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Classical Coulomb Systems Near a Plane Wall. II

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The equilibrium structure of classical Coulomb systems bounded by a plane hard wall is studied near that wall. A general sum rule is derived for the asymptotic form of the charge–charge correlation function along the wall. The exact results which can be obtained for the two-dimensional one-component plasma provide a test for this new sum rule, as well as for other already known sum rules or their generalizations.

KEY WORDS: Coulomb systems; plasmas; surface properties; walls; correlations; sum rules; double electric layer.

1. INTRODUCTION

Near a charged wall, a Coulomb fluid forms a charged layer of opposite sign. The structure of this double electric layer currently attracts much interest.

In a previous paper[(1)] [hereafter referred to as I; equations from I are referred to as (I.1.1), etc.] the equilibrium structure of classical Coulomb systems bounded by a (possibly charged) plane wall was studied near that wall for several models. Only the simplest case of a hard wall with no image forces was considered. It was found that, along the wall, the pair correlation functions decay slowly, only as an inverse power of the distance r, namely, as $r^{-\nu}$ for a ν-dimensional system ($\nu = 2, 3$). One of the models which were studied is the two-dimensional one-component plasma, which happens to be exactly soluble[(2-4)] for the special value of the coupling constant $\Gamma = 2$.

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Smith, who studied independently the surface properties of this model,[5] also obtained exact results in a case with image forces.[6] He assumed that the dielectric constant of the wall is zero. In that case, images, carrying charges of the same sign and magnitude as the real particles, are set up in the wall; the model is still soluble when $\Gamma = 2$.

The present paper deals with several sum rules for the distribution functions of a classical Coulomb system near a plane charged hard wall; image forces may be present. The sum rules, which are of general validity, are checked on specific models, and more especially on the two-dimensional one-component plasma.

In Section 2, we (heuristically) derive a sum rule for the asymptotic behavior of the charge–charge correlation function in the direction parallel to the wall. In Section 3, we check this sum rule for several specific models. In Section 4, we discuss the structure of the screening cloud around a given particle, and show how it is related to suitable generalizations of the sum rules of Gruber *et al.*[7]; we also show that Smith's results are consistent with the sum rule of Blum *et al.*[8] for the dipole moment of the pair correlation function near a charged wall. Section 5 generalizes a known relation between the bulk pressure and the distribution functions near the wall.

Only the case of a fluid phase is considered here.

2. ASYMPTOTIC BEHAVIOR OF THE CHARGE–CHARGE CORRELATION FUNCTION ALONG A PLANE WALL

2.1. Results

We consider a fluid made of several species of charged particles, embedded in a medium the dielectric constant of which is ϵ. The system may be either three dimensional or two dimensional; let ν ($\nu = 2, 3$) be the dimensionality. Two particles of charges e_1 and e_2, at a distance r from one another, interact through a Coulomb potential $e_1 e_2/\epsilon r$ if $\nu = 3$, or $-(e_1 e_2/\epsilon)\ln(r/L)$, where L is an (irrelevant) length scale, if $\nu = 2$. In addition, short-range forces between the particles will also be present in general. The system is a semi-infinite one, which occupies the half-space $x > 0$; we call $\mathbf{y}$ the coordinate(s) normal to x.

The plane $x = 0$ is a hard wall, which may be charged, carrying a uniform surface charge density. We assume the half-space $x < 0$ to be filled with a material the dielectric constant of which is ϵ_W. Therefore, a particle of charge e at the point $(x, \mathbf{y})$ has an electrical image of charge $[(\epsilon - \epsilon_W)/(\epsilon + \epsilon_W)]e$ at the point $(-x, \mathbf{y})$.

Let the microscopic charge density at the point $(x, \mathbf{y})$ be

$$C(x,\mathbf{y}) = \sum_{i\alpha} e_\alpha \delta(x - x_{i\alpha})\delta(\mathbf{y} - \mathbf{y}_{i\alpha}) \tag{2.1}$$

where $(x_{i\alpha}, \mathbf{y}_{i\alpha})$ are the coordinates of particle i of species α and e_α is its charge. Let the canonical average charge density be

$$c^{(1)}(x) = \langle C(x,\mathbf{y})\rangle \tag{2.2}$$

and the canonical average double charge density be

$$c^{(2)}(x,x',|\mathbf{y}'-\mathbf{y}|) = \langle C(x,\mathbf{y})C(x',\mathbf{y}')\rangle \tag{2.3}$$

We also define a truncated double charge density

$$c_T^{(2)}(x,x',|\mathbf{y}'-\mathbf{y}|) = c^{(2)}(x,x',|\mathbf{y}'-\mathbf{y}|) - c^{(1)}(x)c^{(1)}(x') \tag{2.4}$$

For the asymptotic behavior of $c_T^{(2)}$ along the wall, we claim the following sum rule:

$$c_T^{(2)}(x,x',|\mathbf{y}'-\mathbf{y}|) \sim F(x,x',|\mathbf{y}'-\mathbf{y}|), \qquad \text{when} \quad |\mathbf{y}'-\mathbf{y}| \to \infty \tag{2.5}$$

where the asymptotic expression F is a function integrable upon x and x' obeying

$$\int_0^\infty dx' \int_0^\infty dx\, F(x,x',|\mathbf{y}'-\mathbf{y}|) = -\frac{\epsilon_W k_B T}{2[(\nu-1)\pi]^2|\mathbf{y}'-\mathbf{y}|^\nu}, \qquad (\nu = 2,3) \tag{2.6}$$

k_B is Boltzmann's constant and T the temperature.

