Journal of Statistical Physics, Vol. 39, Nos. 3/4, 1985

Surface Correlations in a Quantum Mechanical One-Component Plasma

B. Jancovici[1]

Received November 8, 1984

The time-dependent pair correlation function of a quantum mechanical one-component plasma bounded by a plane hard wall is studied near that wall. Along the wall, this function has an algebraic asymptotic form: it decays only as the inverse cube (square) of the distance for a three (two)-dimensional system (the case of fermions at zero temperature is excluded from the present study). The amplitude of the asymptotic form obeys a universal sum rule. Similar results hold at the plane interface between two different one-component plasmas.

KEY WORDS: Coulomb systems; quantum mechanical one-component plasma; jellium; surface properties; correlations; sum rule.

1. INTRODUCTION

The static correlations between charged particles in classical Coulomb fluids have recently attracted renewed theoretical attention,[1-5] especially as far as surface properties are concerned. For classical Coulomb fluids confined in a half-space by a plane hard wall, it is now clear that the static charge correlations near the wall decay in general only as a power law in directions parallel to the wall; this is in contrast with the decay faster than any power law which occurs in the bulk fluid at least in all cases for which the answer is known. A variety of sum rules obeyed by the correlation functions have been derived both for bulk and semi-infinite fluids.

An extension of some of the above results to time-dependent and quantum effects in a one-component plasma (jellium) is feasible. In the bulk, the classical Stillinger–Lovett sum rules,[6] which give the zeroth and

[1] Laboratoire de Physique Théorique et Hautes Energies, Université de Paris-Sud, 91405 Orsay, France. (This laboratory is associated with the Centre National de la Recherche Scientifique).

0022-4715/85/0500-0427$04.50/0

second moment of the static pair correlation function, or equivalently the long-wavelength behavior of the structure factor,[7] have a time-dependent and quantum mechanical counterpart.[8,9] The present paper deals with the pair correlation function of a semi-infinite one-component plasma, for which the previously obtained classical results[3] will be extended to time-dependent and quantum mechanical phenomena. It will be shown that (except perhaps in the case of fermions at zero temperature) near the wall which confines the semi-infinite plasma, in directions parallel to that wall, the two-body correlation function still decays in general as a power law, i.e., as the inverse cube (square) of the distance, for a three (two)-dimensional system, that the amplitude of this asymptotic form oscillates in time with two characteristic frequencies, and that it obeys a sum rule.

Most of the static classical results are valid for plasmas with an arbitrary number of components. In dealing with time-dependent and quantum mechanical effects, only the one-component plasma will be considered. This is because the dynamical properties (which are not independent of the static properties for a quantum system) have a special feature for the one-component plasma: there is no viscous damping of the long-wavelength plasma oscillations; it will be seen that this absence of damping is an essential ingredient of the argument.

Our results are stated in Section 2. In the classical case, the asymptotic form of the static charge correlation function along a wall had been studied[3] by a linear response argument; this argument will be generalized to the present case in Section 3. An alternative and perhaps physically more transparent argument in terms of long-wavelength collective modes will be presented in Section 4. Another, related, problem, the form of the correlations at the interface between two one-component plasmas, will be treated in Section 5.

2. RESULTS

We consider a three-dimensional one-component plasma (it will be straightforward to adapt the results to the two-dimensional case; see the end of this section). This is a system of particles of charge e, mass m, and bulk number density n, embedded in a neutralizing uniform background of charge density $-en$; furthermore, the background is assumed to have a dielectric constant ε. Thus the interaction potential between two particles at a distance r from each other is $e^2/\varepsilon r$. The system is a semi-infinite one, confined to the half-space $x > 0$; we call $\mathbf{y}$ the coordinates normal to x. We assume the half-space $x < 0$ to be filled with a material described by a dielectric constant ε_W. In addition, the plane $x = 0$ may carry some fixed uniform surface charge density.

The system is in equilibrium; the inverse temperature is β. Let the microscopic charge density at the point $(x, \mathbf{y})$ be

$$C(x, \mathbf{y}) = e \sum_i \delta(x - x_i)\, \delta(\mathbf{y} - \mathbf{y}_i) - en \tag{2.1}$$

where $(x_i, \mathbf{y}_i)$ are the coordinates of particle i. The canonical average charge density is

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

although $c^{(1)}(x, \mathbf{y})$ vanishes far away from the wall, it may differ from zero near the wall. We also introduce a time-dependent microscopic charge density by the Heisenberg operator

$$C(x, \mathbf{y}; t) = \exp(iHt/\hbar)\, C(x, \mathbf{y}) \exp(-iHt/\hbar) \tag{2.3}$$

where H is the Hamiltonian and $\hbar$ is Planck's constant divided by 2π. The time-dependent charge correlation function is defined by

$$c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|; t) = \langle C(x, \mathbf{y}; t)\, C(x', \mathbf{y}'; 0) \rangle - c^{(1)}(x, \mathbf{y})\, c^{(1)}(x', \mathbf{y}') \tag{2.4}$$

its time Fourier transform is

$$c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|; \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t)\, c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|; t) \tag{2.5}$$

