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Charge Correlations in a Coulomb System Along a Plane Wall: A Relation Between Asymptotic Behavior and Dipole Moment

B. Jancovici[1] **and L. Šamaj**[1, 2]

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Classical Coulomb systems at equilibrium, bounded by a plane dielectric wall, are studied. A general two-point charge correlation function is considered. Valid for any fixed position of one of the points, a new relation is found between the algebraic tail of the correlation function along the wall and the dipole moment of that function. The relation is tested first in the weak-coupling (Debye–Hückel) limit, and afterwards, for the special case of a plain hard wall, on the exactly solvable two-dimensional two-component plasma at coupling $\Gamma = 2$, and on the two-dimensional one-component plasma at an arbitrary even integer Γ.

KEY WORDS: Coulomb systems; plasma; surface properties; correlations; sum rules.

1. INTRODUCTION AND SUMMARY

Near a plane wall impenetrable to the particles (hard wall), the charge correlations of a classical (i.e., non-quantum) Coulomb system (plasma, electrolyte, ...) at equilibrium have special features (see review of ref. 1). On one hand, they have only an algebraic decay along the wall (while the bulk charge correlations decay faster than any inverse power law), and their asymptotic form obeys a simple sum rule. On the other hand, the charge correlation function carries a dipole moment (while, in the bulk, there is no such dipole just for symmetry reasons), and this dipole moment obeys another simple sum rule. Some relation between algebraic tail and dipole

[1] Laboratoire de Physique Théorique, Université de Paris-Sud, Bâtiment 210, 91405 Orsay Cedex, France (Unité Mixte de Recherche no. 8627 - CNRS); e-mail: Bernard.Jancovici@th.u-psud.fr and Ladislav.Samaj@th.u-psud.fr

[2] On leave from the Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia.

moment is expected: it is the asymmetry of the screening cloud of a particle sitting near the wall which induces that long-range tail in the charge correlation along the wall. In the present paper, we make this relation quantitative.

The general classical Coulomb systems under consideration consist of s species $\alpha = 1, \ldots, s$ with the corresponding charges q_α, plus perhaps a fixed background of density n_0 and charge density ρ_0. Two cases are of particular interest: the one-component plasma (OCP) which corresponds to $s = 1$ ($q_1 = q$), $\rho_0 = -q n_0 \neq 0$ and the two-component plasma (TCP) which corresponds to $s = 2$ ($q_1 = q$, $q_2 = -q$), $\rho_0 = n_0 = 0$. The presence of a solvent is mimicked by embedding the system in a continuous medium of dielectric constant ϵ. The walls are made of a material of dielectric constant ϵ_W. The particles (and the background if any) interact via the Coulomb potential plus perhaps some short-range forces. For a ν-dimensional system (in what follows, we will restrict ourselves to dimensions $\nu = 2, 3$), the Coulomb potential in vacuum at position $\mathbf{r}$, induced by a unit charge at the origin, defined as the solution of the Poisson equation, is

$$v(\mathbf{r}) = \begin{cases} -\ln\left(\dfrac{|\mathbf{r}|}{r_0}\right), & \nu = 2 \\ \dfrac{1}{|\mathbf{r}|}, & \nu = 3 \end{cases} \tag{1.1}$$

where r_0 is a length scale. It should be remembered that, when $\nu = 2$, the system, with logarithmic interactions, is expected to mimic some general properties of three-dimensional Coulomb systems, but does *not* represent "real" charged particles confined to a plane. For two- and more-component plasmas containing pointlike particles, the singularity of $v(\mathbf{r})$ 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 dimensions for any temperature. In such cases, the above-mentioned short-range forces (e.g., hard cores) are needed, without effect on the results of this paper.

We now define some notations. The microscopic densities of charge and of particles of species α are given respectively by

$$\hat{\rho}(\mathbf{r}) = \rho_0 + \sum_\alpha q_\alpha \hat{n}_\alpha(\mathbf{r}), \qquad \hat{n}_\alpha(\mathbf{r}) = \sum_i \delta_{\alpha,\alpha_i} \delta(\mathbf{r} - \mathbf{r}_i) \tag{1.2}$$

where i indexes the charged particles. The thermal average at the inverse temperature $\beta = 1/(kT)$ will be denoted by $\langle \cdots \rangle$. At one-particle level,

$$\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle, \qquad n_\alpha(\mathbf{r}) = \langle \hat{n}_\alpha(\mathbf{r}) \rangle \tag{1.3}$$

At two-particle level, one introduces the two-body densities

$$n_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i \neq j} \delta_{\alpha, \alpha_i} \delta_{\beta, \alpha_j} \delta(\mathbf{r} - \mathbf{r}_i)\, \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle \tag{1.4a}$$

and the corresponding Ursell functions

$$U_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = n_{\alpha\beta}(\mathbf{r}, \mathbf{r}') - n_\alpha(\mathbf{r})\, n_\beta(\mathbf{r}') \tag{1.4b}$$

The truncated charge-charge correlation (structure function) reads

$$S(\mathbf{r}, \mathbf{r}') = \langle \hat{\rho}(\mathbf{r})\, \hat{\rho}(\mathbf{r}') \rangle^{\mathrm{T}} = \langle \hat{\rho}(\mathbf{r})\, \hat{\rho}(\mathbf{r}') \rangle - \langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\rho}(\mathbf{r}') \rangle \tag{1.5}$$

In the case of the OCP, S takes the form

$$S(\mathbf{r}, \mathbf{r}') = q^2 [U(\mathbf{r}, \mathbf{r}') + n(\mathbf{r})\, \delta(\mathbf{r} - \mathbf{r}')] \tag{1.6}$$

