Sum rules in charged fluids

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The screening effects in fluid phases of charged particles give rise to a variety of exact sum rules for their correlation functions. Some of them have been known for a long time, while others have been derived more recently—in particular, for nonuniform fluids. A presentation of these sum rules for static and time-displaced, classical or quantum-mechanical correlations is given from a unifying viewpoint: they appear as consistency relations imposed by the long range of the Coulomb force in the equilibrium or dynamical equations. The cluster properties and the fluctuations of electrical quantities are also discussed.

CONTENTS

I. INTRODUCTION

Some of the most significant properties of nonrelativistic ordinary matter are the local neutrality and the screening of the Coulomb force: a system in thermal equilibrium does not tolerate any charge inhomogeneity over more than a few intermolecular distances. As a consequence of this very basic fact, the static and the time-displaced correlations of charged particles in thermal equilibrium are subjected to specific constraints. These constraints, which we call sum rules, always express, in one way or another, screening and neutrality in the system. In this paper we review a number of such sum rules in various situations (bulk, inhomogeneous, time-dependent, and quantum-mechanical correlations), as well as their relations to cluster properties and fluctuations in charged fluids. Before entering into a detailed description, it is worth exhibiting some typical features of static screening with the help of simple physical arguments.

A. Debye-Hückel theory

To begin with old and familiar ideas on the subject we recall the reasoning that Debye and Hückel presented in 1923 (Debye and Hückel, 1923). One considers a mixture of s species of positive and negative point ions with charges e_α, $\alpha=1,2,\ldots,s$. The electric potential $\phi(\mathbf{r})$ in the vicinity of an ion of type α fixed at the origin is determined by the Poisson equation

$$\begin{aligned}&\Delta\phi(\mathbf{r})=-4\pi c(\mathbf{r}), \quad \mathbf{r}\neq\mathbf{0}\ ,\\ &c(\mathbf{r})=\sum_{\gamma=1}^{s} e_\gamma n(\gamma,\mathbf{r})\ ,\end{aligned} \tag{1.1}$$

where $n(\gamma,\mathbf{r})$ is the density of particles of type γ at $\mathbf{r}$ when a charge e_α is present at $\mathbf{r}=0$, and $c(\mathbf{r})$ is the associated total charge density. Debye and Hückel assumed that the density may be given by the Boltzmann distribution in the potential $\phi(\mathbf{r})$ at temperature T:

$$n(\gamma,\mathbf{r})=\rho_\gamma \exp[-\beta e_\gamma\phi(\mathbf{r})], \quad \beta=(k_B T)^{-1}\ , \tag{1.2}$$

ρ_γ being the homogeneous density far from the origin. The set of coupled equations (1.1) and (1.2) are the Poisson-Boltzmann equations. In the linear approximation, and taking into account the overall neutrality

$$\sum_{\gamma=1}^{s} e_\gamma\rho_\gamma=0\ , \tag{1.3}$$

the Poisson-Boltzmann equations reduce to the linear Debye-Hückel equation

$$\Delta\phi(\mathbf{r})-\kappa^2\phi(\mathbf{r})=0\ , \tag{1.4}$$

where

$$\kappa=\left[4\pi\beta\sum_{\gamma=1}^{s}\rho_\gamma e_\gamma^2\right]^{1/2}=\lambda^{-1} \tag{1.5}$$

is the inverse of the Debye screening length λ. For $\mathbf{r}\neq\mathbf{0}$, Eq. (1.4) obviously has a solution that vanishes at infinity:

$$\phi(\mathbf{r})=b\frac{e^{-\kappa|\mathbf{r}|}}{|\mathbf{r}|}\ . \tag{1.6}$$

The still unknown constant b is determined by the requirement that as $|\mathbf{r}|\to 0$, $\phi(\mathbf{r})$ should approach the Coulomb potential of a point charge e_α at the origin, i.e., $b=e_\alpha$. Comparing Eqs. (1.1) and (1.4) leads to the following equation for the charge density around the ion α (the ion atmosphere or the screening cloud):

$$c(\mathbf{r})=-\frac{\kappa^2 e_\alpha}{4\pi}\frac{e^{-\kappa|\mathbf{r}|}}{|\mathbf{r}|}\ . \tag{1.7}$$

We can now compute the total charge that is carried by the particles surrounding the ion e_α, and we find from Eq. (1.7)

$$\int d\mathbf{r}\, c(\mathbf{r})=-e_\alpha\ . \tag{1.8}$$

Equation (1.8) expresses the fact that the total amount of charge in the ion atmosphere exactly counterbalances that ion's own charge: it is called the charge or electroneutrality sum rule. Alternatively, Eq. (1.8) may be postulated and used to determine the constant b in Eq. (1.6).

Charge sum rules have probably been known and used from the very beginning of the molecular theory of electrolytes. Gouy (1910) and Chapman (1913) have written and solved the one-dimensional Poisson-Boltzmann equations to study the charge distribution $c(x)$ near a charged electrode (x is the direction perpendicular to the electrode). Here the total charge of the molecular layers compensates the surface charge σ of the electrode:

$$\int_0^\infty dx\, c(x)=-\sigma\ . \tag{1.9}$$

The sum rule (1.8) implies a constraint on the correlation functions of a homogeneous state if one equates the density $n(\gamma,\mathbf{r})$ around the ion α to the density of particles γ in this state when a particle α is known to be located in $\mathbf{r}=\mathbf{0}$:

$$n(\gamma,\mathbf{r})=\frac{\rho(\gamma,\mathbf{r},\alpha,\mathbf{0})}{\rho_\alpha}\ . \tag{1.10}$$

Here, $\rho(\alpha_1,\mathbf{r}_1,\alpha_2,\mathbf{r}_2)$ is the usual two-point correlation function of the homogeneous fluid. Using Eqs. (1.3) and (1.10), the charge sum rule (1.8) can be written as

$$\int d\mathbf{r}\sum_{\gamma=1}^{s} e_\gamma[\rho(\gamma,\mathbf{r},\alpha,\mathbf{0})-\rho_\gamma\rho_\alpha]=-e_\alpha\rho_\alpha\ , \tag{1.11}$$

a relation which is typical for charged particles, and is not true in a fluid with short-range interactions.