A stronger statement, that we present only as a conjecture, is the following:

$$c_T^{(2)}(x,x',|\mathbf{y}'-\mathbf{y}|) \sim \frac{f(x,x')}{|\mathbf{y}'-\mathbf{y}|^\nu}, \qquad \text{when} \quad |\mathbf{y}'-\mathbf{y}| \to \infty, \qquad (\nu = 2,3) \tag{2.7}$$

where $f(x,x')$ is an integrable function obeying

$$\int_0^\infty dx' \int_0^\infty dx\, f(x,x') = -\frac{\epsilon_W k_B T}{2[(\nu-1)\pi]^2} \qquad (\nu = 2,3) \tag{2.8}$$

Obviously, (2.7) and (2.8) imply (2.5) and (2.6), but the reverse is not true.

In the special extreme case $\epsilon_W = 0$, the coefficient of the algebraic tail $|\mathbf{y}'-\mathbf{y}|^{-\nu}$ in (2.6) or (2.8) vanishes; we conjecture that the decay becomes faster than any inverse-power law.

The other extreme case $\epsilon_W = \infty$ corresponds to a perfectly conducting wall; we have no valid results in that case.

2.2. Derivation

The (heuristic) derivation we shall give for (2.5), (2.6) is based on a perfect-screening argument in the long-wavelength limit, closely related to similar arguments used in bulk systems.[9] We phrase the argument for a three-dimensional system; only minor modifications in the numerical factors are required for dealing with a two-dimensional system.

First, we relate the double charge density and the linear response to an external charge density. In addition to the uniform surface charge density which may be carried by the wall, we put on it a periodic external surface charge density of the form $\alpha \exp(i\mathbf{l} \cdot \mathbf{y})$. This surface charge density creates an electrostatic potential

$$\phi(x, \mathbf{y}) = \frac{4\pi\alpha}{(\epsilon + \epsilon_W)l} \exp(i\mathbf{l} \cdot \mathbf{y} - l|x|) \tag{2.9}$$

it is indeed easy to check that the Laplacian of ϕ vanishes outside the plane $x = 0$, that ϕ is continuous on that plane, and that the normal component of the electrical displacement has the proper jump $4\pi\alpha \exp(i\mathbf{l} \cdot \mathbf{y})$ on that plane. Therefore, the external charge density is coupled to the charge density (2.1) of the fluid; the Hamiltonian acquires an additional term

$$\alpha H' = \int d\mathbf{y}' \int_0^\infty dx' \, \phi(x', \mathbf{y}') C(x', \mathbf{y}') \tag{2.10}$$

From the definition of the canonical average of any observable A, one derives the linear response relation

$$\left. \frac{\partial \langle A \rangle_\alpha}{\partial \alpha} \right|_{\alpha=0} = -\beta(\langle AH' \rangle - \langle A \rangle \langle H' \rangle) \tag{2.11}$$

where $\beta = 1/k_B T$; $\langle \; \rangle_\alpha$ denotes a canonical average taken in presence of the term $\alpha H'$ in the Hamiltonian, and $\langle \; \rangle$ denotes a canonical average taken at $\alpha = 0$.

Let us now use for A the integrated charge density

$$A = \int_0^\infty dx \, C(x, \mathbf{y}) \tag{2.12}$$

In the long-wavelength (macroscopic) limit $l \to 0$, we expect that every element of the external surface charge density will be perfectly screened by charges in the fluid surface layer adjacent to this element:

$$\langle A \rangle_\alpha - \langle A \rangle \sim -\alpha \exp(i\mathbf{l} \cdot \mathbf{y}), \qquad \text{when} \quad l \to 0 \tag{2.13}$$

This is our basic assumption. Using it in (2.11), we obtain

$$\int d\mathbf{y}' \int_0^\infty dx' \exp\left[i\mathbf{l} \cdot (\mathbf{y}' - \mathbf{y}) - lx' \right] \int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|)$$
$$\sim \frac{(\epsilon + \epsilon_W) k_B T}{4\pi} l, \qquad \text{when} \quad l \to 0 \tag{2.14}$$

It is convenient to subtract from (2.14) a bulk contribution which comes from the large values of x'. Far away from the wall, $c_T^{(2)}$ becomes the bulk double-charge density, and its Fourier transform (which is essentially the charge density structure factor) has a well-known long-wavelength behavior,[10] obtained by a perfect-screening argument in the bulk:

$$\int d\mathbf{y}' \exp\left[i\mathbf{l} \cdot (\mathbf{y}' - \mathbf{y}) \right] \lim_{x' \to +\infty} \int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|)$$
$$\sim \frac{\epsilon k_B T}{4\pi} l^2, \qquad \text{when} \quad l \to 0 \tag{2.15}$$

Therefore

$$\int d\mathbf{y}' \int_0^\infty dx' \exp\left[i\mathbf{l} \cdot (\mathbf{y}' - \mathbf{y}) - lx' \right] \lim_{x' \to +\infty} \int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|)$$
$$\sim \frac{\epsilon k_B T}{4\pi} l, \qquad \text{when} \quad l \to 0 \tag{2.16}$$

It is also possible to derive (2.16) directly by an argument similar to the one leading to (2.14), but assuming that the bulk fluid occupies both sides of the plane $x = 0$.