In the following, it will be argued that (except perhaps for fermions at zero temperature) near the wall $c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|; \omega)$ has an algebraic decay when $|\mathbf{y}' - \mathbf{y}|$ becomes large for fixed values of x and x'. More precisely,

$$c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|; \omega) \sim \frac{a(x, x'; \omega)}{|\mathbf{y}' - \mathbf{y}|^3}, \qquad \text{when } |\mathbf{y}' - \mathbf{y}| \to \infty \tag{2.6}$$

where $a(x, x'; \omega)$ is a function which has a fast decay as x or x' increases and which obeys the sum rule

$$\begin{aligned} &\int_0^{\infty} dx' \int_0^{\infty} dx\, a(x, x'; \omega) \\ &= \frac{1}{(4\pi)^2} \left\{ -(\varepsilon + \varepsilon_W)\, \hbar\omega_s \left[\frac{\delta(\omega - \omega_s)}{1 - \exp(-\beta\hbar\omega_s)} - \frac{\delta(\omega + \omega_s)}{1 - \exp(\beta\hbar\omega_s)} \right] \right. \\ &\quad \left. + \varepsilon\hbar\omega_p \left[\frac{\delta(\omega - \omega_p)}{1 - \exp(-\beta\hbar\omega_p)} - \frac{\delta(\omega + \omega_p)}{1 - \exp(\beta\hbar\omega_p)} \right] \right\} \end{aligned} \tag{2.7}$$

where ω_p and ω_s are the bulk and surface plasma frequencies:

$$\omega_p = \left(\frac{4\pi n e^2}{\varepsilon m}\right)^{1/2}, \qquad \omega_s = \left[\frac{4\pi n e^2}{(\varepsilon + \varepsilon_W)\, m}\right]^{1/2} \tag{2.8}$$

By integration upon ω, one gets the static result

$$c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|; t = 0) \sim \frac{f(x, x')}{|\mathbf{y}' - \mathbf{y}|^3}, \qquad \text{when } |\mathbf{y}' - \mathbf{y}| \to \infty \tag{2.9}$$

where

$$\int_0^\infty dx' \int_0^\infty dx\, f(x, x') = \frac{1}{(4\pi)^2}\left[-(\varepsilon + \varepsilon_W)\, \hbar\omega_s \operatorname{ctnh}(\beta\hbar\omega_s/2) + \varepsilon\hbar\omega_p \operatorname{ctnh}(\beta\hbar\omega_p/2)\right] \tag{2.10}$$

In the classical limit $\hbar \to 0$, one finds

$$\int_0^\infty dx' \int_0^\infty dx\, a(x, x'; \omega) = \frac{1}{(4\pi)^2 \beta}\{-(\varepsilon + \varepsilon_W)[\delta(\omega - \omega_s) + \delta(\omega + \omega_s)] + \varepsilon[\delta(\omega - \omega_p) + \delta(\omega + \omega_p)]\} \tag{2.11}$$

and one recovers[3]

$$\int_0^\infty dx' \int_0^\infty dx\, f(x, x') = -\frac{2\varepsilon_W}{(4\pi)^2 \beta} \tag{2.12}$$

For a two-dimensional one-component plasma, with an interaction potential $-(e^2/\varepsilon) \ln r$, one finds similar results; however, $|\mathbf{y}' - \mathbf{y}|^{-3}$ has to be replaced by $|\mathbf{y}' - \mathbf{y}|^{-2}$ in (2.6) and (2.9), the plasma frequencies (2.8) have a factor 2π instead of 4π, and $(4\pi)^{-2}$ must be replaced by $(2\pi)^{-2}$ in (2.7), (2.10), (2.11), and (2.12).

3. LINEAR RESPONSE DERIVATION

We derive the results in Section 2 by a time-dependent and quantum mechanical generalization of the static classical linear response argument of Ref. 3.

We introduce on the wall $x = 0$ an external surface charge density[2] of

[2] As usual, the actual physical quantity is the real part of the complex expression.

the form $\alpha \exp(i\mathbf{q}\cdot\mathbf{y} - i\omega t)$, where $\mathbf{q}$ is a two-dimensional vector parallel to the wall; this charge creates an electrostatic potential

$$\phi(x, \mathbf{y}; t) = \frac{4\pi\alpha}{(\varepsilon + \varepsilon_W)\, q} \exp(i\mathbf{q}\cdot\mathbf{y} - q\,|x| - i\omega t) \tag{3.1}$$

and therefore is coupled to the microscopic charge density (2.1) by the coupling Hamiltonian $\alpha V \exp(-i\omega t)$ with

$$V = \frac{4\pi}{(\varepsilon + \varepsilon_W)\, q} \int d\mathbf{y}' \int_0^\infty dx' \exp(i\mathbf{q}\cdot\mathbf{y}' - qx')\, C(x', \mathbf{y}') \tag{3.2}$$

We look at the linear response of the operator

$$A(\mathbf{y}) = \int_0^\infty C(x, \mathbf{y})\, dx \tag{3.3}$$

assuming that ω has a small positive imaginary part which ensures that the coupling is introduced adiabatically. To first order in α, the presence of the coupling Hamiltonian changes the average value[3] of $A(\mathbf{y})$ at time t by an amount

$$\delta A(\mathbf{y}; t) = \alpha\chi(q; \omega) \exp(i\mathbf{q}\cdot\mathbf{y} - i\omega t) \tag{3.4}$$