B. Linear response and sum rules

Another convenient method for generating sum rules in Coulomb systems is linear-response theory. In order to illustrate this method in a simple case we consider a classical charged fluid at equilibrium, in the presence of an external static point charge e_0 located at the origin. The potential energy of the fluid particles with this charge is

$$U_0=e_0\int d\mathbf{r}\frac{C(\mathbf{r})}{|\mathbf{r}|}\ , \tag{1.12}$$

where

$$C(\mathbf{r})=\sum_\alpha e_\alpha N(\alpha,\mathbf{r})\ , \tag{1.13}$$

$$N(\alpha,\mathbf{r})=\sum_j \delta_{\alpha,\alpha_j}\delta(\mathbf{r}-\mathbf{r}_j)\ , \tag{1.14}$$

are the microscopic densities of the charge and of particles of species α. To first order in e_0 the equilibrium average $\langle A\rangle_{e_0}$ of a quantity A in the presence of the external charge e_0 is

$$\langle A\rangle_{e_0}=\langle A\rangle-e_0\beta\int d\mathbf{r}\frac{\langle C(\mathbf{r})A\rangle_T}{|\mathbf{r}|}\ , \tag{1.15}$$

with

$$\langle C(\mathbf{r})A\rangle_T=\langle C(\mathbf{r})A\rangle-\langle C(\mathbf{r})\rangle\langle A\rangle\ . \tag{1.16}$$

In Eqs. (1.15), (1.16), and the following, it is understood that the thermal average $\langle\cdots\rangle$ is defined for an infinitely extended system, and no finite-size effects are taken into account.

We choose for A a localized observable such as a product of densities $N(\alpha_1,\mathbf{r}_1)\cdots N(\alpha_n,\mathbf{r}_n)$, and denote by $A(\mathbf{a})$ the space translate of A from the origin to $\mathbf{a}$. If the charge e_0 is screened, as in the Debye-Hückel theory, the state $\langle\cdots\rangle_{e_0}$ will differ from the unperturbed state $\langle\cdots\rangle=\langle\cdots\rangle_{e_0=0}$ only in a neighborhood of the origin over distances on the order of the screening length λ. Assuming that the state is homogeneous, and that $\langle A(\mathbf{a})\rangle_{e_0}-\langle A\rangle$ decreases exponentially as $|\mathbf{a}|\to\infty$, we conclude from Eq. (1.15) that

$$\begin{aligned}\langle A(\mathbf{a})\rangle_{e_0}-\langle A\rangle&=-e_0\beta\int d\mathbf{r}\frac{\langle C(\mathbf{r})A(\mathbf{a})\rangle_T}{|\mathbf{r}|}\\&=-e_0\beta\int d\mathbf{r}\frac{\langle C(\mathbf{r})A\rangle_T}{|\mathbf{r}+\mathbf{a}|}\end{aligned} \tag{1.17}$$

decays faster than any inverse power of $|\mathbf{a}|$. Then, using the multipolar expansion of the Coulomb potential produced at $\mathbf{a}$ by the charge distribution $\langle C(\mathbf{r})A\rangle_T$ implies that this distribution does not carry multipoles of any order:

$$\int d\mathbf{r}\,\mathcal{Y}_l(\mathbf{r})\langle C(\mathbf{r})A\rangle_T=0 \tag{1.18}$$

for all harmonic polynomials $\mathcal{Y}_l(\mathbf{r})$ of order l, $l=0,1,2,\ldots$.

If $l=0$ and $A=N(\alpha,\mathbf{0})$, one recovers the charge sum rule (1.11). This is immediately seen if one writes $\langle C(\mathbf{r})N(\alpha,\mathbf{0})\rangle$ in terms of the correlation functions, singling out the contribution of coincident particles:

$$\langle C(\mathbf{r})N(\alpha,\mathbf{0})\rangle_T=\sum_\gamma e_\gamma[\rho(\gamma,\mathbf{r},\alpha,\mathbf{0})-\rho_\gamma\rho_\alpha]+e_\alpha\rho_\alpha\delta(\mathbf{r})\ . \tag{1.19}$$

But Eq. (1.18) provides a number of additional nontrivial sum rules for various choices of l and A. To interpret these new sum rules we define the excess particle density of species α at $\mathbf{r}$, when there are particles of species $\alpha_1,\ldots,\alpha_n$ fixed at $\mathbf{r}_1,\ldots,\mathbf{r}_n$, $\mathbf{r}_1\neq\cdots\neq\mathbf{r}_n$:[1]

$$\begin{aligned}\rho_T(\alpha,\mathbf{r}\,|\,\alpha_1,\mathbf{r}_1,\ldots,\alpha_n,\mathbf{r}_n)&\\=\langle N(\alpha,\mathbf{r})N(\alpha_1,\mathbf{r}_1)\cdots N(\alpha_n,\mathbf{r}_n)\rangle&-\langle N(\alpha,\mathbf{r})\rangle\langle N(\alpha_1,\mathbf{r}_1)\cdots N(\alpha_n,\mathbf{r}_n)\rangle\\=\rho(\alpha,\mathbf{r},\alpha_1,\mathbf{r}_1,\ldots,\alpha_n,\mathbf{r}_n)&+\left[\sum_{j=1}^n\delta_{\alpha,\alpha_j}\delta(\mathbf{r}-\mathbf{r}_j)\right]\rho(\alpha_1,\mathbf{r}_1,\ldots,\alpha_n,\mathbf{r}_n)-\rho(\alpha,\mathbf{r})\rho(\alpha_1,\mathbf{r}_1,\ldots,\alpha_n,\mathbf{r}_n)\ ,\end{aligned} \tag{1.20}$$

and the corresponding excess charge density

$$c(\mathbf{r}\,|\,\alpha_1,\mathbf{r}_1,\ldots,\alpha_n\mathbf{r}_n)=\sum_\alpha e_\alpha\rho_T(\alpha,\mathbf{r}\,|\,\alpha_1,\mathbf{r}_1,\ldots,\alpha_n,\mathbf{r}_n)\ . \tag{1.21}$$

Choosing now $A=N(\alpha_1,\mathbf{r}_1)\cdots N(\alpha_n,\mathbf{r}_n)$, we immediately deduce from these definitions that the excess charge density (1.21) does not carry multipoles of any order

$$\int d\mathbf{r}\,\mathcal{Y}_l(\mathbf{r})c(\mathbf{r}\,|\,\alpha_1,\mathbf{r}_1,\ldots,\alpha_n,\mathbf{r}_n)=0\ . \tag{1.22}$$

This set of constraints, $l=0,1,2,\ldots$, $n=1,2,\ldots$ [the (l,n) multipole sum rules], expresses the remarkable fact that typical configurations in a phase having exponential clustering shield the multipoles induced by specifying any arrangement of the system's charges.

