form (2.6) is enough for correctly giving, by integration upon **r**,

$$\beta \int d\mathbf{r}\, \langle \rho(\mathbf{r})\, \phi(\mathbf{r}') \rangle^T = 1 \tag{2.7}$$

which is the Carnie–Chan sum rule.(7)

In the case of a homogeneous fluid, the Carnie–Chan sum rule is equivalent to the Stillinger–Lovett(2) sum rule. We can retrieve that equivalence by taking the Laplacian on **r**′ in both sides of (2.7), with the result

$$-4\pi\beta \langle \rho(\mathbf{r})\, \rho(\mathbf{r}') \rangle^T = \Delta\delta(\mathbf{r}-\mathbf{r}') \tag{2.8}$$

(Here the assumption that the fluid is homogeneous is necessary, because δ actually stands for some peaked function of $\mathbf{r}-\mathbf{r}'$; if the fluid were nonhomogeneous, the microscopic width of that peak would be a function of **r**′, and taking the Laplacian on **r**′ would generate additional terms.) From (2.8), one obtains

$$\int \langle \rho(\mathbf{r})\, \rho(\mathbf{r}') \rangle^T d\mathbf{r}' = 0 \tag{2.9a}$$

and (after an integration by parts)

$$-\frac{2\pi\beta}{3} \int \langle \rho(\mathbf{r})\, \rho(\mathbf{r}') \rangle^T (\mathbf{r}-\mathbf{r}')^2\, d(\mathbf{r}-\mathbf{r}') = 1 \tag{2.9b}$$

Equations (2.9a) and (2.9b) are the well-known Stillinger–Lovett sum rules; it is amusing that they can be written in the form (2.8), which, again, disregards the microscopic detail.

3. OUTSIDE A COULOMB SYSTEM

We now consider correlations involving at least one point outside the boundaries of a conductor.

3.1. Potential and Field Correlations Across the Boundary

We want to compute the potential–potential correlation $\langle \phi(\mathbf{r})\, \phi(\mathbf{r}') \rangle^T$ when **r** is inside the Coulomb fluid and **r**′ is outside. We can repeat the reasoning of Section 2.1, considering the response to an infinitesimal test charge q at **r**. The only difference is that the induced surface charge q, which appears in the case of an insulated conductor, creates at $\mathbf{r}'$ outside the conductor a potential $qF(\mathbf{r}')$ rather than q/C. This function $F(\mathbf{r}')$ is determined by macroscopic electrostatics: it is the potential created at $\mathbf{r}'$ when the conductor carries the total charge 1. Its explicit form can be obtained for simple shapes of the conductor.[2] From (2.2), we now obtain

$$\beta\langle\phi(\mathbf{r})\,\phi(\mathbf{r}')\rangle^T=\frac{1}{|\mathbf{r}-\mathbf{r}'|}-F(\mathbf{r}') \tag{3.1}$$

The same result can be obtained by assuming that the test charge is put at $\mathbf{r}'$; the total potential of the conductor then is $qF(\mathbf{r}')$, because F can be regarded as an element of an inverse capacitance matrix, which is known to be symmetrical.

The last term of (3.1) must be omitted in the case of grounded conductor. It vanishes anyhow in the limit of an infinitely large conductor (such as, for instance, a conducting fluid filling a half-space).

From (3.1), one finds a field-field correlation which is again (2.3).

3.2. Potential and Field Correlations Outside

Finally, we want to compute the potential–potential correlation $\langle\phi(\mathbf{r})\,\phi(\mathbf{r}')\rangle^T$ when both points $\mathbf{r}$ and $\mathbf{r}'$ are outside the Coulomb fluid. We still consider the response to an infinitesimal test charge q at $\mathbf{r}$. The total potential change at $\mathbf{r}'$ is some function $qG(\mathbf{r},\mathbf{r}')$, with $G(\mathbf{r},\mathbf{r}')$ determined by macroscopic electrostatics: $G(\mathbf{r},\mathbf{r}')$ is the total potential change at $\mathbf{r}'$ when a unit point charge is put at $\mathbf{r}$. In the case of a finite conductor, for determining G one must specify whether the conductor is insulated or grounded. G is explicitly computable for simple shapes of the conductor.