The response function $\chi(q; \omega)$ is related by the fluctuation-dissipation theorem[(10)] to the correlation between A and V computed for the non-coupled system ($\alpha = 0$):

$$\begin{aligned}
&\frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(-i\mathbf{q}\cdot\mathbf{y} + i\omega t)[\langle A(\mathbf{y}; t)\, V\rangle - \langle A(\mathbf{y})\rangle\langle V\rangle] \\
&\quad = -\frac{\hbar}{\pi} \frac{1}{1 - \exp(-\beta\hbar\omega)} \operatorname{Im} \chi(q; \omega)
\end{aligned} \tag{3.5}$$

We now use (3.5) in the long-wavelength limit $q \to 0$ where we know $\chi(q; \omega)$. In this limit, indeed, the response is given by macroscopic considerations. The external surface charge density induces in the plasma a charge density localized near the surface, and, in the macroscopic limit $q \to 0$, $\delta A(\mathbf{y}; t)$ can be viewed as an induced surface charge density; thus the total surface charge density is $(1 + \chi)\, \alpha \exp(i\mathbf{q}\cdot\mathbf{y} - i\omega t)$. Correspondingly, the total potential is

$$\phi_{\text{tot}} = (1 + \chi) \frac{4\pi\alpha}{(\varepsilon + \varepsilon_W)\, q} \exp(i\mathbf{q}\cdot\mathbf{y} - q\,|x| - i\omega t) \tag{3.6}$$

[3] If the wall also carries a fixed uniform surface charge density $-\sigma_0$, it is screened by $A(\mathbf{y})$. When $\alpha = 0$, $\langle A(\mathbf{y})\rangle = \sigma_0$.

The current density induced by that potential is

$$\mathbf{j} = -i\frac{ne^2}{m\omega}\nabla\phi_{\text{tot}} \tag{3.7}$$

On the wall $x=0$, j_x and δA are related by the charge conservation equation

$$i\omega\,\delta A = j_x\,|_{x=0} \tag{3.8}$$

Combining these equations, we obtain

$$\chi = \frac{\omega_s^2}{\omega^2 - \omega_s^2} \tag{3.9}$$

where ω_s is defined by (2.8); ω_s is indeed the resonance frequency of surface waves, the surface plasmons.

Since ω has a small positive imaginary part,

$$\operatorname{Im}\chi = -\frac{\pi\omega_s}{2}\left[\delta(\omega-\omega_s) - \delta(\omega+\omega_s)\right] \tag{3.10}$$

Using (3.10) in (3.5), we find

$$\int d\mathbf{y}'\exp(i\mathbf{q}\cdot(\mathbf{y}'-\mathbf{y}))\int_0^\infty dx'\exp(-qx')\int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}'-\mathbf{y}|;\omega)$$
$$\sim \frac{\varepsilon+\varepsilon_W}{8\pi}\hbar\omega_s\left[\frac{\delta(\omega-\omega_s)}{1-\exp(-\beta\hbar\omega_s)} - \frac{\delta(\omega+\omega_s)}{1-\exp(\beta\hbar\omega_s)}\right]q, \qquad \text{when } q\to 0 \tag{3.11}$$

Equation (3.11) is a sum rule which might be of some interest by itself. However, it is also possible to transform it into another form which no longer contains the factor $\exp(-qx')$. For this purpose, we use the known long-wavelength form of the bulk structure factor,[8] which can be written as

$$\lim_{x'\to\infty}\int d\mathbf{y}'\exp[i\mathbf{q}\cdot(\mathbf{y}'-\mathbf{y})]\int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}'-\mathbf{y}|;\omega)$$
$$\sim \frac{\varepsilon}{8\pi}\hbar\omega_p\left[\frac{\delta(\omega-\omega_p)}{1-\exp(-\beta\hbar\omega_p)} - \frac{\delta(\omega+\omega_p)}{1-\exp(\beta\hbar\omega_p)}\right]q^2, \qquad \text{when } q\to 0 \tag{3.12}$$

where ω_p is the bulk plasma frequency defined by (2.8). Multiplying both sides of (3.12) by $\int_0^\infty \exp(-qx')\,dx' = 1/q$ and substracting it from (3.11), we obtain

$$\int d\mathbf{y}' \exp[i\mathbf{q}\cdot(\mathbf{y}'-\mathbf{y})] \int_0^\infty dx' \exp(-qx') \left[\int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}'-\mathbf{y}|; \omega) - \lim_{x'\to\infty} \int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}'-\mathbf{y}|; \omega)\right]$$
$$\sim \left\{\frac{\varepsilon+\varepsilon_W}{8\pi}\hbar\omega_s \left[\frac{\delta(\omega-\omega_s)}{1-\exp(-\beta\hbar\omega_s)} - \frac{\delta(\omega+\omega_s)}{1-\exp(\beta\hbar\omega_s)}\right] - \frac{\varepsilon}{8\pi}\hbar\omega_p \left[\frac{\delta(\omega-\omega_p)}{1-\exp(-\beta\hbar\omega_p)} - \frac{\delta(\omega+\omega_p)}{1-\exp(\beta\hbar\omega_p)}\right]\right\} q, \quad \text{when } q\to 0 \tag{3.13}$$