Subtracting (2.16) from (2.15), we obtain

$$\int d\mathbf{y}' \int_0^\infty dx' \exp\left[i\mathbf{l} \cdot (\mathbf{y}' - \mathbf{y}) - lx' \right]$$
$$\times \left[\int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|) - \lim_{x' \to +\infty} \int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|) \right]$$
$$\sim \frac{\epsilon_W k_B T}{4\pi} l, \qquad \text{when} \quad l \to 0 \tag{2.17}$$

The last bracket in the left-hand-side of (2.17) goes to zero as x' increases, on a microscopic length scale which is the thickness of the surface region. Therefore, in the limit $l \to 0$, the factor $\exp(-lx')$ may be omitted (note that this factor $\exp(-lx')$ *cannot* be omitted in (2.14) where it is needed for the integral to be convergent). One obtains

$$\int d\mathbf{y}' \exp\left[i\mathbf{l} \cdot (\mathbf{y}' - \mathbf{y}) \right] \int_0^\infty dx' \left[\int_0^\infty dx \, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|) - \lim_{x' \to +\infty} \int_0^\infty dx \, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|) \right] \sim \frac{\epsilon_W k_B T}{4\pi} l, \qquad \text{when} \quad l \to 0 \tag{2.18}$$

The function of $\mathbf{l}$ defined by (2.18) is the Fourier transform of a function of $\mathbf{y}' - \mathbf{y}$. The function of $\mathbf{l}$ has a kink at $\mathbf{l} = 0$ which governs the asymptotic behavior of the function of $\mathbf{y}' - \mathbf{y}$; this asymptotic behavior is[11]

$$\int_0^\infty dx' \left[\int_0^\infty dx \, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|) - \lim_{x' \to +\infty} \int_0^\infty dx \, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|) \right] \sim - \frac{\epsilon_W k_B T}{8\pi^2 |\mathbf{y}' - \mathbf{y}|^3}, \qquad \text{when} \quad |\mathbf{y}' - \mathbf{y}| \to \infty \tag{2.19}$$

We expect that long-range correlations are a specific surface feature and that the bulk term

$$\lim_{x' \to +\infty} \int_0^\infty dx \, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|)$$

has a faster decay as a function of $|\mathbf{y}' - \mathbf{y}|$ and does not contribute to the asymptotic behavior. Therefore, (2.19) and its analog in the two-dimensional case lead to the sum rule expressed by (2.5) and (2.6).

In the special case $\epsilon_W = 0$, the kink term $(\epsilon_W k_B T / 4\pi) l$ in (2.18) vanishes. This suggests that $c_T^{(2)}$ might have no algebraic tail as a function of $|\mathbf{y}' - \mathbf{y}|$ in that case.

A perfectly conducting wall would be described by an infinite value of ϵ_W. In that extreme case, our whole argument breaks down, because (2.9) vanishes and therefore the external periodic surface charge density is not coupled to the system.

The argument leading to (2.14) can be slightly modified for studying the charge–charge correlation function for a system of particles confined in a two-dimensional plane and interacting through the usual three-dimensional Coulomb potential $e_1 e_2 / r$. One obtains

$$\int d\mathbf{y}' \exp\left[i\mathbf{l} \cdot (\mathbf{y}' - \mathbf{y}) \right] c_T^{(2)}(|\mathbf{y}' - \mathbf{y}|) \sim \frac{k_B T}{2\pi} l, \qquad \text{when} \quad l \to 0 \tag{2.20}$$

and

$$c_T^{(2)}(|\mathbf{y}' - \mathbf{y}|) \sim - \frac{k_B T}{4\pi^2 |\mathbf{y}' - \mathbf{y}|^3}, \qquad \text{when} \quad |\mathbf{y}' - \mathbf{y}| \to \infty \tag{2.21}$$

where $c_T^{(2)}(|\mathbf{y}' - \mathbf{y}|)$ now is the truncated double *surface* charge density. Since no bulk term has to be subtracted, (2.20) ad (2.21) differ by a factor 2 from their counterparts (2.18) and (2.19).

3. SPECIFIC MODELS

3.1. Plain Hard Wall (No Image Forces)

In I, we studied one-component plasmas near a hard wall, in the case $\epsilon = \epsilon_W = 1$. In such a case, there are no image forces. For a one-component plasma, made of particles of charge e and bulk number density ρ embedded in a background of charge density $-e\rho$, the truncated double-charge density (2.4) is

$$c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|) = e^2 \rho^{(1)}(x, \mathbf{y}) \delta(x' - x) \delta(\mathbf{y}' - \mathbf{y}) + e^2 \rho_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|) \tag{3.1}$$

where $\rho^{(1)}$ and $\rho_T^{(2)}$ are the one-body and truncated two-body number densities. The asymptotic form of $c_T^{(2)}$ is the same as the asymptotic form of $e^2 \rho_T^{(2)}$.

For the two-dimensional one-component plasma, when the coupling constant $\Gamma = \beta e^2$ has the special value $\Gamma = 2$, the asymptotic behavior of $\rho_T^{(2)}$ near a hard wall (which may carry a uniform "surface" charge density $-e\sigma$) is given by (I.2.21). For a two-dimensional or three-dimensional one-component plasma in the weak-coupling limit, $\rho_T^{(2)}$ is equivalent to $\rho^2 h$, and the asymptotic behavior of the pair correlation function h near an (uncharged) hard wall is given by (I.3.15). It is straightforward to check that the sum rule of Section 2, in its strong form (2.7), (2.8), is indeed satisfied in these cases.