The screening of the system's charges and of external charges gives useful information on the truncated charge-charge correlation function (the structure function) of the fluid:

[1]The properly normalized conditional one-particle excess density would be the quantity (1.20) divided by $\rho(\alpha_1,\mathbf{r}_1,\ldots,\alpha_n,\mathbf{r}_n)$. It is convenient to use definition (1.20).

$$S(\mathbf{r}\,|\,\mathbf{r}')=\langle C(\mathbf{r})C(\mathbf{r}')\rangle-\langle C(\mathbf{r})\rangle\langle C(\mathbf{r}')\rangle$$
$$=\sum_{\alpha\alpha'} e_\alpha e_{\alpha'}\rho_T(\alpha,\mathbf{r}\,|\,\alpha',\mathbf{r}')$$
$$=\sum_{\alpha\alpha'} e_\alpha e_{\alpha'}[\rho(\alpha,\mathbf{r},\alpha',\mathbf{r}')-\rho(\alpha,\mathbf{r})\rho(\alpha',\mathbf{r}')]$$
$$+\delta(\mathbf{r}-\mathbf{r}')\sum_\alpha e_\alpha^2\rho(\alpha,\mathbf{r})\ . \tag{1.23}$$

With the choice $A=C(\mathbf{r}')$ and $l=0$, Eq. (1.18) obviously implies

$$\int d\mathbf{r}\, S(\mathbf{r}\,|\,\mathbf{r}')=0\ . \tag{1.24}$$

When one sets $A=C(\mathbf{r}')$ in Eq. (1.15), the screening of the external charge

$$\int d\mathbf{r}'[\langle C(\mathbf{r}')\rangle_{e_0}-\langle C(\mathbf{r}')\rangle]=-e_0 \tag{1.25}$$

leads to

$$\beta\int d\mathbf{r}'\int d\mathbf{r}\frac{1}{|\mathbf{r}|}S(\mathbf{r}\,|\,\mathbf{r}')=1\ . \tag{1.26}$$

If the fluid is invariant under translations and rotations, $S(\mathbf{r}\,|\,\mathbf{r}')$ depends only on $|\mathbf{r}-\mathbf{r}'|$, and we simply write $S(\mathbf{r}\,|\,\mathbf{r}')=S(\mathbf{r}-\mathbf{r}')$. Then Eq. (1.26) becomes

$$\beta\int d\mathbf{r}'\int d\mathbf{r}\frac{1}{|\mathbf{r}'-\mathbf{r}|}S(\mathbf{r})=1\ . \tag{1.27}$$

Applying the convolution theorem of Fourier transforms, this is equivalent to

$$2\pi(\nu-1)\beta\lim_{|\mathbf{k}|\to 0}\frac{\widetilde{S}(\mathbf{k})}{|\mathbf{k}|^2}=1\ , \tag{1.28}$$

where $\widetilde{S}(\mathbf{k})=\int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}S(\mathbf{r})$ and $2\pi(\nu-1)|\mathbf{k}|^{-2}$ is the Fourier transform of the Coulomb potential in dimension $\nu=2,3$. Alternatively, expanding $\widetilde{S}(\mathbf{k})$ to second order in $\mathbf{k}$ and using spherical symmetry, Eq. (1.28) is also equivalent to

$$\beta\int d\mathbf{r}\,|r^j|^2S(\mathbf{r})=\frac{\beta}{\nu}\int d\mathbf{r}\,|\mathbf{r}|^2S(\mathbf{r})$$
$$=-\frac{1}{\pi(\nu-1)},\quad j=1,\ldots,\nu\ . \tag{1.29}$$

The sum rule (1.29) is known as the second-moment Stillinger-Lovett condition (Stillinger and Lovett, 1968a, 1968b; Outhwaite, 1973). Any one of Eqs. (1.27)–(1.29) is equivalent to the property that the inverse dielectric function $\varepsilon^{-1}(\mathbf{k})$ vanishes in the limit of small wave numbers. This follows from the well-known relation

$$\varepsilon^{-1}(\mathbf{k})=1-2\pi(\nu-1)\beta\frac{\widetilde{S}(\mathbf{k})}{|\mathbf{k}|^2}\ , \tag{1.30}$$

obtained from the response of the fluid to an external spatially modulated charge density. When the conditions (1.27)–(1.29) hold, the fluid completely shields any external charge inhomogeneity and behaves as a conducting medium.

C. Reduced growth of charge fluctuations

Another striking consequence of screening is the reduced growth of charge fluctuations. In a gas of neutral atoms or molecules, each charge belongs to a neutral entity that has an extension of the order of the atomic or molecular diameter d. One can also say that a free charge in a plasma always carries its neutralizing cloud (of radius on the order of the Debye length λ), constituting with it a neutral entity. In a macroscopic region Λ of volume $|\Lambda|$, with $|\Lambda|$ much larger than d^ν or λ^ν, only those entities cutting the boundary $\partial\Lambda$ of Λ at random contribute to the net charge $C_\Lambda=\int_\Lambda d\mathbf{r}\, C(\mathbf{r})$ in Λ. The mean-square fluctuations of this charge may then be expected to be proportional to the surface $|\partial\Lambda|$ of Λ, and not to its volume, as are the usual fluctuations of extensive thermodynamical quantities (outside of critical points).

This can be seen as a consequence of the charge sum rule (1.24). Let us choose, for simplicity, a cubic subdomain of side L, in a homogeneous fluid in ν dimensions. Then, with the definitions (1.23), the charge fluctuations in Λ [with characteristic function $\chi_\Lambda(\mathbf{r})$] are

$$\langle C_\Lambda^2\rangle=\int_\Lambda d\mathbf{r}\int_\Lambda d\mathbf{r}'S(\mathbf{r}-\mathbf{r}')$$
$$=\int d\mathbf{r}\,\gamma_\Lambda(\mathbf{r})S(\mathbf{r})\ , \tag{1.31}$$

where $\gamma_\Lambda(\mathbf{r})=\int d\mathbf{r}'\chi_\Lambda(\mathbf{r}')\chi_\Lambda(\mathbf{r}+\mathbf{r}')$ is the volume of the intersection of Λ with its $\mathbf{r}$-translate ($\langle C_\Lambda\rangle=0$ because of local neutrality). We have, clearly, with $\mathbf{r}=(r^1,r^2,\ldots,r^\nu)$, $\nu=2,3$,

$$\gamma_\Lambda(\mathbf{r})=L^\nu-\sum_{i=1}^{\nu}|r^i|L^{\nu-1}+O(L^{\nu-2})\ . \tag{1.32}$$

When the expansion (1.32) is introduced into Eq. (1.31), we find that the volumic contribution vanishes because of the charge sum rule (1.24), and $\langle C_\Lambda^2\rangle$ is indeed on the order of the surface $|\partial\Lambda|=2\nu L^{\nu-1}$ of the cube:

$$\lim_{|\Lambda|\to\infty}\frac{\langle C_\Lambda^2\rangle}{|\partial\Lambda|}=-\frac{1}{2\nu}\int d\mathbf{r}\sum_{i=1}^{\nu}|r^i|\,S(\mathbf{r})\ . \tag{1.33}$$