For our purpose, it is useful to introduce "conditional" densities. Let $n_\alpha(\mathbf{r} \mid Q, \mathbf{R})$ be the density of α-particles at point $\mathbf{r}$ when there is a charge Q fixed at $\mathbf{R}$. Evidently, if $\beta = 1,..., s$ belongs to the set of charged species forming the plasma, it holds

$$n_\alpha(\mathbf{r} \mid q_\beta, \mathbf{r}')\, n_\beta(\mathbf{r}') = n_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \tag{1.7}$$

The excess charge density at point $\mathbf{r}$, due to the presence of the charge Q fixed at $\mathbf{R}$, then is

$$\rho^{\mathrm{ex}}(\mathbf{r} \mid Q, \mathbf{R}) = \left\{ \sum_\alpha q_\alpha [n_\alpha(\mathbf{r} \mid Q, \mathbf{R}) - n_\alpha(\mathbf{r})] \right\} + Q\delta(\mathbf{r} - \mathbf{R}) \tag{1.8}$$

In terms of ρ^{ex}, S is expressible as follows

$$\begin{aligned} S(\mathbf{r}, \mathbf{r}') &= \sum_\beta q_\beta n_\beta(\mathbf{r}')\, \rho^{\mathrm{ex}}(\mathbf{r} \mid q_\beta, \mathbf{r}') \\ &= \sum_\beta q_\beta n_\beta(\mathbf{r})\, \rho^{\mathrm{ex}}(\mathbf{r}' \mid q_\beta, \mathbf{r}) \end{aligned} \tag{1.9}$$

Here, we consider a semi-infinite Coulomb system which occupies the half-space $x > 0$ filled with a medium of dielectric constant ϵ; we denote by $\mathbf{y}$ the set of $(\nu - 1)$ coordinates normal to x. The plane at $x = 0$ is a hard wall impenetrable to the particles. It may be charged by a uniform surface charge density σ. The half-space $x < 0$ is assumed to be filled with a material of dielectric constant ϵ_W. As a consequence, a particle of charge q at the point $\mathbf{r} = (x, \mathbf{y})$ has an electric image of charge $[(\epsilon - \epsilon_W)/(\epsilon + \epsilon_W)]\, q$

at the point $\mathbf{r}^* = (-x, \mathbf{y})$.[2] Due to invariance with respect to translations along the wall and rotations around the x direction,

$$S(\mathbf{r}, \mathbf{r}') = S(x, x'; |\mathbf{y}-\mathbf{y}'|) = S(x', x; |\mathbf{y}-\mathbf{y}'|) \tag{1.10}$$

The cases $\epsilon_W = \infty$ (ideal conductor wall) and $\epsilon_W = 0$ (ideal dielectric wall) are special and will not be considered here. For finite ϵ_W, the charge structure factor $S(x, x'; |\mathbf{y}-\mathbf{y}'|)$ has several general properties: It obeys a condition of electroneutrality

$$\int_0^\infty \mathrm{d}x' \int \mathrm{d}\mathbf{y}\, S(x, x'; \mathbf{y}) = 0 \tag{1.11}$$

The Carnie and Chan generalization to nonuniform fluids of the second-moment Stillinger–Lovett condition[3] results for the present geometry in the dipole sum rule[4, 5]

$$\int_0^\infty \mathrm{d}x \int_0^\infty \mathrm{d}x' \int \mathrm{d}\mathbf{y}\, x' S(x, x'; \mathbf{y}) = -\frac{\epsilon}{2\beta\pi(\nu-1)}, \qquad \nu = 2, 3 \tag{1.12}$$

The charge-charge correlations decay slowly along the wall.[6, 7] One expects an asymptotic power-law behavior

$$S(x, x'; \mathbf{y}) \simeq \frac{f(x, x')}{|\mathbf{y}|^\nu}, \qquad |\mathbf{y}| \to \infty \tag{1.13}$$

where $f(x, x')$, which as a function of x or x' has a fast decay away from the wall, obeys the sum rule[8, 9]

$$\int_0^\infty \mathrm{d}x \int_0^\infty \mathrm{d}x'\, f(x, x') = -\frac{\epsilon_W}{2\beta[\pi(\nu-1)]^2}, \qquad \nu = 2, 3 \tag{1.14}$$

In this work, we establish a general relation between the structure function S and its asymptotic characteristics f. Namely, for any value of $x \geqslant 0$ it is proven that

$$\int_0^\infty \mathrm{d}x' \int \mathrm{d}\mathbf{y}\, x' S(x, x'; \mathbf{y}) = \frac{\epsilon}{\epsilon_W} \pi(\nu-1) \int_0^\infty \mathrm{d}x'\, f(x, x'), \qquad \nu = 2, 3 \tag{1.15}$$

The lhs of (1.15) is a dipole moment (in its expression, due to the electroneutrality property (1.11), x' can be replaced by $x'-x$). In contrast with the sum rules (1.12) and (1.14), the relation (1.15) holds for a given x, without integration over it. However, when both sides of (1.15) are integrated over x from 0 to ∞, it is seen that the sum rule (1.14) for f is a direct consequence of the dipole sum rule (1.12), and vice versa.