In the weak-coupling limit, the case of a symmetrical two-component plasma was also considered in I; the pair correlation functions were found to be essentially the same as in the one-dimensional case, except for changes in the numerical factors. Again, it is straightforward to check that the sum rule (2.7), (2.8) is satisfied.

3.2. Hard Wall with Zero Dielectric Constant

Smith[6] studied the two-dimensional one-component plasma near an uniformly charged hard wall which has a dielectric constant $\epsilon_W = 0$; the plasma is embedded in a medium of finite dielectric constant ϵ. For the other quantities, we shall use here the notations of our paper I; in these notations, the unit of length is the average interparticle distance, and therefore the bulk number density ρ is π^{-1}. When the coupling constant $\Gamma = \beta e^2/\epsilon$ has the special value $\Gamma = 2$, the one-body number density can be written as

$$\rho^{(1)}(x) = \rho \frac{2}{\sqrt{\pi}} \exp\left[-2(x+\pi\sigma)^2\right] \int_{-\infty}^{\infty} \frac{dt \exp(-t^2) \sinh 2xt\sqrt{2}}{Q(t)} \tag{3.2}$$

where

$$\begin{aligned} Q(t) &= \frac{4}{\sqrt{\pi}} \exp(-t^2) \int_0^{\infty} d\zeta \exp\left[-\left(\zeta + \pi\sigma\sqrt{2}\right)^2\right] \sinh 2\zeta t \\ &= \exp\left(-2\pi\sigma t\sqrt{2}\right)\left[1 + \Phi\left(t - \pi\sigma\sqrt{2}\right)\right] \\ &\quad - \exp\left(2\pi\sigma t\sqrt{2}\right)\left[1 - \Phi\left(t + \pi\sigma\sqrt{2}\right)\right] \end{aligned} \tag{3.3}$$

Φ is the error function

$$\Phi(t) = \frac{2}{\sqrt{\pi}} \int_0^t \exp(-\zeta)\, d\zeta \tag{3.4}$$

and $-e\sigma$ is the "surface" charge density on the wall. The truncated two-body number density is

$$\begin{aligned} &\rho_T^{(2)}(x, x', |y'-y|) \\ &\quad = -\exp\left[-(x'-x)^2 - (y'-y)^2\right] \\ &\qquad \times \left\{ |\rho^{(1)}[(x+x'+i|y'-y|)/2]|^2 \right. \\ &\qquad\quad \left. - \exp(-4xx' - 8\pi\sigma x)|\rho^{(1)}[(x'-x+i|y'-y|)/2]|^2 \right\} \end{aligned} \tag{3.5}$$

The asymptotic behaviors of these distribution functions are studied in Appendix A with the following results. As $x \to \infty$, $\rho^{(1)}(x) - \rho$ decays essentially like a Gaussian. The asymptotic behavior of $\rho_T^{(2)}(x, x', |y'-y|)$ when both points (x, y) and (x', y') are far away from the wall $(x, x' \gg 1$, for given values of $x - x'$ and $y - y')$ is the bulk function:

$$\rho_T^{(2)}(x, x', |y'-y|) \sim -\rho^2 \exp\left[-(x'-x)^2 - (y'-y)^2\right] \tag{3.6}$$

The asymptotic behavior of $\rho_T^{(2)}(x, x', |y'-y|)$ as (x', y') recedes to infinity while (x, y) stays at a fixed position depends upon the direction. If (x', y') recedes in the direction normal to the wall, $\rho_T^{(2)}$ decays like $\exp[-(x'-x)^2]$; in an oblique direction, $\rho_T^{(2)}$ decays faster than $\exp[-(x'-x)^2]$. But, for a direction *parallel* to the wall (x and x' keep fixed values while

$|y'-y|\to\infty$), $\rho_T^{(2)}$ decays only with *exponentially* damped oscillations:

$$\begin{aligned}
&\rho_T^{(2)}(x,x',|y'-y|)\\
&\quad\sim -A\exp\left[-2(x+\pi\sigma)^2-2(x'+\pi\sigma)^2-b|y'-y|\right]\\
&\qquad\times\left\{\exp\left[a(x+x')\right]\cos\left[a|y'-y|+b(x+x')+\varphi\right]\right.\\
&\qquad\quad+\exp\left[-a(x+x')\right]\cos\left[a|y'-y|-b(x+x')+\varphi\right]\\
&\qquad\quad-\exp\left[a(x'-x)\right]\cos\left[a|y'-y|+b(x'-x)+\varphi\right]\\
&\qquad\quad\left.-\exp\left[-a(x'-x)\right]\cos\left[a|y'-y|-b(x'-x)+\varphi\right]\right\} \qquad (3.7)
\end{aligned}$$

where A, a, b, φ are constants ($A,a,b>0$). In the special case $\sigma=0$ of an uncharged wall, $A=\pi^2\rho^2$ ($=1$ in our units), $a=2.051$, $b=2.660$, $\varphi=0$.

Therefore, this soluble case supports the conjecture that $c_T^{(2)}$ has no algebraic tail as a function of $|y'-y|$ in the case $\epsilon_W=0$.