Finally, since the last square bracket in the left-hand side of (3.13) goes rapidly to zero as x' increases, in the small-q limit we can erase the factor $\exp(-qx')$. Thus, the left-hand side of (3.13) is just a two-dimensional Fourier transform with respect to $\mathbf{y}'-\mathbf{y}$, and (3.13) states that it behaves like $|\mathbf{q}|$ for small q. Since the inverse Fourier transform[12] of $|\mathbf{q}|$ is $-1/2\pi\,|\mathbf{y}'-\mathbf{y}|^3$, *if* the left-hand side of (3.13) has no other singularity on the q real axis one obtains

$$\int_0^\infty dx' \left[\int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}'-\mathbf{y}|; \omega) - \lim_{x'\to\infty} \int_0^\infty dx\, c_T^{(2)}(x, x', |\mathbf{y}'-\mathbf{y}|; \omega)\right]$$
$$\sim \frac{1}{(4\pi)^2}\left\{-(\varepsilon+\varepsilon_W)\hbar\omega_s \left[\frac{\delta(\omega-\omega_s)}{1-\exp(-\beta\hbar\omega_s)} - \frac{\delta(\omega+\omega_s)}{1-\exp(\beta\hbar\omega_s)}\right] + \varepsilon\hbar\omega_p \left[\frac{\delta(\omega-\omega_p)}{1-\exp(-\beta\hbar\omega_p)} - \frac{\delta(\omega+\omega_p)}{1-\exp(\beta\hbar\omega_p)}\right]\right\} \frac{1}{|\mathbf{y}'-\mathbf{y}|^3},$$
$$\text{when } |\mathbf{y}'-\mathbf{y}| \to \infty \tag{3.14}$$

Assuming that no subtle cancellations occur when the asymptotic form of $c_T^{(2)}(x, x', |\mathbf{y}'-\mathbf{y}|; \omega)$ is integrated upon x and x', we infer from (3.14) that this asymptotic form is (2.6). Assuming also that the bulk term in the left-hand side of (3.14) has a faster decay, and does not contribute to the asymptotic form, we can rewrite (3.14) as the sum rule (2.7).

It should be noted that (3.11) and (3.13) remain valid in the zero-temperature limit. Actually, by integrating (3.13) [with the factor $\exp(-qx')$ erased] upon ω, one recovers at zero temperature an equation previously derived by Langreth and Perdew.[13] However, at zero temperature, for fermions, one expects some singularity related to the existence of a sharp Fermi surface. For instance, one knows that the bulk static response function $\chi(q, 0)$ is singular at $q = 2f$ (where f is the Fermi wave number); this singularity gives rise to the well-known Friedel oscillations.[14] In our surface problem, we may also expect singularities for other values of q than $q = 0$, and therefore the asymptotic behavior of $c_T^{(2)}(x, x', |\mathbf{y}' - \mathbf{y}|; \omega)$ might be not as simple as (2.6). This is why we exclude the case of fermions at zero temperature.

Finally, let us note that the simple form (3.9) for the response function in the limit $q \to 0$ is valid for a one-component plasma but not for a many-component one. For a many-component plasma, the different components will not oscillate in phase with one another, and the oscillation will be damped by the mutual friction of the different components. The resonance at ω_s (and the one at ω_p for the bulk plasmons) will be both broadened and displaced in a nonuniversal way, and the simple equation (2.7) will no longer be valid.

4. COLLECTIVE MODE FLUCTUATIONS

We now present an alternative argument, which is essentially equivalent to the previous one, but instead of using the linear response approach, we directly look at the fluctuations of the collective modes. The behavior of the correlations is governed by the long-wavelength collective modes, which can be studied macroscopically. The correlations near the wall will be ascribed to those modes which involve the surface density. Indeed, from a macroscopic point of view, the total charge at time t can be separated into a volume charge density $\rho(x, \mathbf{y}; t)$ and a surface charge density $\sigma(\mathbf{y}; t)$; the microscopic charge density (2.1) can be replaced by an expression of the form $\rho(x, \mathbf{y}; t) + \delta(x)\, \sigma(\mathbf{y}; t)$, which can in turn be expanded as a superposition of collective modes. These modes are of two different types: surface plasmons and volume plasmons. We shall first describe them classically, and quantize then afterwards.