The surface behavior, Eq. (1.33), can also be found by another simple argument based on the Gauss law:

$$C_\Lambda=\frac{1}{2\pi(\nu-1)}\int_{\partial\Lambda}d\mathbf{s}\cdot\mathbf{E}(\mathbf{r}),\quad \nu=2,3, \tag{1.34}$$

where $\mathbf{E}(\mathbf{r})$ is the electric field at $\mathbf{r}$ due to a particle configuration in the fluid. We divide the surface $\partial\Lambda$ into N cells Δ_j of size $|\Delta|$ (i.e., $|\partial\Lambda|=N|\Delta|$). Then we have approximately

$$\int_{\partial\Lambda}d\mathbf{s}\cdot\mathbf{E}(\mathbf{r})\simeq|\Delta|\sum_{j=1}^{N}E_j\ ,$$

where E_j is the projection of the electric field on the direction normal to the surface of the cell Δ_j. If the electric fields at different points can be treated as weakly correlated random variables, we can apply the law of large numbers to conclude that

$$\langle C_\Lambda^2 \rangle \simeq \left[\frac{|\Delta|}{2\pi(\nu-1)} \right]^2 \sum_{i,j=1}^{N} \langle E_i E_j \rangle$$
$$\simeq (\text{const})N \simeq (\text{const}) \, |\partial\Lambda| \ . \qquad (1.35)$$

D. Scope of the review

In the derivation of sum rules presented in this Introduction, several approximations have been made. For instance, in the Debye-Hückel theory, one introduces a mean potential in Eq. (1.2), and the linearized equation (1.4). One expects, however, that the sum rule (1.11) is exact and holds under very general conditions (otherwise, individual charges in matter would produce a Coulomb field at large distances). The same remark applies to the second-moment condition (1.29) derived here by linear response. The purpose of this paper is to review various kinds of exact sum rules that have been obtained in recent years, and to present more fundamental derivations in the framework of statistical mechanics. We shall also discuss the characteristic fluctuation properties of electric quantities.

There is no need to emphasize the importance of sum rules in the study of charged fluids, for instance, liquid electrolytes and strongly coupled plasmas, where the Coulomb interaction between the particles plays the essential role and cannot be regarded as a weak perturbation. In these cases, not much is known about the correlations, and any exact relation provides useful information. Such relations also serve as guiding constraints in building approximation schemes.

From a more basic viewpoint we would like to understand better the properties of Gibbs states of ordinary matter, whose constituents interact with the Coulomb force. The beautiful work on the stability of matter (see the review by Lieb, 1976) was concerned with establishing the saturation of bulk matter and its thermodynamic stability. It is then a natural question to ask what the general implications of the long range of the Coulomb force on the structure of an equilibrium state are. In this sense, the multipolar sum rules (1.22) are a set of constraints that are inherent in the structure of the Gibbs state of a uniform classical plasma.

Progress on this problem has been achieved along three different and complementary lines. The first, and most fundamental, uses field-theoretic methods to establish the thermodynamic limit of the state and cluster properties in suitable domains of the thermodynamic parameters (see the review articles by Brydges and Federbush, 1981; Fröhlich and Spencer, 1981c). These methods are constructive and completely rigorous. They are of rather high technical complexity and apply at the moment to a limited (yet important) number of situations. A second line of investigation, which we shall adopt here, is to explore the constraints imposed by the long range of the Coulomb force, provided that the correlation functions exist in the thermodynamic limit, and obey appropriate equilibrium equations and cluster conditions. The results obtained in this way are exact (i.e., do not follow from approximations), but not all of them are rigorously proven, insofar as some reasonable properties (e.g., the type of decay of the correlations) are assumed to hold *a priori.* Using the usual integral-equation approach to the theory of fluids, this allows us to keep a simple mathematical language, and give a unified presentation of the classical static and dynamical as well as quantum-mechanical situations. Finally, much effort has gone into the search and the solution of explicit models (lately, mainly in two dimensions). In addition to their own mathematical interest, they enable one to understand detailed mechanisms, and check the validity of general sum rules. Two-dimensional models have been reviewed in part by Alastuey (1987), and one-dimensional models by Choquard *et al.* (1981).

Notwithstanding their intrinsic beauty and richness, the mathematics of the field-theoretic methods and of the solvable models cannot be presented here, for this would lead beyond the scope of this paper. We shall content ourselves with describing the results that are relevant to the matter under consideration. We also cannot give credit to the large body of literature on approximate methods, numerical simulations, and other approaches to the properties of charged fluids. For this, we refer, in particular, to the review articles by Baus and Hansen (1980), Ichimaru (1982), and Alastuey (1986).

Section II is devoted to the bulk properties of homogeneous classical fluids and is more extended. We give the derivation of sum rules in some detail; it is also in this simple situation that more results, old and new, are known. The properties of inhomogeneous fluids have attracted much attention lately; they are reviewed in Sec. III, where recent works concerned with the link between the statistical mechanics of Coulomb systems and macroscopic electrostatics are also reported (Sec. III.G). Crystalline states are not considered, except for some general aspects of the spontaneous breaking of translational invariance (Sec. III.F). Screening in classical dynamics and in quantum mechanics share several common features: it is less efficient than in classical statics because of the absence of Debye regime (i.e., of exponential clustering) in both cases. This is the subject of Secs. IV and V. Parts of the material presented here have already been reviewed by Gruber and Martin (1980a), Lebowitz (1981), Martin (1986, 1987), and Jancovici (1987).

II. BULK PROPERTIES OF HOMOGENEOUS FLUIDS

A. Equilibrium equations

1. General setting

In this section we are concerned with the bulk properties of homogeneous phases of classical charged particles in dimensions $\nu=1,2,3$. We can have s species of charges e_α, $\alpha=1,\ldots,s$, and a fixed uniform background of charge density c_b. We speak of a Coulomb gas when $c_b=0$, and of a jellium system when $c_b\neq 0$. A Coulomb gas has at least two components with charges of opposite signs. The jellium can have several components with charges of the same sign and opposite to that of the background. The one-component jellium is usually abbreviated OCP (one-component plasma). We denote by $q=(\alpha,\mathbf{r})$ the species α and the position $\mathbf{r}$ of a particle of this species.

A configuration of N particles in the volume V has potential energy

$$U(q_1,\ldots,q_n)=\sum_{i<j}^{N} e_{\alpha_i}e_{\alpha_j}\phi(\mathbf{r}_i-\mathbf{r}_j)+c_b\sum_{i=1}^{N} e_{\alpha_i}\int_V d\mathbf{r}\,\phi(\mathbf{r}_i-\mathbf{r})+\tfrac{1}{2}c_b^2\int_V d\mathbf{r}\int_V d\mathbf{r}'\phi(\mathbf{r}-\mathbf{r}') . \quad (2.1)$$

The Coulomb potential $\phi^c(\mathbf{r})$ is the solution of the Poisson equation in dimension $\nu=1,2,3$:

$$\Delta\phi^c(\mathbf{r})=-\varepsilon_\nu\delta(\mathbf{r}) ,\qquad \varepsilon_1=2,\quad \varepsilon_2=2\pi,\quad \varepsilon_3=4\pi , \quad (2.2)$$

namely,

$$\phi^c(\mathbf{r})=\begin{cases}\dfrac{1}{|\mathbf{r}|}, & \nu=3,\\ -\ln\dfrac{|\mathbf{r}|}{r_0}, & \nu=2\ (r_0 \text{ is a length scale}),\\ -|r|, & \nu=1.\end{cases} \quad (2.3)$$