4. ELECTRICAL MOMENTS OF THE SCREENING CLOUD

4.1. Systems with No Image Forces

Gruber *et al.*[7] have given a rigorous derivation of sum rules for inhomogeneous Coulomb systems, under the assumption that the correlations decay fast enough. These rules state that the total excess charge carried by a particle (i.e., its own charge plus the charge of the screening cloud it induces in its vicinity) is zero (perfect screening), and that this excess charge has no dipole nor quadrupole moment. On the basis of a heuristic argument, we state the following more general rule:

If the two-point correlation functions decay faster than any inverse-power law in every direction, the total excess charge carried by a particle is zero and has no electrical moment of any order.

The argument for this statement is that, if the excess charge had a 2^n-pole electrical moment, this moment would create at a large distance r an electrostatic potential decaying as $r^{2-\nu-n}$ (for a ν-dimensional system), and therefore would induce an excess charge density decaying as $r^{2-\nu-n}$, in contradiction with the assumption of no inverse-power law correlations.

The sum rule can be tested on the exactly known bulk correlation functions[3] of the two-dimensional one-component plasma at $\Gamma=2$. The inhomogeneity in the system can be introduced by fixing one of the particles at the origin and considering it as an external charge. In terms of the n-body densities $\rho^{(n)}$ $(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)$ of the homogeneous system, the one- and two-body densities of the inhomogeneous system are

$$\rho_I^{(1)}(\mathbf{r}_1) = \frac{\rho^{(2)}(0,\mathbf{r}_1)}{\rho} = \rho\left[1 - \exp(-r_1^2)\right] \tag{4.1}$$

and

$$\begin{aligned}\rho_I^{(2)}(\mathbf{r}_1,\mathbf{r}_2) &= \frac{\rho^{(3)}(0,\mathbf{r}_1,\mathbf{r}_2)}{\rho} \\ &= \rho^2\left\{1 - \exp(-r_1^2) - \exp(-r_2^2) - \exp\left[-(\mathbf{r}_2-\mathbf{r}_1)^2\right]\right. \\ &\qquad \left. + 2\exp(-r_1^2 - r_2^2 + r_1 r_2\cos\theta)\cos(r_1 r_2 \sin\theta)\right\} \end{aligned} \tag{4.2}$$

where θ is the angle $(\mathbf{r}_1, \mathbf{r}_2)$. The truncated two-body density

$$\rho_{IT}^{(2)} = \rho_I^{(2)}(\mathbf{r}_1,\mathbf{r}_2) - \rho_I^{(1)}(\mathbf{r}_1)\rho_I^{(1)}(\mathbf{r}_2) \tag{4.3}$$

decays like a Gaussian for large values of r_2, and therefore the conditions of applicability of the sum rule are fulfilled. The excess charge density carried by particle 1 is, at $\mathbf{r}_2$,

$$c(\mathbf{r}_2 \mid \mathbf{r}_1) = e\left[\delta(\mathbf{r}_2 - \mathbf{r}_1) + \frac{\rho_{IT}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)}{\rho_I^{(1)}(r_1)}\right] \tag{4.4}$$

The sum rule states that the two-dimensional 2^n-pole moment of $c(\mathbf{r}_2 \mid \mathbf{r}_1)$ should vanish:

$$\int_0^\infty dr_2\, r_2 \int_0^{2\pi} d\theta\, r_2^n \cos(n\theta)\, c(\mathbf{r}_2 \mid \mathbf{r}_1) = 0 \tag{4.5}$$

That (4.5) is satisfied for all non-negative integer values of n can indeed be checked by a rather straightforward calculation of the integral.

Along a hard wall, as discussed in I, the pair correlation decays only like r^{-2} in two dimensions, and the conditions of applicability of the sum rule are not fulfilled. As discussed in I, only the monopole moment (i.e., the total excess charge) vanishes.

4.2. Hard Wall with Zero Dielectric Constant

In presence of a flat hard wall with zero dielectric constant, the sum rule discussed in Section 4.1 must be modified. The electrostatic potential at any point in the fluid is due to both the real charges and their images. Let us consider a particle at (x, y) and let us choose the origin at the intersection of the wall and of the normal to it drawn through the particle; the coordinates of the particle are now $(x, 0)$. The screening cloud is invariant under rotations around the x axis. Furthermore, since each charge has an image of the same magnitude and sign, the total excess charge plus its image is symmetrical with respect to the plane of the wall $x = 0$. Therefore, with respect to the origin, the odd electrical moments of the real excess charge are canceled by their images and they do not contribute to the electrostatic field created in the fluid. The argument of Section 4.1 now applies only to the even moments. The sum rule becomes the following:

If the two-point correlation functions decay faster than any inverse-power law in any direction, the real total excess charge carried by a particle is zero and has no *even* electrical moment of any order with respect to the projection of the particle on the wall.

As discussed in Section 2, it is likely that the condition that the pair correlation decays faster than any inverse-power law is indeed always fulfilled near a wall of zero dielectric constant.

The sum rule can be tested on the two-dimensional one-component plasma at $\Gamma = 2$. In Section 3.2, the pair correlation function was shown to decay exponentially along the wall, and faster in any other direction. The sum rule should be applicable; the densities (3.2) and (3.5) should obey the relation

$$\int_0^\infty dx' \int_{-\infty}^\infty dy' (x' + iy')^{2n} \rho_T^{(2)}(x, x', |y'|) = -x^{2n} \rho^{(1)}(x, 0) \qquad (4.6)$$

for all non-negative integer values of n. Showing that (4.6) is actually satisfied involves some algebra which is described in Appendix B.