The potential change due to the fluid only is $q[G(\mathbf{r},\mathbf{r}')-|\mathbf{r}-\mathbf{r}'|^{-1}]$, and (2.2) gives

$$\beta\langle\phi(\mathbf{r})\,\phi(\mathbf{r}')\rangle^T=\frac{1}{|\mathbf{r}-\mathbf{r}'|}-G(\mathbf{r},\mathbf{r}') \tag{3.2}$$

From (3.2), one finds for the field–field correlation

$$\beta\langle E_\mu(\mathbf{r})\,E_\nu(\mathbf{r}')\rangle^T=\frac{\partial^2}{\partial r_\mu\,\partial r'_\nu}\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|}-G(\mathbf{r},\mathbf{r}')\right] \tag{3.3}$$

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[2] In most textbooks about electrostatics, it is stated that the potential is continuous at the surface of a conductor. This would imply that (3.1) and (2.4) become identical when $\mathbf{r}'$ is on the surface. Actually, there is usually a potential difference across the surface of a conductor, due to the formation of an electrical double layer. However, a constant shift of the potential is of no effect on the electric field.

4. SURFACE CHARGE CORRELATIONS

In the present macroscopic approach, it is natural to introduce a surface charge dénsity σ, which will be associated with the electrical field discontinuity at the surface of the conductor. At some point $\mathbf{r}$ on the surface,

$$4\pi\sigma(\mathbf{r}) = E_n^{\text{out}}(\mathbf{r}) - E_n^{\text{in}}(\mathbf{r}) \tag{4.1}$$

where the index n denotes the component normal to the surface (with the positive direction defined as pointing toward the outside) and $E_n^{\text{out(in)}}(\mathbf{r})$ is the limit of that field component as $\mathbf{r}$ is approached from the outside (inside). Therefore, the surface change density correlation function is

$$\langle \sigma(\mathbf{r})\, \sigma(\mathbf{r}')\rangle^T = \frac{1}{(4\pi)^2} \langle [E_n^{\text{out}}(\mathbf{r}) - E_n^{\text{in}}(\mathbf{r})][E_n^{\text{out}}(\mathbf{r}') - E_n^{\text{in}}(\mathbf{r}')]\rangle^T \tag{4.2}$$

Using the field correlations (2.5) and (3.3), one finds the final result

$$\beta\langle \sigma(\mathbf{r})\, \sigma(\mathbf{r}')\rangle^T = -\frac{1}{(4\pi)^2} \frac{\partial^2 G(\mathbf{r}, \mathbf{r}')}{\partial r_n\, \partial r'_n}\bigg|_{\mathbf{r},\mathbf{r}' \in \text{surface}} \tag{4.3}$$

Of course, this approach is valid only if the distance $|\mathbf{r} - \mathbf{r}'|$ is large compared to the microscopic scale. Also, the surface charge density σ has to be understood as being the microscopic volume charge density integrated on some microscopic depth. Within these liminations, the computation of the correlation function (4.3) has been reduced to a problem in the macroscopic electrostatics of conductors.

A method for obtaining the charge correlations near the surface of a Coulomb system was devised by Choquard *et al.*(8) a few years ago. This method was presented as an approximation to the Debye–Hückel approximation. However, it can be seen that the surface charge densities provided by the method of Choquard *et al.* have to be identical to ours (their kernel G_{ext} is identical to our function G). Therefore, our approach rephrases the method of Choquard *et al.*, without any need for invoking the Debye–Hückel approximation.

5. A FEW SPECIFIC CASES

In order to illustrate how the present method works, we now consider a few specific cases.