More generally, it can be assumed that the excess charge density (1.8) also obeys a condition of electroneutrality similar to (1.11) and has an asymptotic behavior similar to (1.13)

$$\rho^{\text{ex}}(\mathbf{r} \mid Q, \mathbf{R}) \simeq \frac{F(x \mid Q, X)}{|\mathbf{y}|^{\nu}}, \qquad |\mathbf{y}| \to \infty \tag{1.16}$$

where we have chosen $\mathbf{R} = (X, \mathbf{0})$, with F as a function of x or X having a fast decay away from the wall. Under these assumptions, we derive the relation

$$\int \mathrm{d}\mathbf{r}\, x\rho^{\text{ex}}(\mathbf{r} \mid Q, \mathbf{R}) = \frac{\epsilon}{\epsilon_W}\, \pi(\nu-1) \int_0^{\infty} \mathrm{d}x\, F(x \mid Q, X), \qquad \nu = 2, 3 \tag{1.17}$$

valid for an arbitrary Q. Here too, in the lhs of (1.17), x can be replaced by $x-X$. On account of (1.9), this more general relation immediately leads to (1.15) with $f(x, X) = \sum_{\beta} q_{\beta} n_{\beta}(X)\, F(x \mid q_{\beta}, X)$.

The paper is organized as follows. Section 2 is devoted to a general derivation of the basic result (1.17). The validity of this result is checked in the Debye–Hückel limit $\beta \to 0$ (Section 3) and in two dimensions at the special value of the coupling constant $\Gamma = \beta q^2 = 2$, for both the TCP[10] (Section 4) and the OCP[7] (Section 5) in contact with a plain hard wall ($\epsilon_W = \epsilon = 1$). In the case of the two-dimensional OCP, we were able to document the validity of formula (1.15) even for an arbitrary even integer Γ by a non-trivial application of sum rules derived in ref. 11 using the technique of Grassmann variables.

2. GENERAL DERIVATION

In this section, the abbreviated notation $\rho^{\text{ex}}(\mathbf{r})$ will be used for the excess charge distribution $\rho^{\text{ex}}(\mathbf{r} \mid Q, \mathbf{R})$ defined in (1.8), with $\mathbf{R} = (X, \mathbf{0})$. For simplicity, we first consider the case when there are no dielectric media ($\epsilon = \epsilon_W = 1$). Our derivation of (1.17) is based on the assumption that there are good screening properties in the bulk: the charge distribution $\rho^{\text{ex}}(\mathbf{r})$ is localized near the wall and the electric potential $\phi(\mathbf{r})$ it creates in the plasma at a macroscopic distance from the wall vanishes. This electric potential is

$$\phi(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'\, v(\mathbf{r}-\mathbf{r}')\, \rho^{\text{ex}}(\mathbf{r}') \tag{2.1}$$

where $v(\mathbf{r}-\mathbf{r}')$ is the Coulomb interaction (1.1). When x is large enough for the charge distribution $\rho^{\text{ex}}(\mathbf{r})$ to be negligible, $v(\mathbf{r}-\mathbf{r}')$ can be expanded in powers of x' (with the notation $\mathbf{r}=(x, \mathbf{y})$, etc...), and one obtains

$$\phi(\mathbf{r}) = \int \mathrm{d}\mathbf{y}'\, v(x, \mathbf{y}-\mathbf{y}') \int_0^\infty \mathrm{d}x'\, \rho^{\text{ex}}(x', \mathbf{y}') \\ - \int \mathrm{d}\mathbf{y}'\, \frac{\partial v(x, \mathbf{y}-\mathbf{y}')}{\partial x} \int_0^\infty \mathrm{d}x'\, x' \rho^{\text{ex}}(x', \mathbf{y}') + \cdots \tag{2.2}$$

where the higher-order terms of the expansion involve higher-order derivatives of v with respect to x.

We shall now consider the Fourier transform of (2.2) with respect to $\mathbf{y}$, using the convolution theorem. In (2.2), let us define

$$\sigma^{\text{ex}}(\mathbf{y}') = \int_0^\infty \mathrm{d}x'\, \rho^{\text{ex}}(x', \mathbf{y}') \tag{2.3}$$

(from a macroscopic point of view, $\sigma^{\text{ex}}(\mathbf{y}')$ can be regarded as a surface charge density). The total charge $\int \mathrm{d}\mathbf{y}\, \sigma^{\text{ex}}(\mathbf{y})$ vanishes, as required by the perfect screening of Q. Also, it results from (1.16) that $\sigma^{\text{ex}}(\mathbf{y})$ has the asymptotic behavior

$$\sigma^{\text{ex}}(\mathbf{y}) \simeq \frac{A}{|\mathbf{y}|^{\nu}} \tag{2.4}$$

where

$$A = \int_0^\infty \mathrm{d}x\, F(x \mid Q, X) \tag{2.5}$$

Therefore, the Fourier transform of $\sigma^{\text{ex}}(\mathbf{y})$ with respect to $\mathbf{y}$ has the small wave number behavior

$$\tilde{\sigma}^{\text{ex}}(\boldsymbol{l}) = \int \mathrm{d}\mathbf{y}\, \exp(-i\boldsymbol{l}\cdot\mathbf{y})\, \sigma^{\text{ex}}(\mathbf{y}) \simeq -(\nu-1)\, \pi A\, |\boldsymbol{l}| \tag{2.6}$$

The Fourier transform of $v(x, \mathbf{y})$ is $(\nu-1)\, \pi \exp(-|\boldsymbol{l}|\, x)/|\boldsymbol{l}|$ and thus the Fourier transform of $\partial v/\partial x$ is $-(\nu-1)\, \pi \exp(-|\boldsymbol{l}|\, x)$ and so on for higher-order derivatives of v. Using these transforms in the convolution theorem gives the Fourier transform $\tilde{\phi}(x, \boldsymbol{l})$ of (2.2), which, at $\boldsymbol{l}=\mathbf{0}$, is found to be

$$\tilde{\phi}(x, \mathbf{0}) = (\nu-1)\, \pi[-(\nu-1)\, \pi A + P] \tag{2.7}$$

where

$$P = \int d\mathbf{r}\; x\rho^{\text{ex}}(\mathbf{r}) \tag{2.8}$$

Since x has been assumed to be large, $\tilde{\phi}(x, \mathbf{0}) = 0$ and (2.7) results into

$$-(\nu - 1)\, \pi A + P = 0 \tag{2.9}$$

On account of (2.5) and (2.8), (2.9) is (1.17) in the special case ($\epsilon = \epsilon_W = 1$).