4.1. Surface Plasmons

A surface plasmon is defined as a mode for which the volume charge density ρ vanishes. There is only a surface charge density, which we choose of the form

$$\sigma(\mathbf{y}; t) = \sigma_{\mathbf{q}}(t) \exp(i\mathbf{q} \cdot \mathbf{y}) + \sigma_{-\mathbf{q}}(t) \exp(-i\mathbf{q} \cdot \mathbf{y}) \tag{4.1}$$

Reality requires $\sigma_{-\mathbf{q}} = \sigma_{\mathbf{q}}^*$. This surface charge density creates a potential

$$\phi(x, \mathbf{y}; t) = \sigma(\mathbf{y}; t) \frac{4\pi}{(\varepsilon + \varepsilon_W) q} \exp(-q|x|) \tag{4.2}$$

which induces a current density $\mathbf{j}(x, \mathbf{y}; t)$ obeying

$$\frac{\partial \mathbf{j}}{\partial t} = -\frac{e^2 n}{m} \nabla \phi \tag{4.3}$$

charge conservation on the plane $x = 0$ requires

$$\frac{\partial \sigma}{\partial t} + j_x(0, \mathbf{y}; t) = 0 \tag{4.4}$$

Combining these equations, we easily find that the motion of $\sigma_{\mathbf{q}}(t)$ is described by a harmonic oscillator Hamiltonian

$$H_{\mathbf{q}} = A \frac{4\pi}{(\varepsilon + \varepsilon_W) q} \left[\frac{1}{\omega_s^2} |\dot{\sigma}_{\mathbf{q}}|^2 + |\sigma_{\mathbf{q}}|^2 \right] \tag{4.5}$$

where A is the area of the wall, and the frequency ω_s is given by (2.8).

4.2. Volume Plasmons in a Half-Space

We now consider the volume plasmons, which are the modes for which the volume charge density ρ does not vanish. Combining Poisson's equation

$$\Delta \phi = -(4\pi/\varepsilon) \rho \tag{4.6}$$

with current conservation

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \mathbf{j} = 0 \tag{4.7}$$

and the mechanical equation (4.3), we find that ρ obeys an harmonic oscillator equation with the bulk plasma frequency ω_p given by (2.8). For the present half-space problem, there is an important additional feature: a surface charge density σ must appear on the wall $x = 0$, in order that (4.4) be satisfied. From (4.3) and (4.4), which are also valid for the present mode, we find

$$-\varepsilon \left. \frac{\partial \phi}{\partial x} \right|_{x=0^+} = 4\pi\sigma \tag{4.8}$$

Since $-\varepsilon\partial\phi/\partial x$ has to jump by $4\pi\sigma$ across the plane $x=0$, it vanishes for $x=0^-$, and we can choose $\phi=0$ for $x<0$.

Thus we look for a volume charge density of the form

$$\rho(x, \mathbf{y}; t) = [\rho_{\mathbf{q}k}(t)\exp(i\mathbf{q}\cdot\mathbf{y}) + \rho_{-\mathbf{q}k}(t)\exp(-i\mathbf{q}\cdot\mathbf{y})]\sin kx \tag{4.9}$$

(where $\rho_{-\mathbf{q}k} = \rho_{\mathbf{q}k}^*$) to which is associated a potential

$$\phi = \frac{4\pi}{\varepsilon(q^2+k^2)}\rho \tag{4.10}$$

obeying (4.6) and a surface charge density

$$\sigma(\mathbf{y}; t) = -\frac{k}{q^2+k^2}[\rho_{\mathbf{q}k}(t)\exp(i\mathbf{q}\cdot\mathbf{y}) + \rho_{-\mathbf{q}k}(t)\exp(-i\mathbf{q}\cdot\mathbf{y})] \tag{4.11}$$

obeying (4.8). All these quantities oscillate at the frequency ω_p, and their motion is found to be decribed by the harmonic oscillator Hamiltonian

$$H_{\mathbf{q}k} = AL\frac{2\pi}{\varepsilon(q^2+k^2)}\left[\frac{1}{\omega_p^2}|\dot{\rho}_{\mathbf{q}k}|^2 + |\rho_{\mathbf{q}k}|^2\right] \tag{4.12}$$

where A is again the area of the wall and L the length of the system in the x direction.

4.3. Thermal Averages

It is easy to show that the surface and volume waves are independent from one another for different values of the wave vectors (except for the fact that a given wave involves both $\mathbf{q}$ and $-\mathbf{q}$), i.e., that for a superposition of waves the total Hamiltonian is just a sum of terms of the forms (4.5) and (4.12). Each wave behaves like a *two-dimensional* independent harmonic oscillator (the oscillator is two-dimensional because $\sigma_\mathbf{q}$ and $\rho_{\mathbf{q}k}$ are complex quantities, the real and imaginary parts of which are independent variables). These collective variables can be approximately considered as canonical "position" variables.[7] Quantizing them, we find the nonzero thermal averages to be

$$\langle\sigma_\mathbf{q}(t)\,\sigma_\mathbf{q}^*(0)\rangle = \frac{1}{A}\frac{(\varepsilon+\varepsilon_W)\,q}{8\pi}\hbar\omega_s\left[\frac{\exp(-i\omega_s t)}{1-\exp(-\beta\hbar\omega_s)} - \frac{\exp(i\omega_s t)}{1-\exp(\beta\hbar\omega_s)}\right] \tag{4.13}$$

and

$$\langle\rho_{\mathbf{q}k}(t)\,\rho_{\mathbf{q}k}^*(0)\rangle = \frac{1}{AL}\frac{\varepsilon(q^2+k^2)}{4\pi}\hbar\omega_p\left[\frac{\exp(-i\omega_p t)}{1-\exp(-\beta\hbar\omega_p)} - \frac{\exp(i\omega_p t)}{1-\exp(\beta\hbar\omega_p)}\right] \tag{4.14}$$