5.1. Coulomb Fluid in a Half-Space

The surface of the Coulomb fluid is the plane $x0y$, which acts as an impenetrable wall, confining the particles to the half-space $z<0$. The method of images gives, in the empty half-space,

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{|\mathbf{r}^*-\mathbf{r}'|} \tag{5.1}$$

where $\mathbf{r}^* = (x, y, -z)$ is the image of $\mathbf{r} = (x, y, z)$. One readily finds from (4.3), on the plane $x0y$,

$$\beta\langle\sigma(\mathbf{r})\,\sigma(\mathbf{r}')\rangle^T = -\frac{1}{8\pi^2\,|\mathbf{r}-\mathbf{r}'|^3} \tag{5.2}$$

Which is the result obtained in ref. 9 in the equivalent microscopic language: the volume charge density correlation function $\langle\rho(\mathbf{r})\,\rho(\mathbf{r}')\rangle^T$ behaves asymptotically, when $(x-x')^2+(y-y')^2$ becomes large, as $F(z, z', (x-x')^2 + (y-y')^2)$, where F is a function integrable upon z and z' obeying

$$\begin{aligned}\beta\int_{-\infty}^{0} dz \int_{-\infty}^{0} dz'\, F(z, z', (x-x')^2+(y-y')^2) \\ = -\frac{1}{8\pi^2[(x-x')^2+(y-y')^2]^{3/2}}\end{aligned} \tag{5.3}$$

5.2. Coulomb Fluid in a Ball

A ball of macroscopic radius R centered at the origin is filled by a Coulomb fluid. The method of images now gives, outside the ball,

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} - \frac{R}{r}\frac{1}{|\mathbf{r}'-\mathbf{r}^*|} + \frac{R}{rr'} \tag{5.4}$$

where the image of $\mathbf{r}$ has the coordinate $\mathbf{r}^* = R^2\mathbf{r}/r^2$. The presence of the last term in (5.4) is appropriate for an insulated ball, i.e., if we want to study the fluctuations in an ensemble such that the total charge on the ball is constant, for instance, the canonical ensemble; on the contrary, if the ball is assumed to be allowed to exchange charge with some reservoir, say at zero potential (grounded ball), the last term of (5.4) must be omitted.

Using (5.4) in (4.3) gives, for an insulated ball,

$$\beta\langle\sigma(\mathbf{r})\,\sigma(\mathbf{r}')\rangle^T = -\frac{1}{8\pi^2}\left[\frac{1}{[2R\sin(\theta/2)]^3} + \frac{1}{2R^3}\right] \tag{5.5}$$

where θ is the angle between $\mathbf{r}$ and $\mathbf{r}'$. In the case of a grounded ball, the last term in (5.5) must be suppressed, i.e., one must add the contribution $+1/(4\pi)^2 R^3$ from the total charge fluctuations.

This contribution from the fluctuations of the total charge Q can be alternatively derived by assuming that, for typical configurations, Q is uniformly spread on the surface. Then, the corresponding energy is $Q^2/2R$. If one further assumes that the average of this energy has the harmonic oscillator value $(1/2)\beta^{-1}$, using $\sigma = Q/4\pi R^2$, one finds the contribution $1/(4\pi)^2 R^3$ to $\beta\langle\sigma\sigma\rangle$.

5.3. Coulomb Fluid in a Wedge

Our method reproduces the results of Choquard *et al.*(8) These authors had expressed some doubts about the reliability of their result, because it was not obvious that their derivation, presented as an approximation to the Debye–Hückel theory, was valid for a nonsmooth surface such as a wedge. The present approach now puts things on the firmer basis of macroscopic electrostatics, which we believe to be true, even in the case of a wedge.

The results in ref. 8 are different from those obtained by Jancovici *et al.*(10) It is now apparent that the section Wedge in ref. 10 is erroneous,[3] as well as its quotation in Eqs. (10a) and (10b) of ref. 3.

6. CONDUCTING SURFACES

This section is about two-dimensional Coulomb fluids, with an interaction potential which is the usual $1/r$ one. The surface charge correlations can be studied by a slightly modified version of the method used in Section 4. The field correlation function in three-dimensional space is still given by (3.3), and the surface charge correlations still can be expressed in terms of the correlations between the field discontinuities on the surface.