The singularity of $\phi^c(\mathbf{r})$ at the origin prevents the thermodynamic stability of systems containing point charges of opposite signs in two dimensions for strong enough coupling, and in three dimensions for all values of the coupling (classical collapse). In these cases we introduce an appropriate regularization of the potential at $\mathbf{r}=0$, which we will not specify here (for instance, by dealing with spherically symmetric extended charges). The regularization is not necessary for the jellium when all components have charges of equal sign. In the energy (2.1), $\phi(\mathbf{r})$ denotes the regularized Coulomb potential when this is needed. In fact, all the properties of interest to us are due to the long range of the Coulomb potential, and we will allow local modifications of the potential (2.3) such that the force $\mathbf{F}(\mathbf{r})=-\nabla\phi(\mathbf{r})$ remains locally integrable.[2]

It is well known that the finite-volume canonical or grand canonical distributions $\rho_V(q_1,\ldots,q_n)$, associated with the energy (2.1), satisfy the BGY (Born-Green-Yvon) equations (Yvon, 1969; Hansen and McDonald, 1976)

$$\beta^{-1}\nabla_1\rho_V(q_1,\ldots,q_n)=\left[\mathbf{F}_b(q_1)+\sum_{j=2}^{n}\mathbf{F}(q_1,q_j)\right]\rho_V(q_1,\ldots,q_n)+\int_V dq\,\mathbf{F}(q_1,q)\rho_V(q,q_1,\ldots,q_n) , \quad (2.4)$$

where

$$\mathbf{F}(q_1,q_2)=e_{\alpha_1}e_{\alpha_2}\mathbf{F}(\mathbf{r}_1-\mathbf{r}_2) \quad (2.5)$$

is the two-body (regularized) Coulomb force, and

$$\mathbf{F}_b(q)=e_\alpha c_b\int_V d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}') \quad (2.6)$$

is the electric force on the particle e_α at $\mathbf{r}$ due to the background charge density. In Eq. (2.4), $\int_V dq=\int_V d\mathbf{r}\sum_{\alpha=1}^{s}$ means integration over V and summation over all species.

For the purpose of taking the thermodynamic limit and studying the bulk properties, it is convenient to rewrite Eq. (2.4) in terms of the electric field due to all charges (background plus system's charges) as

$$\mathbf{E}_V(\mathbf{r})=\int_V d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')c_V(\mathbf{r}') , \quad (2.7)$$

where

$$c_V(\mathbf{r})=\sum_{\alpha=1}^{s} e_\alpha\rho_V(\alpha,\mathbf{r})+c_b \quad (2.8)$$

is the total charge density. Equation (2.4) then becomes

$$\beta^{-1}\nabla_1\rho_V(q_1,\ldots,q_n)=\left[e_{\alpha_1}\mathbf{E}_V(\mathbf{r}_1)+\sum_{j=2}^{n}\mathbf{F}(q_1,q_j)\right]\rho_V(q_1,\ldots,q_n)+\int_V dq\,\mathbf{F}(q_1,q)[\rho_V(q,q_1,\ldots,q_n)-\rho_V(q)\rho_V(q_1,\ldots,q_n)] . \quad (2.9)$$

2. Thermodynamic limit

In a number of cases, it has been proven that the thermodynamic limit of the finite-volume correlations exists, and the corresponding infinitely extended state is invariant under translations and rotations. In the cases described below (except the last one), the finite-volume

[2]Strongly repulsive short-range forces, or hard cores, can also be considered. This requires us to explicitly separate the contributions of the short-range parts of the force from those of the long-range parts: the demonstrations become slightly longer, but the results are the same for the problems under consideration.

correlations are defined in the grand canonical ensemble with temperature T and activities z_α.

(a) Edwards and Lenard (1962) have explicitly solved the problem of the one-dimensional Coulomb gas ($c_b=0$) when the charges are rationally related, for all values of T and z_α. They have shown that the thermodynamic limit can be taken by usual method of the transfer matrix in one-dimensional systems.

(b) The thermodynamic limit of the three-dimensional Coulomb gas ($c_b=0$) can be controlled in the Debye screening regime (Brydges, 1978; Brydges and Federbush, 1980). The charges e_α are integer multiples of a charge e. The Debye regime is characterized by the dimensionless plasma parameter $\Gamma=\beta e^2/\lambda_D$ small enough, where

$$\lambda_D=\left[\beta\sum_{\alpha=1}^{s} z_\alpha e_\alpha^2\right]^{-1/2} .$$

The Coulomb potential is taken as the inverse of the Laplacian with Dirichlet boundary conditions, corresponding to perfectly conducting walls. The methods are based on the sine-Gordon representation of the Coulomb gas and cluster expansions developed in the context of the constructive field theory. In this treatment constraints (i) $\sum_\alpha e_\alpha z_\alpha=0$ and (ii) $z_\alpha/\max_\alpha\{z_\alpha\}\geq C>0$ are imposed. Condition (i), related to overall neutrality, has been removed in particular cases, and free boundary conditions can also be used (Federbush and Kennedy, 1985). The thermodynamic limit of the two-dimensional Coulomb gas has been established by the same field-theoretic methods in the Debye regime characterized by the plasma parameter $\Gamma=\beta e^2$ small enough (Yang, 1987).

(c) The results of (b) have been generalized by Imbrie (1983) to systems with arbitrary charges, including the jellium. The jellium limit formally corresponds to $z_\alpha\to\infty$, with $z_\alpha e_\alpha$ fixed for one species α, namely, to relaxing condition (ii) in (b).

(d) Fröhlich and Park (1978) have shown the existence of the thermodynamic limit of charge-symmetric systems in all dimensions, and for all values of the thermodynamic parameters. A charge-symmetric system has $c_b=0$, and an even number of charges, with $e_\alpha=-e_{\alpha+1}$ and $z_\alpha=z_{\alpha+1}$. One uses here correlation inequalities for Gaussian measures. For charge-symmetric systems it is possible to prove that the correlations are asymptotic to the approximation given by the Debye-Hückel theory as the parameter $\Gamma=\beta e^2/\lambda_D$ tends to zero (Kennedy, 1983). Moreover, in the presence of an external charge distribution, the correlations converge as $\Gamma\to 0$, after an appropriate scaling, to those of an ideal gas in the external mean potential determined by the Poisson-Boltzmann equations (Kennedy, 1984).

(e) The two-dimensional OCP is exactly solvable in the canonical ensemble for the special value of the coupling parameter $\Gamma=\beta e^2=2$ and all densities (Alastuey and Jancovici, 1981a; Caillol, 1981; Jancovici, 1981a). The reason is that at this value of the temperature, the Boltzmann factor takes the form of a Vandermonde determinant that can be computed. We add that Gaudin (1985) was able to solve, at $\Gamma=2$, a lattice version of a two-component Coulomb gas. This model is further studied and extended by Cornu and Jancovici (1987).