4.4. Charge Correlations

An arbitrary charge fluctuation can be expanded on the basis of the surface[4] and volume modes:

$$\rho(x, \mathbf{y}; t) = \sum_{\mathbf{q}k} \rho_{\mathbf{q}k}(t) \exp(i\mathbf{q}\cdot\mathbf{y}) \sin kx \tag{4.15}$$

$$\delta\sigma(\mathbf{q}; t) = \sum_{\mathbf{q}} \left[\sigma_{\mathbf{q}}(t) - \sum_{k} \frac{k}{q^2+k^2} \rho_{\mathbf{q}k}(t) \right] \exp(i\mathbf{q}\cdot\mathbf{y}) \tag{4.16}$$

The sums upon $\mathbf{q}$ and k in (4.15) and (4.16) can be replaced in the usual way by $A \int d\mathbf{q}/(2\pi)^2$ and $L \int_0^\infty dk/\pi$. Using the independence of the different modes, we find the correlation functions

$$\langle \rho(x, \mathbf{y}; t)\, \rho(x, \mathbf{y}; 0) \rangle = AL \int \frac{d\mathbf{q}}{(2\pi)^2} \int_0^\infty \frac{dk}{\pi} \exp[i\mathbf{q}\cdot(\mathbf{y}-\mathbf{y}')]$$
$$\times \sin kx \sin kx' \langle \rho_{\mathbf{q}k}(t)\, \rho^*_{\mathbf{q}k}(0) \rangle \tag{4.17}$$

$$\langle \rho(x, \mathbf{y}; t)\, \delta\sigma(\mathbf{y}'; 0) \rangle = -AL \int \frac{d\mathbf{q}}{(2\pi)^2} \int_0^\infty \frac{dk}{\pi} \exp[i\mathbf{q}\cdot(\mathbf{y}-\mathbf{y}')]$$
$$\times \sin kx \frac{k}{q^2+k^2} \langle \rho_{\mathbf{q}k}(t)\, \rho^*_{\mathbf{q}k}(0) \rangle \tag{4.18}$$

$$\langle \delta\sigma(\mathbf{y}; t)\, \delta\sigma(\mathbf{y}'; 0) \rangle = A \int \frac{d\mathbf{q}}{(2\pi)^2} \exp[i\mathbf{q}\cdot(\mathbf{y}-\mathbf{y}')] \Bigg\{ \langle \sigma_{\mathbf{q}}(t)\, \sigma^*_{\mathbf{q}}(0) \rangle$$
$$+ L \int_0^\infty \frac{dk}{\pi} \frac{k^2}{(q^2+k^2)^2} \langle \rho_{qk}(t)\, \rho^*_{qk}(0) \rangle \Bigg\} \tag{4.19}$$

where $\langle \rho_{\mathbf{q}k}(t)\, \rho^*_{\mathbf{q}k}(0) \rangle$ and $\langle \sigma_{\mathbf{q}}(t)\, \sigma^*_{\mathbf{q}}(0) \rangle$ are given by (4.14) and (4.13) for *small* values of q and k (what happens for larger values of q and k cannot be inferred from the present macroscopic analysis, but we expect that we can account for it by assuming that these correlation functions as functions of q and k decay fast enough for making the integrals convergent at infinity, or equivalently that we can introduce some upper cutoffs in q and k at some inverse microscopic length). Thus, the correlation functions (4.17), (4.18), (4.19) appear as Fourier transforms and their behavior at

[4] We use the notation $\delta\sigma$ rather than σ for the surface charge density *fluctuation* for emphasizing that $\sigma = \delta\sigma + \sigma_0$ has a static part σ_0 if the wall carries a static external charge $-\sigma_0$.

large separations is governed by the behavior at the origin in wave-number space (we exclude the case of fermions at zero temperature).

In the volume correlations (4.17) and the volume–surface correlations (4.18), the integrands are regular at the origin, and these correlation functions will have a faster than algebraic decay as $(x, \mathbf{y})$ recedes in any direction. Furthermore, one can check that (4.17) goes to the correct bulk form far away from the wall. Indeed, since

$$\sin kx \sin kx' = \tfrac{1}{2}[\cos k(x'-x) - \cos k(x'+x)] \tag{4.20}$$

and since the contribution from $\cos k(x'+x)$ goes to zero as $x'+x \to \infty$ (a general property of Fourier transforms), using the symmetries one is left with

$$\langle \rho(x, \mathbf{y}; t)\, \rho(x', \mathbf{y}'; 0)\rangle \sim \int \frac{d\mathbf{q}\, dk}{(2\pi)^3} \times \exp[i\mathbf{q}\cdot(\mathbf{y}-\mathbf{y}') + ik(x-x')]\, S((q^2+k^2)^{1/2}; t) \quad 2(4.21)$$

where the bulk time-dependent structure factor

$$S((q^2+k^2)^{1/2}; t) = \tfrac{1}{2}AL\langle \rho_{\mathbf{q}k}(t)\, \rho^*_{\mathbf{q}k}(0)\rangle \tag{4.22}$$

has from (4.14) the known[8] small wave-number behavior equivalent to (3.12); in the static classical limit $t=0$, $\hbar=0$, (4.22) takes the perhaps more familiar form

$$S((q^2+k^2)^{1/2}) = \frac{\varepsilon}{4\pi\beta}(q^2+k^2) \tag{4.23}$$

which is equivalent to the Stillinger–Lovett rules.[6]