In the case of a conducting plane, one finds

$$\beta\langle\sigma(\mathbf{r})\,\sigma(\mathbf{r}')\rangle^T = -\frac{1}{4\pi^2\,|\mathbf{r}-\mathbf{r}'|^3} \tag{6.1}$$

(This result could also have been derived by considering a slab(3,10) in the zero-thickness limit.) It should be noted that the plane result (6.1) is not identical to the half-space result (5.2). This shows that, in the case of a three-dimensional Coulomb fluid with boundaries, there must be some coupling between the surface charge and the volume charge densities.

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[3] The mistake in ref. 10 can be traced to the assumption following Eq. (A.5); this assumption is just not true.

In the case of an insulated conducting spherical surface of radius R centered at the origin, one finds

$$\beta\langle\sigma(\mathbf{r})\,\sigma(\mathbf{r}')\rangle^T = -\frac{1}{4\pi^2}\left[\frac{1}{[2R\sin(\theta/2)]^3}+\frac{1}{4R^3}\right] \tag{6.2}$$

where θ is the angle between $\mathbf{r}$ and $\mathbf{r}'$. In the case of a grounded surface, the last term of (6.2) must be suppressed. Therefore, $1/(4\pi)^2R^3$ is again the contribution from the total charge fluctuations, just as for a grounded ball filled with a three-dimensional Coulomb fluid, in agreement with the assumption that in this latter case the fluctuations of the total charge are localized on the surface only. The rest of $\langle\sigma(\mathbf{r})\,\sigma(\mathbf{r}')\rangle^T$, however, is different for a spherical surface and for a ball filled with the fluid, as seen in (6.2) and (5.5); again, in the case of a ball, there is some coupling between the surface and the volume.

7. TWO-DIMENSIONAL COULOMB INTERACTION

The above method and results can be easily transposed to two-dimensional or one-dimensional systems with a two-dimensional Coulomb interaction: the potential at $\mathbf{r}$ created by a unit point charge at the origin is $-\ln(r/L)$, where L is some given length. These systems are interesting for a variety of reasons. In some cases they are exactly solvable models. Some of them appear in the theory of random matrices.

One now obtains for the potential–potential correlations inside an insulated two-dimensional conductor

$$\beta\langle\phi(\mathbf{r})\,\phi(\mathbf{r}')\rangle^T = -\ln\frac{|\mathbf{r}-\mathbf{r}'|}{L}-\frac{1}{C} \tag{7.1}$$

where C is the capacitance; for instance, for a disk of radius R, $C^{-1} = -\ln(R/L)$. Now, if the system becomes infinite, $C^{-1}\to\infty$ and (7.1) has no well-behaved thermodynamic limit.(11) However, the corresponding field–field correlation function is given by

$$\beta\langle E_\mu(\mathbf{r})\,E_\nu(\mathbf{r}')\rangle^T = -\frac{2(\mathbf{r}-\mathbf{r}')_\mu(\mathbf{r}-\mathbf{r}')_\nu-\delta_{\mu\nu}(\mathbf{r}-\mathbf{r}')^2}{|\mathbf{r}-\mathbf{r}'|^4} \tag{7.2}$$

while $\langle E_\mu(\mathbf{r})\rangle = 0$, and these expressions remain finite for infinite systems. The analog of the surface charge density is now a charge per unit length that we still call $\sigma(\mathbf{r})$. Following the same other steps as in Sections 2–4, one finds again that obtained the "surface" charge correlations $\langle\sigma\sigma\rangle$

for two-dimensional or one-dimensional systems with logarithmic interactions reduces (for macroscopic distances) to a macroscopic electrostatics problem: finding $G(\mathbf{r}, \mathbf{r}')$, the total potential at $\mathbf{r}'$ outside a conductor when a unit point charge has been put at $\mathbf{r}$ (also outside). For the explicit calculation of G, a specifically two-dimensional tool is provided by the theory of functions of a complex variable and conformal transformations.