The generalization to other values of the dielectric constants is straightforward. In (2.2), one must add to $\rho^{\text{ex}}(x', \mathbf{y}')$ its electric image[2] $[(\epsilon - \epsilon_W)/(\epsilon + \epsilon_W)]\, \rho^{\text{ex}}(-x', \mathbf{y}')$. This is equivalent to keeping the integration range $(0, \infty)$ for x', but multiplying the first integral in (2.2) by $2\epsilon/(\epsilon + \epsilon_W)$ and the second integral by $2\epsilon_W/(\epsilon + \epsilon_W)$. This gives the general form of (1.17).

3. DEBYE–HÜCKEL LIMIT

We check the relation (1.17) for the general Coulomb system defined in the Introduction, along a plane wall, in the weak coupling limit $\beta \to 0$ (Debye–Hückel limit). It is convenient to introduce the Fourier transform with respect to $\mathbf{y}$ of the excess charge density (1.8)

$$\tilde{\rho}_Q^{\text{ex}}(x, X, |\mathbf{l}|) = \int d\mathbf{y}\, \exp(-i\mathbf{l} \cdot \mathbf{y})\, \rho^{\text{ex}}(\mathbf{r} \mid Q, \mathbf{R}) \tag{3.1}$$

One defines a bulk inverse Debye length κ by

$$\kappa^2 = 2\pi(\nu - 1)\, \beta \left(\sum_{\alpha} q_\alpha^2 n_\alpha \right) \Big/ \epsilon \tag{3.2}$$

where n_α is the bulk density of species α. A minor generalization of the calculation in ref. 7 gives $\tilde{\rho}_Q^{\text{ex}}$ as a sum of its bulk Debye–Hückel form plus a "reflected" term:

$$\begin{aligned} \tilde{\rho}_Q^{\text{ex}}(x, X, \mathbf{l}) = &- \frac{Q\kappa^2}{2(\kappa^2 + l^2)^{1/2}} \Big\{ \exp[-(\kappa^2 + l^2)^{1/2}\, |x - X|] \\ &+ \frac{\epsilon(\kappa^2 + l^2)^{1/2} - \epsilon_W\, |\mathbf{l}|}{\epsilon(\kappa^2 + l^2)^{1/2} + \epsilon_W\, |\mathbf{l}|} \exp[-(\kappa^2 + l^2)^{1/2}\, (x + X)] \Big\} \\ &+ Q\delta(x - X) \end{aligned} \tag{3.3}$$

The asymptotic behavior of $\rho^{\mathrm{ex}}(\mathbf{y})$ is determined by the kink of its Fourier transform $\tilde{\rho}^{\mathrm{ex}}(\boldsymbol{l})$ at $|\boldsymbol{l}|=0$, $Q(\epsilon_W/\epsilon)\exp[-\kappa(x+X)]\,|\boldsymbol{l}|$ (in the sense of distributions, the inverse Fourier transform of $|\boldsymbol{l}|$ is $-1/[(\nu-1)\,\pi\,|\mathbf{y}|^{\nu}]$). One does find the asymptotic behavior (1.16) with

$$F(x\mid Q,X)=-\frac{Q\epsilon_W}{\pi(\nu-1)\,\epsilon}\exp[-\kappa(x+X)] \tag{3.4}$$

Therefore

$$\int_0^{\infty} \mathrm{d}x\, F(x\mid Q,X)=-\frac{Q\epsilon_W}{\pi(\nu-1)\,\kappa\epsilon}\exp(-\kappa X) \tag{3.5}$$

For finding the dipole moment associated to $\rho^{\mathrm{ex}}(\mathbf{r}\mid Q,\mathbf{R})$, one first notes that the integral of ρ^{ex} over $\mathbf{y}$ is the Fourier transform (3.3) taken at $\boldsymbol{l}=0$. The integral over x is easily computed, and one checks that (1.17) is obeyed.

4. TWO-DIMENSIONAL TWO-COMPONENT PLASMA

We now check (1.17) on the two-dimensional TCP at the special value of the coupling constant $\Gamma=\beta q^2=2$, in the case of a plain rectilinear hard wall. Without loss of generality, we shall take the charges $\pm q$ as ± 1. The corresponding correlation functions are known.[(10)] We would like to consider the excess charge density (1.8) in the special case $Q=q=1$, i.e., when the particle fixed at $\mathbf{R}=(X,0)$ is one of the particles (say a positive one) of the system. Although, at $\Gamma=2$, for a given fugacity, the densities diverge, the Ursell functions are finite. Therefore, instead of $\rho^{\mathrm{ex}}(\mathbf{r}|+1,\mathbf{R})$, we consider the finite quantity proportional to its non-self part

$$n_+(\mathbf{R})[\rho^{\mathrm{ex}}(\mathbf{r}|+1,\mathbf{R})-Q\delta(\mathbf{r}-\mathbf{R})]=U_{++}(\mathbf{r},\mathbf{R})-U_{-+}(\mathbf{r},\mathbf{R}) \tag{4.1}$$

($U_{s_1 s_2}$ was called $\rho^{(2)T}_{s_1 s_2}$ in ref. 10). In that same reference, the possible surface charge density carried by the wall was chosen as $-\sigma$ and we shall keep this choice in the present section.