3. The BGY hierarchy for the bulk correlation functions

In all the above-mentioned cases, the bulk correlations $\rho(q_1,\ldots,q_n)=\lim_{V\to\mathbb{R}^\nu}\rho_V(q_1,\ldots,q_n)$ obey the hierarchy of equations obtained by formally taking the infinite-volume limit in Eq. (2.9). More precisely, one shows for the two- and three-dimensional systems of cases (b)–(e) that the bulk correlations satisfy the equations (Fontaine and Martin, 1984)

$$\beta^{-1}\nabla_1\rho(q_1,\ldots,q_n)=\sum_{j=2}^{n}\mathbf{F}(q_1,q_j)\rho(q_1,\ldots,q_n)+\int dq\,\mathbf{F}(q_1,q)[\rho(q,q_1,\ldots,q_n)-\rho(q)\rho(q_1,\ldots,q_n)] \tag{2.10}$$

under the clustering condition

$$|\rho(q,q_1,\ldots,q_n)-\rho(q)\rho(q_1,\ldots,q_n)|\leq\frac{M}{|\mathbf{r}|^\eta},\quad \eta>1 . \tag{2.11}$$

This condition is verified in cases (b), (c), and (e) (see Sec. II.B). It ensures that the integral in the last term of Eq. (2.10) is absolutely convergent. The corresponding states are locally neutral:

$$\sum_{\alpha=1}^{s} e_\alpha\rho_\alpha+c_b=0 , \tag{2.12}$$

and, as $V\to\mathbb{R}^\nu$, the electric field (2.7) vanishes in the bulk. A uniform state that verifies Eqs. (2.10) and (2.11) cannot sustain a nonvanishing electric field in the bulk.[3]

The correlations of the one-dimensional Coulomb gas [case (a)] also obey Eq. (2.10) in the thermodynamic limit

[3]Indeed, writing the infinite-volume limit of Eq. (2.9) for $n=1$, and for a general $\mathbf{E}=\lim_{V\to\mathbb{R}^\nu}\mathbf{E}_V(\mathbf{r})$, gives

$$e_\alpha\mathbf{E}+e_\alpha\sum_{\alpha_1}e_{\alpha_1}\int d\mathbf{r}_1\mathbf{F}(\mathbf{r}-\mathbf{r}_1)[\rho(\alpha,\mathbf{r},\alpha_1,\mathbf{r}_1)-\rho_\alpha\rho_{\alpha_1}]=0$$

The invariance of the two-point correlation under translations and rotations together with the antisymmetry of the force imply that this integral vanishes, and thus $\mathbf{E}=\mathbf{0}$.

(Gruber, Lugrin, and Martin, 1978; Aizenman and Martin, 1980; Aizenman, 1981). However, this system shows a dielectric behavior: in an external applied field, it admits states where the electric field is also different from zero in the bulk (see Sec. II.F).

It will be useful to write Eq. (2.10) in an alternative form, introducing the electric field at $\mathbf{r}_1$,

$$\mathbf{E}(\mathbf{r}_1 \mid q_2, \ldots, q_n) = \int d\mathbf{r}\, \mathbf{F}(\mathbf{r}_1 - \mathbf{r}) c(\mathbf{r} \mid q_2, \ldots, q_n) , \tag{2.13}$$

which is generated by the excess charge density (1.21) when particles are fixed at $q_2, \ldots, q_n$. For this we introduce the abbreviated notation $Q = (q_2, \ldots, q_n)$, and the truncated functions defined by

$$\rho_T(q_1, Q) = \rho(q_1, Q) - \rho(q_1)\rho(Q) , \tag{2.14}$$

$$\rho_T(q, q_1, Q) = \rho(q, q_1, Q) - \rho(q_1)\rho_T(q, Q) - \rho(q)\rho_T(q_1, Q) - \rho(Q)\rho(q, q_1) . \tag{2.15}$$

When Q consists of a single point, Eq. (2.15) is the usual form of the truncated (Ursell) three-point correlation function. Then it is not hard to check that Eq. (2.10) is equivalent to

$$\beta^{-1}\nabla_1 \rho_T(q_1, Q) = e_{\alpha_1}\rho(q_1)\mathbf{E}(\mathbf{r}_1 \mid Q) + \sum_{j=2}^{n} \mathbf{F}(q_1, q_j)\rho_T(q_1, Q) + \int dq\, \mathbf{F}(q_1, q)\rho_T(q, q_1, Q) . \tag{2.16}$$

B. Cluster properties

1. Results

Not much is rigorously known about the behavior of the correlations for large spatial separations. In the one-dimensional Coulomb gas [case (a)], the asymptotic form of the truncated correlation functions can be calculated and shown to be exponentially decaying (Edwards and Lenard, 1962). This follows for the fact, familiar in one-dimensional systems, that there is a gap between the lowest eigenvalue of the transfer matrix and the rest of the spectrum.

A remarkable result is the proof of the existence of the Debye-Hückel regime (i.e., exponential clustering) in the two- and three-dimensional Coulomb systems of cases (b) and (c). Brydges and Federbush (1980), Imbrie (1983), and Yang (1987) show that the truncated correlations have an exponential bound, when two groups of particles are separated:

$$| \rho(\alpha_1, \mathbf{r}_1 + \mathbf{a}, \ldots, \alpha_k, \mathbf{r}_k + \mathbf{a}, \alpha_{k+1}, \mathbf{r}_{k+1}, \ldots, \alpha_n, \mathbf{r}_n) - \rho(\alpha_1, \mathbf{r}_1, \ldots, \alpha_k, \mathbf{r}_k)\rho(\alpha_{k+1}, \mathbf{r}_{k+1}, \ldots, \alpha_n, \mathbf{r}_n) | \le C_1 \exp\left[-C_2 \frac{|\mathbf{a}|}{\lambda_D} \right] . \tag{2.17}$$

Constants C_1 and C_2 depend on the thermodynamic parameters and on the short-range regularization. The constant C_2 can be chosen arbitrarily close to one, by taking the plasma parameter Γ sufficiently small.

One can make the following comment to appreciate the difference between one and higher dimensions. Because of screening one can imagine that the charges in a typical configuration can be grouped into neutral entities. As a consequence of Newton's theorem, two neutral groups of particles do not interact in one dimension, as soon as they do not overlap. With this picture in mind the one-dimensional system behaves as a gas of neutral molecules with short-range forces, and the correlations of this gas are known to cluster exponentially fast. In higher dimensions, however, neutral groups of particles do not form spherically symmetric charge distributions and there are always residual multipole forces between such groups. The important and albeit, nontrivial point in the Debye-Hückel regime is that these multipole forces are also screened, on the average, because of very subtle arrangements of particles in the typical equilibrium configuration, thus allowing for exponential clustering.