For a Coulomb fluid in a half-plane (the fluid is assumed to fill the $y<0$ domain of the $xy0$ plane), one finds

$$\beta\langle \sigma(x)\, \sigma(x')\rangle^T = -\frac{1}{2\pi^2(x-x')^2} \tag{7.3}$$

which is the result given in ref. 9 in microscopic language. Similarly, on an infinite conducting line, one finds

$$\beta\langle \sigma(x)\, \sigma(x')\rangle = -\frac{1}{\pi^2(x-x')^2} \tag{7.4}$$

(a result previously derived by a different method$^{(12)}$).

For a Coulomb fluid in a disk of radius R centered at the origin, one finds

$$\beta\langle \sigma(\mathbf{r})\, \sigma(\mathbf{r}')\rangle = -\frac{1}{2\pi^2[2R\sin(\theta/2)]^2} \tag{7.5}$$

where θ is the angle between $\mathbf{r}$ and $\mathbf{r}'$. This result is valid both for an insulated and a grounded disk. In the case of a three-dimensional ball, grounding gave to the surface charge correlation function (5.5) an additional contribution coming from the fluctuations of the total charge. It is remarkable that such an additional term does not occur in two dimensions. The reason is that the energy associated with a total charge fluctuation Q on a disk is infinite, since increasing the charge Q by bringing in an additional charge δQ from far away costs an energy $Q\,\delta Q \int_R^\infty dr/r$, where the integral diverges. Thus, fluctuations of the total charge cannot occur.

As an illustration of the method of conformal transformations, let us consider a Coulomb fluid in a wedge. We use polar coordinates (r, θ). The fluid is assumed to fill the two-dimensional wedge $\gamma<\theta<2\pi$; the domain $0<\theta<\gamma$ is empty. For finding G in the wedge $0<\theta<\gamma$, we can start from its half-plane $(\gamma=\pi)$ expression in terms of complex coordinates $[z = r\exp(i\theta)]$

$$G_{\gamma=\pi} = \ln\left|\frac{\bar{z}-z'}{z-z'}\right| \tag{7.6}$$

and make the conformal transformaton $z \to z^{\pi/\gamma}$ which relates the half-plane and the wedge. Thus,

$$G_\gamma = \frac{1}{2} \ln \frac{r^{2\alpha} + r'^{2\alpha} - 2r^\alpha r'^\alpha \cos \alpha(\theta + \theta')}{r^{2\alpha} + r'^{2\alpha} - 2r^\alpha r'^\alpha \cos \alpha(\theta - \theta')} \tag{7.7}$$

where $\alpha = \pi/\gamma$, and one finds

$$\beta \langle \sigma(\mathbf{r})\, \sigma(\mathbf{r}') \rangle = -\frac{\alpha^2}{2\pi^2} \frac{(rr')^{\alpha - 1}}{(r^\alpha - sr'^\alpha)^2} \tag{7.8}$$

where $s = +1$ (-1) if the two points $\mathbf{r}$ and $\mathbf{r}'$ are on the same side (different sides) of the wedge.

Other specific cases are solved in refs. 13 and 14.

8. GAUSSIAN BEHAVIOR OF THE POTENTIAL AND FIELD FLUCTUATIONS

In Sections 2 and 3, we have obtained the two-point correlations for the electrical potential and field, except for their microscopic distance behavior. We now want to prove the stronger statement that the fluctuations of these quantities are "almost" Gaussian, with the above-mentioned covariances (the meaning of "almost" will be explained later).

Showing that the fluctuations are Gaussian is a step toward better understanding why the finite-size corrections to the free energy of a Coulomb system$^{(15)}$ are similar to those of a critical field theory: the Gaussian model.

The basic ingredient of the proof (already used in wavenumber space in ref. 15) is the assumption that the screening response (2.3) remains of the same form, *linear* in q, even if q is no longer infinitesimal, but is an external point charge of arbitrary magnitude. Now, a *linear* response to a *finite* (noninfinitesimal) perturbation characterizes a Gaussian distribution. As a pedagogical example, consider a particle in a one-dimensional potential $V(x)$. A simple calculation shows that if, in thermal equilibrium, the average displacement of the particle under an additional force q is proportional to q, then $V(x)$ is a harmonic oscillator potential, and the probability density $\exp[-\beta V(x)]$ is Gaussian.