In the surface correlations (4.19), however, the integrand is singular at $q=0$. On one hand, $\langle \sigma_{\mathbf{q}}(t)\, \sigma^*_{\mathbf{q}}(0)\rangle$ behaves like $|\mathbf{q}|$, from (4.13). On the other hand, the integral upon k also is singular like $|\mathbf{q}|$: using (4.14) in (4.19), and introducing some upper cutoff K, one has to compute

$$\int_0^K dk \frac{k^2}{q^2+k^2} = K - \frac{\pi}{2}q + O(q^2) \tag{4.24}$$

Altogether, (4.19) is of the form

$$\langle \delta\sigma(\mathbf{y}; t)\, \delta\sigma(\mathbf{y}'; 0)\rangle = \int \frac{d\mathbf{q}}{(2\pi)^2} \exp[i\mathbf{q}\cdot(\mathbf{y}-\mathbf{y}')]\, s(q; t) \tag{4.25}$$

where, for small q, $s(q; t)$ has a cusplike singularity

$$\left\{\frac{\varepsilon+\varepsilon_W}{8\pi}\hbar\omega_s\left[\frac{\exp(-i\omega_s t)}{1-\exp(-\beta\hbar\omega_s)}-\frac{\exp(i\omega_s t)}{1-\exp(\beta\hbar\omega_s)}\right]-\frac{\varepsilon}{8\pi}\hbar\omega_p\left[\frac{\exp(-i\omega_p t)}{1-\exp(-\beta\hbar\omega_p)}\right.\right.$$
$$\left.\left.-\frac{\exp(i\omega_p t)}{1-\exp(\beta\hbar\omega_p)}\right]\right\} q$$

The space and time Fourier transform of this gives the asymptotic behavior in space

$$\int \frac{dt}{2\pi}\exp(i\omega t)\langle\delta\sigma(\mathbf{y}; t)\,\delta\sigma(\mathbf{y}'; 0)\rangle$$
$$\sim\frac{1}{(4\pi)^2}\left\{-(\varepsilon+\varepsilon_W)\,\hbar\omega_s\left[\frac{\delta(\omega-\omega_s)}{1-\exp(-\beta\hbar\omega_s)}-\frac{\delta(\omega+\omega_s)}{1-\exp(\beta\hbar\omega_s)}\right]\right.$$
$$\left.+\varepsilon\hbar\omega_p\left[\frac{\delta(\omega-\omega_p)}{1-\exp(-\beta\hbar\omega_p)}-\frac{\delta(\omega+\omega_p)}{1-\exp(\beta\hbar\omega_p)}\right]\right\}\frac{1}{|\mathbf{y}'-\mathbf{y}|^3}$$
$$\text{when } |\mathbf{y}'-\mathbf{y}|\to\infty \qquad (4.26)$$

Coming back now to the microscopic point of view, in which only volume charge densities are defined (the distribution $\sigma\delta(x)$ is actually smeared on some microscopic distance in the x direction), we can interpret (4.26) [and the fast decay of (4.17) and (4.18)] by assuming that the correlation function (2.5) has a algebraically decaying part, *localized near the wall*, of the form (2.6). The macroscopic expression (4.26) must be identified with the integral upon x and x' of the microscopic expression (2.6), and therefore the sum rule (2.7) follows from (4.26).

It should be emphasized that the *volume* plasmons do contribute to the *surface* charge density fluctuations, and this is the physical reason for which the bulk plasma frequency ω_p appears in (2.7).

5. INTERFACE BETWEEN TWO ONE-COMPONENT PLASMAS

The above results and derivations can be easily extended to the plane interface between two one-component plasmas. The interface is chosen as the plane $x=0$. The region $x<0$ ($x>0$) is a one-component plasma made of particles of charge e_1 (e_2), mass m_1 (m_2), and bulk number density n_1 (n_2), embedded in a neutralizing background of charge density $-e_1 n_1$ ($-e_2 n_2$) and dielectric constant ε_1 (ε_2). The plane $x=0$ must be assumed impermeable to the particles if they are different on each side; it may be permeable or impermeable if the particles are identical on both sides.