The model has a rescaled fugacity m [which has the dimension of an inverse length such that the bulk correlation length is $1/(2m)$]. The Ursell functions in (4.1) are expressible in terms of auxiliary functions $g_{s+}(x,X,y)$, where $s=\pm$, as[3]

$$U_{s+}(\mathbf{r},\mathbf{R})=-sm^2\,|g_{s+}(x,X,y)|^2 \tag{4.2}$$

[3] We use the symmetry relations (2.15) of ref. 10, the first one of which is misprinted: its rhs should be replaced by its complex conjugate.

The g functions are given by their Fourier transforms

$$\tilde{g}_{s+}(x, X, l) = \int_{-\infty}^{\infty} \mathrm{d}y \, \exp(-\mathrm{i}ly) \, g_{s+}(x, X, y) \tag{4.3}$$

which are

$$\tilde{g}_{++}(x, X, l) = \frac{m}{2k} \{\exp(-k\,|x-X|) - \exp[-k(x+X)]\}, \qquad l<0 \tag{4.4a}$$

$$\tilde{g}_{++}(x, X, l) = \frac{m}{2k} \left\{\exp(-k\,|x-X|) + \frac{k-l+2\pi\sigma}{k+l-2\pi\sigma} \exp[-k(x+X)]\right\}, \quad l>0 \tag{4.4b}$$

$$\tilde{g}_{-+}(x, X, l) = \frac{1}{2k} \{[l-2\pi\sigma + k \,\mathrm{sign}(x-X)] \exp(-k\,|x-X|) - (k+l-2\pi\sigma) \exp[-k(x+X)]\}, \qquad l<0 \tag{4.4c}$$

$$\tilde{g}_{-+}(x, X, l) = \frac{1}{2k} \{[l-2\pi\sigma + k \,\mathrm{sign}(x-X)] \exp(-k\,|x-X|) + (k-l+2\pi\sigma) \exp[-k(x+X)]\}, \qquad l>0 \tag{4.4d}$$

where $k = [m^2 + (l-2\pi\sigma)^2]^{1/2}$.

The asymptotic behavior of the $g(y)$ functions is governed by the discontinuity of their Fourier transforms $\tilde{g}(l)$ at $l=0$. In the sense of distributions, the inverse Fourier transform of $\mathrm{sign}(l)$ is $\mathrm{i}/(\pi y)$. Thus,

$$g_{++}(x, X, y) \simeq \frac{\mathrm{i}m}{2\pi(k_0 - 2\pi\sigma)\, y} \exp[-k_0(x+X)] \tag{4.5a}$$

$$g_{-+}(x, X, y) \simeq \frac{\mathrm{i}}{2\pi y} \exp[-k_0(x+X)] \tag{4.5b}$$

where $k_0 = [m^2 + (2\pi\sigma)^2]^{1/2}$. Using (4.5) in (4.2) and (4.1) gives

$$U_{++}(\mathbf{r}, \mathbf{R}) - U_{-+}(\mathbf{r}, \mathbf{R}) \simeq \frac{F(x \mid X)}{y^2}, \qquad |y| \to \infty \tag{4.6}$$

where

$$F(x \mid X) = -\frac{k_0}{2\pi^2}(k_0 + 2\pi\sigma)\exp[-2k_0(x+X)] \tag{4.7}$$

Therefore

$$\int_0^\infty \mathrm{d}x\, F(x \mid X) = -\frac{1}{4\pi^2}(k_0 + 2\pi\sigma)\exp(-2k_0 X) \tag{4.8}$$

For computing the dipole moment

$$P = \int_0^\infty \mathrm{d}x(x-X)\int_{-\infty}^\infty \mathrm{d}y[U_{++}(\mathbf{r}, \mathbf{R}) - U_{-+}(\mathbf{r}, \mathbf{R})] \tag{4.9}$$

one first considers the integral over y. With regard to (4.2) and (4.3),

$$\begin{aligned}\int_{-\infty}^\infty \mathrm{d}y[U_{++}(\mathbf{r}, \mathbf{R}) - U_{-+}(\mathbf{r}, \mathbf{R})]\\ = -\frac{m^2}{2\pi}\int_{-\infty}^\infty \mathrm{d}l\,\{[\tilde{g}_{++}(x, X, l)]^2 + [\tilde{g}_{-+}(x, X, l)]^2\}\end{aligned} \tag{4.10}$$

In the special case $\sigma = 0$, using (4.4) in (4.10) gives for the dipole moment, after some calculation,

$$\begin{aligned}P = -\frac{m^2}{2\pi}\int_0^\infty \mathrm{d}x\,(x-X)\\ \times \int_0^\infty \mathrm{d}l\left\{\exp(-2k\,|x-X|) + \frac{k-l}{m}\exp[-2k(x+X)]\right\}, \qquad \sigma = 0\end{aligned} \tag{4.11}$$

Performing the integral over x before the one over l gives

$$P = -\frac{m}{4\pi}\exp(-2mX), \qquad \sigma = 0 \tag{4.12}$$

Comparing (4.8) when $\sigma = 0$ with (4.12), one checks that (1.17) is obeyed (here $\epsilon = \epsilon_W = 1$).