For a proof in the present case of a Coulomb fluid, we study the cumulants, considering, for instance, an insulated fluid with three-dimensional Coulomb interactions. The argument is an follows. Place at $n=1$ points $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n-1}$ (chosen inside or outside the fluid) point charges $q_1, q_2, \ldots, q_{n-1}$. Let $\mathbf{r}_n$ be some point, inside or outside; if inside, $\mathbf{r}_n$ is assumed to be at a distance large compared to the microscopic scale from those points among $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n-1})$ which are inside. Since macroscopic electrostatics says that the potential–charge relations are linear, the response of $\phi(\mathbf{r}_n)$ is given by an obvious generalization of what has been derived in Sections 2 and 3:

$$\langle \phi(\mathbf{r}_n) \rangle_{\{q_i\}} = \langle \phi(\mathbf{r}_n) \rangle + \sum_{i=1}^{n-1} a_i q_i \tag{8.1}$$

where $\langle \cdot \rangle_{\{q_i\}}$ means an average computed with the full Hamiltonian including the interaction term $\sum_{i=1}^{n-1} q_i \phi(\mathbf{r}_i)$, while $\langle \cdot \rangle$ means the average when there are no charges q_i. The coefficients a_i are those ones obtained in Sections 2 and 3:

$$\begin{aligned}
a_i &= -\frac{1}{|\mathbf{r}_i - \mathbf{r}_n|} + \frac{1}{C} && \text{if both } \mathbf{r}_i \text{ and } \mathbf{r}_n \text{ are inside} \\
a_i &= -\frac{1}{|\mathbf{r}_i - \mathbf{r}_n|} + F(\mathbf{r}_{\text{out}}) && \text{if one member } (\mathbf{r}_{\text{out}}) \text{ of the pair } (\mathbf{r}_i, \mathbf{r}_n) \\
& && \text{is outside and the other one inside} \\
a_i &= -\frac{1}{|\mathbf{r}_i - \mathbf{r}_n|} + G(\mathbf{r}_i, \mathbf{r}_n) && \text{if both } \mathbf{r}_i \text{ and } \mathbf{r}_n \text{ are outside}
\end{aligned} \tag{8.2}$$

By definition,

$$\langle \phi(\mathbf{r}_n) \rangle_{\{q_i\}} = \frac{\langle \{\exp[-\beta \sum_{i=1}^{n-1} q_i \phi(\mathbf{r}_i)]\} \, \phi(\mathbf{r}_n) \rangle}{\langle \exp[-\beta \sum_{i=1}^{n-1} q_i \phi(\mathbf{r}_i)] \rangle} \tag{8.3}$$

Rewriting the r.h.s. of (8.3) as a logarithmic derivative and combining (8.1) and (8.3), one obtains

$$-\frac{1}{\beta} \frac{\partial}{\partial q_n} \ln \left\langle \exp\left[-\beta \sum_{i=1}^{n} q_i \phi(\mathbf{r}_i) \right] \right\rangle \Bigg|_{q_n = 0} = \langle \phi(\mathbf{r}_n) \rangle + \sum_{i=1}^{n-1} a_i q_i \tag{8.4}$$

Since the cumulants (or truncated correlation functions) $\langle \cdots \rangle^T$ of the potential ϕ are defined by the expansion in powers of q_i

$$\begin{aligned}
&\ln \left\langle \exp\left[-\beta \sum_{i=1}^{n} q_i \phi(\mathbf{r}_i) \right] \right\rangle \\
&= {\sum_{0}^{\infty}}' \frac{\langle \phi(\mathbf{r}_1)^{m_1} \phi(\mathbf{r}_2)^{m_2} \cdots \phi(\mathbf{r}_n)^{m_n} \rangle^T}{m_1! \, m_2! \cdots m_n!} (-\beta q_1)^{m_1} (-\beta q_2)^{m_2} \cdots (-\beta q_n)^{m_n}
\end{aligned} \tag{8.5}$$

(where the prime indicates the absence of the term with all m's simultaneously vanishing), a comparison between (8.4) and (8.5) shows that all cumulants of total order $m_1 + m_2 + \cdots + m_n$ higher than 2 and with $m_n = 1$ vanish.