Finally, the correlations of the two-dimensional OCP at $\Gamma = 2$ [case (e)] can be calculated explicitly (Jancovici, 1981a), and they have a Gaussian decay. The structure function (1.23) has the particularly simple form

$$S(\mathbf{r}) = e^2 \rho [\delta(\mathbf{r}) - \rho e^{-\pi\rho |\mathbf{r}|^2}] . \tag{2.18}$$

2. Type of clustering compatible with the equilibrium equations

A simple argument based on the harmonicity of the Coulomb potential shows that all types of asymptotic behavior are not possible in a homogeneous classical charged fluid: if the truncated correlations are integrable and monotonously decreasing at infinity, they have to decay faster than any inverse power.

We consider the homogeneous OCP in three dimensions. A short-range regularization of the Coulomb potential is not needed here. Denoting $\rho_T(r) = \rho_T(\mathbf{r}, \mathbf{0})$, $(|\mathbf{r}| = r)$, the spherically symmetric truncated two-point function, Eq. (2.16) for $n = 2$, simplifies in this case to

$$\beta^{-1}\frac{d}{dr}\rho_T(r)=e\rho E(r)+\frac{e^2}{r^2}\rho_T(r)+e^2\hat{r}\cdot\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\rho_T(\mathbf{r},\mathbf{r}',\mathbf{0})\;,\qquad \hat{r}=\frac{\mathbf{r}}{|\mathbf{r}|}\;, \tag{2.19}$$

with $E(r)=\hat{r}\cdot\mathbf{E}(\mathbf{r}\,|\,\mathbf{0})$ the radial component of the electric field (2.13). It is therefore determined by the Poisson equation

$$\frac{1}{4\pi r^2}\frac{d}{dr}[r^2E(r)]=c(\mathbf{r}\,|\,\mathbf{0})=e[\rho_T(r)+\rho\delta(r)]\;. \tag{2.20}$$

Then we have (Alastuey and Martin, 1985) the following proposition.

Proposition 2.1. Assume that $\rho_T(\mathbf{r},\mathbf{0})$ is integrable and tends monotonously to zero as $r\to\infty$. Moreover, for r large enough, $|\rho_T(\mathbf{r},\mathbf{r}',\mathbf{0})|\le M(t)|\rho_T(r)|$, $t=\min(|\mathbf{r}-\mathbf{r}'|,\;|\mathbf{r}'|)$, and $\lim_{t\to\infty}M(t)=0$, then $\lim r^p\rho_T(r)=0$ for all $p>0$.

The assumed bound on the three-point truncated function $\rho_T(\mathbf{r},\mathbf{r}',\mathbf{0})$ requires that the latter does not decay more slowly than the two-point function itself, and also has some joint decay as a second particle is sent to infinity. This bound is compatible with known exact results, and bounds indicated by perturbative expansions.

Proof. Let us first assume for simplicity that $\rho_T(r)$ has a power-law decay

$$\lim_{r\to\infty} r^p\rho_T(r)=A \quad \text{for some } p>3\;. \tag{2.21}$$

Integrating the Poisson equation (2.20) gives, for $r\neq 0$,

$$E(r)=\frac{C}{r^2}-\frac{4\pi e}{r^2}\int_r^\infty dr' r'^2\rho_T(r')=\frac{C}{r^2}-\frac{4\pi e}{p-3}\frac{A}{r^{p-1}}+o\left[\frac{1}{r^{p-1}}\right]\;, \tag{2.22}$$

where $C=e\int d\mathbf{r}[\rho_T(r)+\rho\delta(\mathbf{r})]$ is the total charge of the right-hand side of Eq. (2.20). Moreover, the condition on the three-point function implies that[4]

$$\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\rho_T(\mathbf{r},\mathbf{r}',0)=o\left[\frac{1}{r^{p-1}}\right]\;. \tag{2.23}$$

Hence inserting Eqs. (2.22) and (2.23) in Eq. (2.19) gives

$$\beta^{-1}\frac{d}{dr}\rho_T(r)=e\rho\frac{C}{r^2}-\frac{4\pi e^2\rho}{p-3}\frac{A}{r^{p-1}}+o\left[\frac{1}{r^{p-1}}\right]\;, \tag{2.24}$$

and, therefore, by integration

$$\beta^{-1}\rho_T(r)=-e\rho\frac{C}{r}+\frac{4\pi e^2\rho}{(p-3)(p-2)}\frac{A}{r^{p-2}}+o\left[\frac{1}{r^{p-2}}\right]\;. \tag{2.25}$$

Thus we conclude from assumption (2.21) that $C=0$ and $A=0$. The relation $C=0$ is simply the charge sum rule (1.24), and $A=0$ means that the decay cannot be like an inverse power of the distance. The *a priori* assumption (2.21) can be removed, to also exclude all kinds of monotonous (nonalgebraic) decays that are not faster than inverse powers.

We conclude from the proposition that if the structure function of the homogeneous OCP does not decay faster than any inverse power, it must either have oscillations, or be nonintegrable. The local relation between the electric field and the charge distribution given by the Poisson equation (2.20), together with the monotonicity hypothesis, play an essential role. We cannot exclude an oscillatory behavior as $\cos\lambda r/r^p$, because then the field and the charge density are of the same order at infinity.

These arguments can be extended to multicomponent systems, under the assumption that $\rho_T(\alpha_1,\mathbf{r},\alpha_2,\mathbf{0})$ has a definite sign for $|\mathbf{r}|$ large enough, namely,

$$e_{\alpha_1}e_{\alpha_2}\rho_T(\alpha_1,\mathbf{r},\alpha_2,\mathbf{0})<0,\quad |\mathbf{r}|\text{ large enough}\;,$$

an inequality which expresses the electrostatic attraction or repulsion of charges at large distances.