For checking (1.17) in the general case $\sigma \neq 0$, it is enough (and easier) to check that the derivatives with respect to $2\pi\sigma$ of both its sides are equal. From (4.8) one obtains

$$\frac{\mathrm{d}}{\mathrm{d}(2\pi\sigma)}\int_0^\infty \mathrm{d}x\, F(x \mid X) = -\frac{1}{4\pi^2}\left(1+\frac{2\pi\sigma}{k_0}\right)(1-4\pi\sigma X)\exp(-2k_0 X) \tag{4.13}$$

On the other hand, the integrand in the rhs of (4.10) depends on l and σ only through the combination $l' = l - 2\pi\sigma$, and its analytic form changes at $l' = -2\pi\sigma$ from some function $f_1(l')$ to some other function $f_2(l')$, as apparent in (4.4). Therefore, the corresponding integral can be rewritten in the form

$$I = \int_{-\infty}^{-2\pi\sigma} \mathrm{d}l'\, f_1(l') + \int_{-2\pi\sigma}^{\infty} \mathrm{d}l'\, f_2(l') \tag{4.14}$$

and one obtains

$$\frac{\mathrm{d}I}{\mathrm{d}(2\pi\sigma)} = -f_1(2\pi\sigma) + f_2(2\pi\sigma) \tag{4.15}$$

This gives $\mathrm{d}/\mathrm{d}(2\pi\sigma)$ of the integral over y in (4.9). Then, one computes the integral over x, with the result that $\mathrm{d}P/\mathrm{d}(2\pi\sigma)$ is π times (4.13). This completes the check of (1.17) on the present model.

5. TWO-DIMENSIONAL ONE-COMPONENT PLASMA

We consider the two-dimensional OCP in contact with a plain hard wall ($\epsilon_W = \epsilon = 1$), localized at $x = 0$ and charged by a "surface" charge density $q\sigma$, first at the coupling constant $\Gamma = \beta q^2 = 2$, then for any even integer Γ ($\sigma = 0$). We work in units such that $\pi n_0 = 1$, where n_0 is the background density. We intend to check the relation (1.15).

5.1. $\Gamma = 2$

The one-body density at a distance x from the wall is given by (see Eq. (2.16) of ref. 7)

$$n(x) = n_0 \frac{2}{\sqrt{\pi}} \int_{-\pi\sigma\sqrt{2}}^{\infty} \frac{\exp[-(t - x\sqrt{2})^2]}{1+\Phi(t)}\,\mathrm{d}t \tag{5.1}$$

where

$$\Phi(t) = \frac{2}{\sqrt{\pi}} \int_0^t \exp(-u^2)\, \mathrm{d}u \tag{5.2}$$

is the error function. The two-body Ursell function (called $\rho_T^{(2)}$ in Eq. (2.18) of ref. 7) is

$$\begin{aligned} &U(x, x'; |y-y'|) \\ &\quad = -n_0^2 \exp[-(x-x')^2] \\ &\qquad \times \left| \frac{2}{\sqrt{\pi}} \int_{-\pi\sigma\sqrt{2}}^{\infty} \frac{\exp\{-[t-(x+x')/\sqrt{2}]^2 - \mathrm{i}t(y-y')\sqrt{2}\}}{1+\Phi(t)}\, \mathrm{d}t \right|^2 \end{aligned} \tag{5.3}$$

The structure function S is expressed in terms of n and U in formula (1.6). The asymptotic f-function takes the form (see Eq. (2.21) of ref. 7)

$$f(x, x') = -n_0^2 q^2 \frac{2}{\pi} \frac{\exp[-2(x+\pi\sigma)^2 - 2(x'+\pi\sigma)^2]}{[1+\Phi(-\pi\sigma\sqrt{2})]^2} \tag{5.4}$$

It is easy to show that

$$\frac{\pi}{q^2} \int_0^\infty \mathrm{d}x'\, f(x, x') = -\frac{1}{\sqrt{2}\,\pi^{3/2}} \frac{\exp[-2(x+\pi\sigma)^2]}{1+\Phi(-\pi\sigma\sqrt{2})} \tag{5.5}$$

On the other hand, performing first the integration over the y-coordinate, one obtains

$$\begin{aligned} &\frac{1}{q^2} \int_0^\infty \mathrm{d}x' \int_{-\infty}^{\infty} \mathrm{d}y\, x' S(x, x'; y) \\ &\quad = x \frac{2}{\pi^{3/2}} \int_{-\pi\sigma\sqrt{2}}^{\infty} \frac{\exp[-(t-x\sqrt{2})^2]}{1+\Phi(t)}\, \mathrm{d}t \\ &\qquad - \frac{8}{\sqrt{2}\,\pi^2} \exp(-2x^2) \int_{-\pi\sigma\sqrt{2}}^{\infty} \frac{\exp(-2t^2 + 2\sqrt{2}\,tx)}{[1+\Phi(t)]^2} I(t)\, \mathrm{d}t \end{aligned} \tag{5.6}$$

where

$$\begin{aligned} I(t) &= \int_0^\infty \mathrm{d}x'\, x' \exp(-2x'^2 + 2\sqrt{2}\,tx') \\ &= \frac{1}{4} + \frac{\sqrt{\pi}}{4} t[1+\Phi(t)] \exp(t^2) \end{aligned} \tag{5.7}$$

After simple algebra, one arrives at

$$\frac{1}{q^2}\int_0^\infty \mathrm{d}x' \int_{-\infty}^{\infty} \mathrm{d}y\, x' S(x, x'; y) = J_1 + J_2 \tag{5.8}$$

where

$$J_1 = \frac{1}{\sqrt{2}\,\pi^{3/2}} \int_{-\pi\sigma\sqrt{2}}^{\infty} \mathrm{d}t\, \frac{1}{1+\Phi(t)} \frac{\partial}{\partial t} \exp[-(t-x\sqrt{2})^2] \tag{5.9a}$$

$$J_2 = -\frac{2}{\sqrt{2}\,\pi^2} \int_{-\pi\sigma\sqrt{2}}^{\infty} \mathrm{d}t\, \frac{\exp(-t^2)}{[1+\Phi(t)]^2} \exp[-(t-x\sqrt{2})^2] \tag{5.9b}$$