The above result can be rephrased as follows. Consider the cumulant $\langle \phi(\mathbf{r}_1)\, \phi(\mathbf{r}_2) \cdots \phi(\mathbf{r}_p) \rangle^T$, with $p > 2$. That cumulant vanishes provided that one point at least, say $\mathbf{r}_p$, is at a distance large compared to the microscopic scale from all those other points which are inside the fluid; these other points, however, might be at arbitrary distances (including zero) from each other. Similar properties hold for the electric fields.

Were it not for the restriction about the position of $\mathbf{r}_p$, the vanishing of the cumulants of order larger than 2 would imply that the $\phi(\mathbf{r}_i)$ are jointly Gaussian. With the restriction added, the statistics become "generalized Gaussian." This restriction actually is not very drastic, or at least is of a kind which currently occurs in field theory. In the simple case of a homogeneous infinite system, the covariance $\beta \langle \phi(r_1)\, \phi(r_2) \rangle = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ corresponds to a Gaussian probability density proportional to $\exp[-(\beta/8\pi) \int (\nabla\phi)^2\, d^3\mathbf{r}]$, a form which is not unexpected since $(1/8\pi)(\nabla\phi)^2$ is just the Coulomb energy density expressed in terms of the electrical field $-\nabla\phi$. It is well known that this Gaussian field theory actually becomes singular for short distances and the average $\langle \phi(\mathbf{r}_1)\, \phi(\mathbf{r}_2) \cdots \phi(\mathbf{r}_p) \rangle$ is not properly defined when there are coincident points; some regularization is necessary. A most important property is that, at least in the absence of coincident points (i.e., when all distances are large compared to the microscopic cutoff), Wick's theorem can be straightforwardly used for expressing $\langle \phi(\mathbf{r}_1)\, \phi(\mathbf{r}_2) \cdots \phi(\mathbf{r}_p) \rangle$ in terms of the 2-point function $\langle \phi(\mathbf{r}_1)\, \phi(\mathbf{r}_2) \rangle = 1/\beta\, |\mathbf{r}_1 - \mathbf{r}_2|$.

The Gaussian behavior of the electrical fields follows.

Our result about the higher-order cumulants had been previously obtained, by a different method, in the special case of an infinite homogeneous one-component plasma.(16) It should be noted that the quantities V_R^{out} which were shown to have Gaussian fluctuations in ref. 6 are *not* the full potentials ϕ considered here.

The present considerations can be easily transcribed to the case of a two-dimensional (logarithmic) Coulomb potential.

9. CONCLUSION

The universal validity of macroscopic electrostatics implies in particular universal response properties for conductors. Whenever *classical* statistical mechanics is applicable, these response properties imply in turn universal properties for the equilibrium thermal fluctuations. Independent of the details of the microscopic constitution of the conductor, for length scales large compared to the microscopic ones, the potential and field fluctuations are Gaussian with universal covariances (outside the conductor, things depend on its geometry, but again not on its microscopic constitution). The surface charge fluctuations are also universal, depending only on the geometry. The volume charge fluctuation also have universal properties, but in a less explicit way, since the universality then appears only in the form of sum rules.

Unfortunately, when quantum mechanics is used, the universal response properties no longer imply simple universal static (equal-time) correlations, because of the more complicated form of the linear response theory. One can write quantum sum rules for the correlations in the special case of the one-component plasma,(17, 10) but these sum rules involve the nonuniversal plasma frequency. For more general quantum models, no sum rules are known for static or (real) time-dependent correlations.

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