4.3. The Dipole Moment Sum Rule

Blum *et al.*[8] have derived a sum rule which relates the dipole moment of the total excess charge carried by a particle of species α to the derivative of the density of that species with respect to the wall surface charge density. For a one-component plasma in two dimensions, this sum rule becomes, in our notation,

$$\frac{\partial \rho^{(1)}(x)}{\partial \sigma} = -2\pi\beta \frac{e^2}{\epsilon} \int_0^\infty dx' \int_{-\infty}^\infty dy' (x' - x) \rho_T^{(2)}(x, x', |y'|) \qquad (4.7)$$

This sum rule has been tested[8,13] on the two-dimensional one-component plasma at $\Gamma = \beta e^2/\epsilon = 2$, in the case $\epsilon_W = \epsilon$. It can also be tested when $\epsilon_W = 0$, after some algebra, by using (3.2) and (B1).

5. SURFACE STRUCTURE AND BULK PRESSURE

The structure of a fluid near a wall determines the force it exerts on that wall, and therefore this structure must be related to the pressure. In the simplest case of a system of charged hard spheres in a medium of dielectric constant ϵ, near a uniformly charged plane hard wall with no image forces, Henderson *et al.*[14,15] obtained the contact value theorem, which reads, for a ν-dimensional system ($\nu = 2, 3$),

$$p = k_B T \sum_\alpha \rho_\alpha(0) - (\nu - 1)\pi \frac{e^2}{\epsilon}\sigma^2 \qquad (\nu = 2, 3) \tag{5.1}$$

where p is the bulk pressure, $\rho_\alpha(0)$ the number density of species α at the plane of closest approach to the wall, and $-e\sigma$ the surface charge density on the wall.

The case where there are image forces was considered by Carnie and Chan.[16] They showed one must add to (5.1) a contribution from the image forces, which involves the two-body densities.

The case where there is a uniformly charged background was considered by Choquard *et al.*[17] and Totsuji[18]: There are several nonequivalent possible definitions of the pressure[17,19]: Here, p is the bulk "thermal" pressure, i.e., $-p$ is the derivative of the free energy of an overall neutral system with respect to the volume; both the particles and the background are supposed to be subject to the volume change. One must then add to (5.1) a contribution involving the background density and the potential difference across the surface layer.

The case where both image forces and a charged background are present can be dealt with by a straightforward addition of the above-mentioned contributions. For a one-component plasma, in a medium of dielectric constant ϵ, and in presence of a hard wall of dielectric constant ϵ_W, we find, for a ν-dimensional system ($\nu = 2, 3$) of point charges in a background,

$$p = k_B T \rho^{(1)}(0) - (\nu - 1)\pi \frac{e^2}{\epsilon}\sigma^2 - 2(\nu - 1)\pi \frac{e^2}{\epsilon}\rho \int_0^\infty dx\, x\left[\rho^{(1)}(x) - \rho\right]$$
$$- \left(\frac{\epsilon_W - \epsilon}{\epsilon_W + \epsilon}\right)\frac{e^2}{\epsilon}\int_0^\infty dx\left[\frac{\rho^{(1)}(x)}{(2x)^{\nu-1}} + \int_0^\infty dx' \int dy' \frac{\rho_T^{(2)}(x, x', |\mathbf{y}'|)(x + x')}{\left[(x + x')^2 + y'^2\right]^{\nu/2}}\right] \tag{5.2}$$

to avoid divergences, when the image force is attractive, one may replace the point charges by hard spheres of diameter d. In the right-hand side of (5.2) the third term is the contribution from the background and the last term is the contribution from the image forces.

Equation (5.2) can be tested on the two-dimensional one-component plasma for $\Gamma = e^2/(\epsilon k_B T) = 2$ and $\epsilon_W = \epsilon$ or 0. For $\epsilon_W = \epsilon = 1$, (5.2) is equivalent to (I.3.32). For $\epsilon_W = 0$, using (3.2), (B1), and the equation of state[20]

$$p = \rho\left(k_B T - \frac{e^2}{4\epsilon}\right) \tag{5.3}$$

we can also check (5.2) after some algebra (in that case, $\rho^{(1)}(0)$ vanishes).

6. CONCLUSION

The main point of the present paper is the new sum rule of Section 2, which must be obeyed by the asymptotic form of the charge–charge correlation function along a hard wall. Algebraically decaying correlations are present for general values of the wall dielectric constant. There are two special cases. If the wall has zero dielectric constant, it is likely that the correlations decay faster than any inverse-power law. What happens if the wall is a perfect conductor is an open problem.

The exact results which can be obtained for the two-dimensional one-component plasma provide a test for this new sum rule, as well as for other already known sum rules or their generalizations.

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APPENDIX A

We study the asymptotic behaviors of the densities (3.2) and (3.5).

As $x \to \infty$, the dominant contributions to the integral in (3.2) come from two domains of t around $\pm(x + \pi\sigma)\sqrt{2}$, and Φ in (3.3) can be replaced by 1 in one domain and by -1 in the other one. Therefore

$$\rho^{(1)}(x) \sim \frac{\rho}{\sqrt{\pi}} \int_{-\infty}^{\infty} dt \left\{ \exp\left[\left(t - x\sqrt{2} - \pi\sigma\sqrt{2}\right)^2\right] + \exp\left[-\left(t + x\sqrt{2} + \pi\sigma\sqrt{2}\right)^2\right]\right\} = \rho \tag{A1}$$

and it is easy to see that the correction to (A1) decreases like a Gaussian.