Using the equality

$$\frac{\exp(-t^2)}{[1+\Phi(t)]^2} = -\frac{\sqrt{\pi}}{2} \frac{\partial}{\partial t}\left[\frac{1}{1+\Phi(t)}\right] \tag{5.10}$$

in J_2, the consequent integration per partes implies

$$J_2 = -\frac{1}{\sqrt{2}\,\pi^{3/2}} \frac{\exp[-2(x+\pi\sigma)^2]}{1+\Phi(-\pi\sigma\sqrt{2})} - J_1 \tag{5.11}$$

Inserting J_2 into (5.8) and comparing with (5.5) one gets the expected relation (1.15) with $\epsilon_W = \epsilon$ and $\nu = 2$.

5.2. Γ = Even Integer

Let the OCP with logarithmic interactions be confined to a compact two-dimensional domain V. The positively oriented contour enclosing the domain V, denoted by ∂V, is defined parametrically as $x = X(\varphi)$, $y = Y(\varphi)$; $\varphi_0 \leqslant \varphi \leqslant \varphi_1$. For example, the circle enclosing the disk of radius R centered at the origin admits the parametrization $X(\varphi) = R\cos\varphi$, $Y(\varphi) = R\sin\varphi$; $0 \leqslant \varphi \leqslant 2\pi$. Integrals over the V-domain can be expressed in terms of the ∂V-contour integrals according to the rule

$$\int_V \left(\frac{\partial Q}{\partial x} - \frac{\partial P}{\partial y}\right) \mathrm{d}x\, \mathrm{d}y = \int_{\partial V} (P\, \mathrm{d}x + Q\, \mathrm{d}y) \tag{5.12a}$$

where

$$\int_{\partial V} P(x, y)\,\mathrm{d}x = \int_{\varphi_0}^{\varphi_1} \mathrm{d}\varphi\; P[X(\varphi), Y(\varphi)]\; X'(\varphi)$$
$$\int_{\partial V} Q(x, y)\,\mathrm{d}y = \int_{\varphi_0}^{\varphi_1} \mathrm{d}\varphi\; Q[X(\varphi), Y(\varphi)]\; Y'(\varphi) \tag{5.12b}$$

The neutralizing background of uniform density n_0 creates the one-particle potential $-qn_0 v_0(\mathbf{r})$ where

$$v_0(\mathbf{r}) = \int_V \mathrm{d}^2 r'\; v(|\mathbf{r}-\mathbf{r}'|) \tag{5.13}$$

The corresponding electric field is $-qn_0 \mathbf{E}_0(\mathbf{r})$ where

$$\mathbf{E}_0(\mathbf{r}) = E_0^x(\mathbf{r})\,\hat{\mathbf{x}} + E_0^y(\mathbf{r})\,\hat{\mathbf{y}} = -\nabla v_0(\mathbf{r}) \tag{5.14}$$

with $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ being unit vectors in the x and y directions. For the half-plane of interest,

$$v_0(\mathbf{r}) = \text{const} - \pi x^2; \qquad E_0^x = 2\pi x, \quad E_0^y = 0 \tag{5.15}$$

For a disk of radius R centered at the origin $\mathbf{0}$,

$$v_0(\mathbf{r}) = \text{const} - \pi r^2/2; \qquad E_0^x = \pi x, \quad E_0^y = \pi y \tag{5.16}$$

By mapping the two-dimensional OCP onto a discrete one-dimensional Grassmann field theory for the coupling constant $\Gamma =$ even integer, two new kinds of sum rules for the structure function S were established in ref. 11 for an arbitrarily shaped V-domain. The first sum rule reads (see formulae (61a,b) of ref. 11 where U is called n^{T})

$$-\beta n_0 \int_V \mathrm{d}^2 r'\; E_0^x(\mathbf{r}')\, S(\mathbf{r}, \mathbf{r}') = \frac{\partial n(\mathbf{r})}{\partial x} + \int_V \mathrm{d}^2 r'\, \frac{\partial}{\partial x'}\, U(\mathbf{r}, \mathbf{r}') \tag{5.17a}$$

$$-\beta n_0 \int_V \mathrm{d}^2 r'\; E_0^y(\mathbf{r}')\, S(\mathbf{r}, \mathbf{r}') = \frac{\partial n(\mathbf{r})}{\partial y} + \int_V \mathrm{d}^2 r'\, \frac{\partial}{\partial y'}\, U(\mathbf{r}, \mathbf{r}') \tag{5.17b}$$

With the aid of the prescription (5.12), the last terms on the rhs of these sum rules can be rewritten as follows

$$\int_V \mathrm{d}^2 r' \, \frac{\partial}{\partial x'} U(\mathbf{r}, \mathbf{r}') = \int_{\varphi_0}^{\varphi_1} \mathrm{d}\varphi \, U[\mathbf{r}; (X, Y)] \, Y' \tag{5.18a}$$

$$\int_V \mathrm{d}^2 r' \, \frac{\partial}{\partial y'} U(\mathbf{r}, \mathbf{r}') = -\int_{\varphi_0}^{\varphi_1} \mathrm{d}\varphi \, U[\mathbf{r}; (X, Y)] \, X' \tag{5.18b}$$