In the bulk of each plasma, volume plasmons have the frequencies $\omega_1=(4\pi n_1 e_1^2/\varepsilon_1 m_1)^{1/2}$ and $\omega_2=(4\pi n_2 e_2^2/\varepsilon_2 m_2)^{1/2}$, respectively. Along the interface,[11] there are surface plasmons with a frequency

$$\omega_s=\left[\frac{4\pi}{\varepsilon_1+\varepsilon_2}\left(\frac{n_1 e_1^2}{m_1}+\frac{n_2 e_2^2}{m_2}\right)\right]^{1/2} \tag{5.1}$$

Instead of (3.11), one now finds the sum rule

$$\begin{aligned}&\int d\mathbf{y}' \exp[i\mathbf{q}\cdot(\mathbf{y}'-\mathbf{y})] \int_{-\infty}^{\infty} dx' \exp(-q\,|x'|) \int_{-\infty}^{\infty} dx\, c_T^{(2)}(x, x', |\mathbf{y}'-\mathbf{y}|; \omega)\\ &\sim \frac{\varepsilon_1+\varepsilon_2}{8\pi}\hbar\omega_s\left[\frac{\delta(\omega-\omega_s)}{1-\exp(-\beta\hbar\omega_s)}-\frac{\delta(\omega+\omega_s)}{1-\exp(\beta\hbar\omega_s)}\right]q, \quad \text{when } q\to 0\end{aligned} \tag{5.2}$$

Again, one can get rid of the factor $\exp(-q\,|x'|)$ by combining (5.2) with bulk terms. Except perhaps for fermions at zerc temperature, one finds again an algebraic asymptotic behavior of the form (2.6), where now, however,

$$\begin{aligned}&\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx'\, a(x, x'; \omega)\\ &= \frac{1}{(4\pi)^2}\left\{-(\varepsilon_1+\varepsilon_2)\,\hbar\omega_s\left[\frac{\delta(\omega-\omega_s)}{1-\exp(-\beta\hbar\omega_s)}-\frac{\delta(\omega+\omega_s)}{1-\exp(\beta\hbar\omega_s)}\right]\right.\\ &\quad+\varepsilon_1\hbar\omega_1\left[\frac{\delta(\omega-\omega_1)}{1-\exp(-\beta\hbar\omega_1)}-\frac{\delta(\omega+\omega_1)}{1-\exp(\beta\hbar\omega_1)}\right]\\ &\quad\left.+\varepsilon_2\hbar\omega_2\left[\frac{\delta(\omega-\omega_2)}{1-\exp(-\beta\hbar\omega_2)}-\frac{\delta(\omega+\omega_2)}{1-\exp(\beta\hbar\omega_2)}\right]\right\}\end{aligned} \tag{5.3}$$

Yet, in the classical limit $\hbar=0$,

$$\int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx'\, a(x, x'; \omega)=0 \tag{5.4}$$

This is in agreement with the conjecture that, for *classical* systems, the static correlation function $c_T^{(2)}(x, x', |\mathbf{y}'-\mathbf{y}|; t=0)$ has a faster than algebraic decay in every direction near the interface of two *conducting* media.[4,15,16] Apparently, at such an interface, the presence of conducting material everywhere makes the static screening of a given particle efficient enough for the screening cloud to have a fast decay; but the existence of several different resonance frequencies near the interface makes the dynamical screening less efficient, causing an algebraic spatial decay (for a quantum system, even the static screening is spoilt, because the dynamics and the statics cannot be separated).

CONCLUSION

The charge correlations along a wall or an interface have a rather general asymptotic behavior as the inverse cube (square) of the distance for a three (two)-dimensional system. The basic mechanism is that the spherical symmetry, which exists around a point charge in the bulk, is broken near a wall or interface, and a dipole moment appears. The inverse cube (square) law is essentially a dipole–dipole interaction.[17] The universal sum rule which has been obtained for large distances is a consequence of the validity of macroscopic electrostatics and hydrodynamics for large-scale phenomena in jellium.

ACKNOWLEDGMENTS

I thank W. Kohn for having brought Refs. 13 and 17 to my attention, and Ph. A. Martin for a critical reading of the manuscript.

REFERENCES

1. Ch. Gruber, J. L. Lebowitz, and Ph. A. Martin, *J. Chem. Phys.* **75**:944 (1981).
2. L. Blum, D. Henderson, J. L. Lebowitz, Ch. Gruber, and Ph. A. Martin, *J. Chem. Phys.* **75**:5974 (1981).
3. B. Jancovici, *J. Stat. Phys.* **29**:263 (1982).
4. B. Jancovici, *J. Stat. Phys.* **34**:803 (1984).
5. S. L. Carnie and D. Y. C. Chan, *Molec. Phys.* **51**:1047 (1984).
6. F. H. Stillinger and R. Lovett, *J. Chem. Phys.* **49**:1991 (1968).
7. D. Pines and D. Bohm, *Phys. Rev.* **85**:338 (1952).
8. D. Pines and Ph. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).
9. Ph. A. Martin and C. Oguey, *J. Phys. A*, to be published.
10. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Part 1 (Pergamon, Oxford, 1980).
11. E. A. Stern and R. A. Ferrell, *Phys. Rev.* **120**:130 (1960).
12. I. M. Gelfand and G. E. Shilov, *Generalized Functions* (Academic Press, New York, 1964).
13. D. C. Langreth and J. P. Perdew, *Phys. Rev. B* **15**:2884 (1977).
14. J. Friedel, *Philos. Mag.* **43**:153 (1952).
15. M. L. Rosinberg and L. Blum, *J. Chem. Phys.* **81**:3700 (1984).
16. P. J. Forrester, *J. Phys. A*, to be published.
17. W. Kohn and K. H. Lau, *Solid State Commun.* **18**:553 (1976).