For studying the two-body density (3.5), one must investigate the one-body density (3.2) for complex values of the variable. Therefore, let us consider the function $\rho^{(1)}(X + iY)$.

If $X \to +\infty$ for a fixed value of Y, $\rho^{(1)}(X + iY) \to \rho$; this can be shown by the same argument as the one leading to (A1).

When both X and Y go to $+\infty$, the behavior of $\rho^{(1)}(X+iY)$ is found by reexpressing (3.2) in terms of integrals in the complex t plane. The only singularities of the integrand in (3.2) are poles coming from the zeros of $Q(t)$. One of these zeros is on the real axis at $t=0$. All the other zeros are complex, and are in general associated in groups of four of the form $t=\pm p \pm iq$ $(p,q>0)$, since $Q(t)$ is odd and $Q(t^*)=Q^*(t)$. Let q_0 be the smallest value of q; the corresponding zeros are at $t=\pm p_0 \pm iq_0$. Let C be the contour which runs from $-\infty$ to $+\infty$ along the real axis except in the vicinity of the origin where the contour skirts around the origin below it; obviously, the integration in (3.2) can be replaced by an integration along C, since the integrand is regular at the origin. Let C_+ be the contour which runs parallel to the real axis from $-\infty+is$ to $+\infty+is$, where s is some positive constant, and let C_- be the contour which runs parallel to the real axis from $-\infty-is$ to $+\infty-is$. Let us choose for s a value such that $0<s<q_0$. In (3.2), we split the sinh into its two exponential parts; for one of them we shift the integration contour from C to C_+ [the residue of the pole of $Q^{-1}(t)$ at $t=0$ must be taken into account], and for the other exponential part we shift the integration contour from C to C_-. We obtain

$$\rho^{(1)}(X+iY)=\exp\left[-2(X+iY+\pi\sigma)^2\right]$$
$$\times\left\{iA_0+\frac{\rho}{\sqrt{\pi}}\int_{C_+}\frac{dt\exp\left[-t^2+2(X+iY)t\sqrt{2}\right]}{Q(t)}\right.$$
$$\left.-\frac{\rho}{\sqrt{\pi}}\int_{C_-}\frac{dt\exp\left[-t^2-2(X+iY)t\sqrt{2}\right]}{Q(t)}\right\} \tag{A2}$$

where the (pure imaginary) constant iA_0 is the contribution from the pole at $t=0$.

From (A2), we can derive an upper bound for $|\rho^{(1)}(X+iY)|$. Let us first consider the case $\sigma \leqslant 0$. Then $|Q^{-1}(t)|$ remains finite along C_+ and C_-, including at infinity, and therefore it has an upper bound B; writing $t=u+is$, we obtain

$$\left|\int_{C_+}\frac{dt\exp\left[-t^2+2(X+iY)t\sqrt{2}\right]}{Q(t)}\right|$$
$$\leqslant B\int_{-\infty}^{\infty}du\exp\left[s^2-2sY\sqrt{2}-u^2+2Xu\sqrt{2}\right]$$
$$=B\sqrt{\pi}\exp(s^2-2sY\sqrt{2}+2X^2) \tag{A3}$$

A similar inequality holds for the integral along C_-. Replacing each term in (A2) by its modulus or an upper bound to it, we obtain

$$|\rho^{(1)}(X+iY)| \leqslant \exp(2Y^2 - 4\pi\sigma Y)\left[D\exp(-2X^2) + F\exp(-2sY\sqrt{2})\right] \quad (\sigma \leqslant 0) \quad \text{(A4)}$$

where D and F are positive constants independent of X and Y. In the case $\sigma > 0$, $Q(u \pm is) \to 0$ as $u \to \pm\infty$, and the argument needs a slight modification: in the integrands in (A2), the numerators and the denominators are to be multiplied by $\cosh 2\pi\sigma u\sqrt{2}$. Then $|Q(u+is)\cosh 2\pi\sigma u\sqrt{2}|^{-1}$ has an upper bound along C_+ and C_-, and one obtains by similar steps

$$|\rho^{(1)}(X+iY)| \leqslant \exp(2Y^2)\left[D'\exp(-2X^2) + F'\exp(-2sY\sqrt{2})\right] \quad (\sigma > 0) \quad \text{(A5)}$$

where D' and F' are again positive constants independent of X and Y.

Using (A4) or (A5) in (3.5), it is easy to see that $|\rho_T^{(2)}(x, x', |y'-y|)|$ decreases faster than $\exp[-(x'-x)^2]$ when both x' and $|y'-y|$ go to infinity.

Let us now study the behavior of $\rho^{(1)}(X+iY)$ when $Y \to +\infty$ for a fixed value of X. We can derive a formula analogous to (A2), including explicitly now also the contributions from the four complex poles which are closest to the real axis. For this purpose, the constant s which defines the distance to the real axis of the contours C_+ and C_- must now be chosen larger than q_0 (but small enough so that no other poles than $t = 0$ and $t = \pm p_0 \pm iq_0$ lie between C_+ and C_-). We now obtain instead of (A2)

$$\begin{aligned}\rho^{(1)}(X+iY) \sim &\exp\left[-2(X+iY+\pi\sigma)^2\right]\\ &\times\left\{iA_0 + iA_1\exp\left[2(X+iY)(p_0+iq_0)\sqrt{2}\right]\right.\\ &\left.+ iA_1^*\exp\left[2(X+iY)(-p_0+iq_0)\sqrt{2}\right] + \cdots\right\} \quad \text{(A6)}\end{aligned}$$

The dots in (A6) represent the contributions from the integrals on the contours C_+ and C_-; these contributions, as seen from (A3), contain a factor $\exp(-2sY\sqrt{2})$ which decreases faster than the factor $\exp(-2q_0Y\sqrt{2})$ which is present in (A6). Therefore (A6) is the asymptotic form of $\rho^{(1)}(X+iY)$ as $Y \to +\infty$.