The second sum rule reads (see formula (45a) of ref. 11)

$$-\beta n_0 \int_V \mathrm{d}^2 r' [\mathbf{r}' \cdot \mathbf{E}_0(\mathbf{r}')] \, S(\mathbf{r}, \mathbf{r}')$$

$$= 2n(\mathbf{r}) + \mathbf{r} \cdot \nabla n(\mathbf{r}) + \int_{\varphi_0}^{\varphi_1} \mathrm{d}\varphi \, U[\mathbf{r}; (X, Y)](XY' - X'Y) \tag{5.19}$$

For the half-plane, since the Ursell function $U(\mathbf{r}, \mathbf{r}')$ goes to zero at large $|\mathbf{r} - \mathbf{r}'|$, Eq. (5.17a) yields

$$-2\pi\beta n_0 \int_0^\infty \mathrm{d}x' \int_{-\infty}^\infty \mathrm{d}y \, x' S(x, x'; y) = \frac{\mathrm{d}n(x)}{\mathrm{d}x} - \int_{-\infty}^\infty \mathrm{d}y \, U(x, 0; y) \tag{5.20}$$

This is an OCP generalization of the WLMB equations,[12, 13] which were originally derived for neutral systems. It is trivial to obtain the dipole sum rule (1.12) by integrating both sides of (5.20) over x from 0 to ∞, then taking into account that $\lim_{x\to\infty} n(x) = n_0$, and finally considering the electroneutrality condition (1.11) at $x = 0$.

For a disk of radius R, the addition of Eq. (5.17a) multiplied by x and Eq. (5.17b) multiplied by y, with the substitutions (5.18), leads to

$$-\pi\beta n_0 \int_{\text{disk}} \mathrm{d}^2 r' \, (\mathbf{r} \cdot \mathbf{r}') \, S(\mathbf{r}, \mathbf{r}') = r \frac{\mathrm{d}n(r)}{\mathrm{d}r} + \int_0^{2\pi} \mathrm{d}\varphi' \, (\mathbf{r} \cdot \mathbf{R}') \, U(\mathbf{r}, \mathbf{R}') \tag{5.21}$$

where, in polar coordinates, $\mathbf{R}' = (R, \varphi')$. Eq. (5.19) takes the form

$$-\pi\beta n_0 \int_{\text{disk}} \mathrm{d}^2 r' \, |\mathbf{r}'|^2 \, S(\mathbf{r}, \mathbf{r}') = 2n(r) + r \frac{\mathrm{d}n(r)}{\mathrm{d}r} + R^2 \int_0^{2\pi} \mathrm{d}\varphi' \, U(\mathbf{r}, \mathbf{R}') \tag{5.22}$$

Since $|\mathbf{r}-\mathbf{r}'|^2 = |\mathbf{r}|^2 + |\mathbf{r}'|^2 - 2\mathbf{r}\cdot\mathbf{r}'$, the combination of relations (5.21) and (5.22) with the electroneutrality condition (1.11) results in

$$-\pi\beta n_0 \int_{\text{disk}} \mathrm{d}^2 r' \, |\mathbf{r}-\mathbf{r}'|^2 \, S(\mathbf{r},\mathbf{r}') \\ = 2n(r) - r\,\frac{\mathrm{d}n(r)}{\mathrm{d}r} - \int_0^{2\pi} \mathrm{d}\varphi' \, (2\mathbf{r}\cdot\mathbf{R}' - R^2)\, U(\mathbf{r},\mathbf{R}') \tag{5.23}$$

Let us move the origin to the disk boundary by introducing $x = R - r$. Equation (5.23) becomes

$$-\pi\beta n_0 \int_0^{2\pi} \mathrm{d}\varphi' \int_0^R \mathrm{d}x' (R-x') \, |\mathbf{r}-\mathbf{r}'|^2 \, S(\mathbf{r},\mathbf{r}') \\ = 2n(x) + (R-x)\,\frac{\mathrm{d}n(x)}{\mathrm{d}x} - \int_0^{2\pi} \mathrm{d}\varphi' [2R(R-x)\cos(\varphi'-\varphi) - R^2]\, U(\mathbf{r},\mathbf{R}') \tag{5.24}$$

We now take the limit $R \to \infty$. The lhs of (5.24) is dominated by the large values of $|\mathbf{r}-\mathbf{r}'|$. The asymptotic behaviour (1.13) is equivalent to

$$|\mathbf{r}-\mathbf{r}'|^2 \, S(\mathbf{r},\mathbf{r}') \simeq f(x,x') + \cdots \tag{5.25}$$

where the higher-order terms vanish for large $|\mathbf{r}-\mathbf{r}'|$. Substituting $\varphi' \to y = R(\varphi'-\varphi)$ on the rhs of (5.24) and collecting all terms of order R, one finally arrives at the equation

$$-2\pi^2\beta n_0 \int_0^\infty \mathrm{d}x' \, f(x,x') = \frac{\mathrm{d}n(x)}{\mathrm{d}x} - \int_{-\infty}^\infty \mathrm{d}y \, U(x,0;y) \tag{5.26}$$

formulated for the half-plane. This equation is exactly of the form (5.20), with the expected identification (1.15) for the case under consideration $\epsilon = \epsilon_W = 1$ and $\nu = 2$.

6. CONCLUSION

We have derived a general relation between the asymptotic behavior of a charge correlation function along a plane wall and the dipole moment of that correlation function, in the general form (1.17). In the particular case of the charge structure factor, that relation becomes (1.15).

In those exactly solvable models for which the two-body correlations are known, finding their asymptotic behavior is often easier than directly computing the dipole moment. However, in the present paper, we did compute this dipole moment, for the sake of checking the general relation.

The relation (1.15) was first observed in the special case of a two-dimensional one-component plasma, as one more application of a mapping onto a Grassmann field theory.[11] Afterwards, we realized that the relation could be derived in general for any Coulomb system.

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