Using (A6) in (3.5), one finds the asymptotic form (3.7), where $a = p_0\sqrt{2}$ and $b = q_0\sqrt{2}$. In the special case $\sigma = 0$, $Q(t)$ reduces to twice the error function $\Phi(t)$, the complex zeros of which are tabulated[12]; the residues of $\exp(-t^2)\Phi^{-1}(t)$ are all equal to $\sqrt{\pi}/2$, and one obtains the special values listed after Eq. (3.7).

APPENDIX B

We show that (3.2) and (3.5) obey (4.6).

Using the integral representation (3.2) in (3.5), we find, after some rearrangements,

$$\rho_T^{(2)}(x, x', |y'|) = -\rho^2 \frac{8}{\pi} \exp\left[-2(x+\pi\sigma)^2 - 2(x'+\pi\sigma)^2\right] \int_{-\infty}^{\infty} \frac{dt\, \exp(-t^2)}{Q(t)}$$
$$\times \int_{-\infty}^{\infty} \frac{du\, \exp(-u^2)}{Q(u)} \sinh\left[x(t+u)\sqrt{2}\right]$$
$$\times \sinh\left[x'(t+u)\sqrt{2}\right] \exp\left[iy'(u-t)\sqrt{2}\right] \tag{B1}$$

We want to compute

$$P_{2n} = \int_0^{\infty} dx' \int_{-\infty}^{\infty} dy' (x'+iy')^{2n} \rho_T^{(2)}(x, x', |y'|) \tag{B2}$$

If we use the representation (B1), its symmetries allow to replace $(x'+iy')^2$ in (B2) by $(1/2)d^2/du^2$. Furthermore, for integrating upon x', we can use (3.3) where ζ has to be renamed $x'\sqrt{2}$ and t has to be replaced by $(t+u)/2$. One obtains

$$P_{2n} = -\rho^2 2^{1-n}\sqrt{\pi} \exp\left[-2(x+\pi\sigma)^2\right] \int_{-\infty}^{\infty} \frac{dt\, \exp(-t^2)}{Q(t)} \int_{-\infty}^{\infty} \frac{du\, \exp(-u^2)}{Q(u)}$$
$$\times \sinh\left[x(t+u)\sqrt{2}\right] \frac{d^{2n}}{du^{2n}} \left\{ \exp\left[\left(\frac{t+u}{2}\right)^2\right] Q\left(\frac{t+u}{2}\right) \delta(u-t) \right\} \tag{B3}$$

and, by integration by parts,

$$P_{2n} = -\rho^2 2^{1-n}\sqrt{\pi} \exp\left[-2(x+\pi\sigma)^2\right]$$
$$\times \int_{-\infty}^{\infty} dt \left[\frac{d^{2n}}{du^{2n}} \left\{ \frac{\exp(-u^2)}{Q(u)} \sinh\left[x(t+u)\sqrt{2}\right] \right\} \right]_{u=t} \tag{B4}$$

The derivative in (B4) can be written as

$$\left\{\left(\frac{d}{du}+\frac{1}{2}\frac{d}{dt}\right)^{2n}\left[\frac{\exp(-u^2)}{Q(u)}\sinh 2xt\sqrt{2}\right]\right\}_{u=t}$$

$$= \frac{\exp(-t^2)}{Q(t)}\left(\frac{1}{2}\frac{d}{dt}\right)^{2n}\sinh 2xt\sqrt{2}$$

$$+\left\{\left[\left(\frac{d}{du}+\frac{1}{2}\frac{d}{dt}\right)^{2n}-\left(\frac{1}{2}\frac{d}{dt}\right)^{2n}\right]\left[\frac{\exp(-u^2)}{Q(u)}\sinh 2xt\sqrt{2}\right]\right\}_{u=t} \tag{B5}$$

In the curly bracket of (B5), we can factorize out

$$\left(\frac{d}{du}+\frac{1}{2}\frac{d}{dt}\right)+\frac{1}{2}\frac{d}{dt}=\frac{d}{du}+\frac{d}{dt}$$

and this bracket will be a sum of terms of the form

$$\left\{\left(\frac{d}{du}+\frac{d}{dt}\right)F(u)G(t)\right\}_{u=t}=\frac{d}{dt}\left[F(t)G(t)\right]$$

where the functions F and G are such that $F(t)G(t)$ vanishes at infinity; therefore, these terms do not contribute to the integral in (B4). Only the first term of (B5) must be kept, and it gives

$$P_{2n} = -\rho^2 2\sqrt{\pi}\exp\left[-2(x+\pi\sigma)^2\right]x^{2n}\int_{-\infty}^{\infty}\frac{dt\exp(-t^2)\sinh 2xt\sqrt{2}}{Q(t)} \tag{B6}$$

Since $\rho\pi = 1$ in our units, (B2), (B6), and (3.2) result into (4.6).

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