3. Non-Coulombic potentials

To emphasize the special role played by the Coulomb potential, among other long-range potentials, we consider a OCP of particles interacting with a long-range but non-Coulombic potential $\phi(\mathbf{r})$ characterized by

$$\phi(\mathbf{r})\simeq\frac{b}{|\mathbf{r}|^\gamma}\quad \text{as } |\mathbf{r}|\to\infty\quad (b\neq 0)\;, \tag{2.26}$$

with $0<\gamma<\nu$, $\gamma\neq\nu-2$ [$\gamma=\nu-2$ is the Coulomb potential (2.3)], or equivalently

$$\tilde{\phi}(\mathbf{k})\simeq a_\nu b\,|\mathbf{k}|^{\gamma-\nu},\quad |\mathbf{k}|\to 0\;, \tag{2.27}$$

where $\tilde{\phi}(\mathbf{k})$ is the Fourier transform of $\phi(\mathbf{r})$, and a_ν a constant. Assuming that the correlations still verify the BGY hierarchy, an analysis of Eq. (2.16) in Fourier space shows that the Fourier transform $\tilde{S}(\mathbf{k})$ of the structure function necessarily has the form

$$\tilde{S}(\mathbf{k})=(\beta a_\nu b)^{-1}|\mathbf{k}|^{\nu-\gamma}+g(\mathbf{k})\;, \tag{2.28}$$

where $g(\mathbf{k})$ depends on the three-point correlation function. When $\gamma\neq\nu-2$, the first term of Eq. (2.28) is not analytic in $\mathbf{k}$ at $\mathbf{k}=0$, and this singularity induces a term of order $|\mathbf{r}|^{-(2\nu-\gamma)}$ in the asymptotic development of $S(\mathbf{r})$. One of course has to check that the behavior of $g(\mathbf{k})$ as $\mathbf{k}\to 0$ does not cancel the first term of Eq. (2.28): in any case, a more detailed analysis (Alastuey and Martin, 1985) shows that the decay of $S(\mathbf{r})$ has to be algebra-

[4] Lemma 1 in Alastuey and Martin (1985).

ic when $\gamma \neq \nu-2$. Therefore, among all possible long-range potentials, it is only in the Coulomb case, Eq. (2.3), that a decay law of the correlations faster than any inverse power is compatible with the structure of equilibrium equations.

A physical example is the two-dimensional film of electrons at the surface of liquid helium, interacting with the three-dimensional Coulomb potential (i.e., $\nu=2$, $\gamma=1$). If the term $|\mathbf{r}|^{-(2\nu-\gamma)}$ is dominant, the asymptotic behavior of the structure function of the electron film is $|\mathbf{r}|^{-3}$, and it agrees with the results found for the slab geometry in three dimensions (Sec. III.D). The same considerations apply to a one-dimensional system of electrons interacting with the two-dimensional logarithmic Coulomb potential ($\nu=1$, $\gamma=0$).[5] Here, the decay of the charge-charge correlations is $|r|^{-2}$ [a result rigorously established by Dyson (1962) for the value $k_B T=1$ of the temperature], and corresponds to that obtained for the strip geometry in two dimensions (Sec. III.D).

C. Multipolar sum rules

We have seen in Proposition 2.1 that the charge sum rule (1.24) follows from the BGY equation, when the truncated correlations are integrable. The next proposition states that the higher-order multipole sum rules (1.22) have to hold in an equilibrium state that has good cluster properties (Gruber, Lugrin, and Martin, 1980; Gruber, Lebowitz, and Martin, 1981; Blum *et al.*, 1982).

Proposition 2.2. Let the space dimension ν be two or three. If the correlations satisfy Eq. (2.16) and

$$\text{(i)}\, |d^{\eta}\rho_T(q_1,\ldots,q_n)| \leq M, \quad d=\sup_{i,j} |\mathbf{r}_i-\mathbf{r}_j| \;,$$

for $\eta>\nu+l_0$ and $n=2,\ldots,n_0+2$, then the (l,n) multipole sum rules (1.22) hold for $l\leq l_0$, $n\leq n_0$.

Proof. The asymptotic behavior of the BGY equation is analyzed as the particle $(\alpha_1,\mathbf{r}_1)$ is sent to infinity, the other remaining fixed. One integrates Eq. (2.16) over a ball of fixed radius, centered around the point $\mathbf{r}_1=\lambda\hat{u}$, $\hat{u}$ being a fixed unit vector, and let $\lambda\to\infty$ [this has the effect of transforming the gradient on the left-hand side of Eq. (2.16) into the integral of $\rho_T(q_1,Q)$ on the surface of the ball, so no assumptions have to be made on the asymptotic form of the derivatives of the correlations]. The main point is to show that the field $E(\mathbf{r}_1|Q)$ due to the excess charge density has a decay faster than $\lambda^{-\nu+1-l_0}$. This is clearly the case for the LHS (left-hand side) of Eq. (2.16) (after integration over the ball) and for the second term on the RHS (right-hand side) of Eq. (2.16).

The last term on the RHS can be written in the form (Q being fixed)

$$\int dq\, \mathbf{F}(q_1,q)\rho_T(q,q_1,Q)=\int d\mathbf{r}\, \mathbf{F}(\mathbf{r}_1-\mathbf{r})g(\mathbf{r}_1,\mathbf{r}) \;, \tag{2.29}$$

with $g(\mathbf{r}_1,\mathbf{r})=e_{\alpha_1}\sum_\alpha e_\alpha \rho_T(\alpha,\mathbf{r},\alpha_1,\mathbf{r}_1,Q)$. The clustering assumption (i) implies that $|d^{\eta}g(\mathbf{r}_1,\mathbf{r})|\leq M$, $d=\sup(|\mathbf{r}_1|,|\mathbf{r}|)$. Then, the following lemma with the choice $\gamma=\nu-1$ shows that the convolution (2.29) decays faster than $|\mathbf{r}_1|^{-\nu+1-l_0}$.

Lemma. Let $\mathbf{F}(\mathbf{r})$ be a locally integrable function on $\mathbb{R}^\nu$ with $\mathbf{F}(\mathbf{r})=O(|\mathbf{r}|^{-\gamma})$, $0<\gamma<\nu$, and $g(\mathbf{r}_1,\mathbf{r})$ a bounded function on $\mathbb{R}^\nu\times\mathbb{R}^\nu$ such that $g(\mathbf{r}_1,\mathbf{r})=O(d^{-\eta})$, $d=\sup(|\mathbf{r}_1|,|\mathbf{r}|)$, and $\eta>\nu+l$. Then

$$\lim_{|\mathbf{r}_1|\to\infty} |\mathbf{r}_1|^{\gamma+l}\int d\mathbf{r}\, \mathbf{F}(\mathbf{r}_1-\mathbf{r})g(\mathbf{r}_1,\mathbf{r})=0 \;.$$

Thus we conclude that the field $\mathbf{E}(\mathbf{r}_1|Q)$ also decays faster than $|\mathbf{r}_1|^{-\nu+1-l_0}$. Under the same clustering assumptions, $\mathbf{E}(\lambda\hat{u}|Q)$ has a multipole expansion up to order l_0:

$$\mathbf{E}(\lambda\hat{u}|Q)=\sum_{l=0}^{l_0}\frac{(-1)^l}{l!}\frac{\mathbf{G}_l(\hat{u}|Q)}{\lambda^{l+\nu-1}}+o\left[\frac{1}{\lambda^{l+\nu-1}}\right] , \tag{2.30}$$

with

$$G_l^i(\hat{u}|Q)=\sum_{i_1\cdots i_l}^{\nu}(\partial_{i_1}\cdots\partial_{i_l}F^i)(\mathbf{r})\Big|_{\mathbf{r}=\hat{u}} \times\int d\mathbf{r}\, r^{i_1}\cdots r^{i_l}c(\mathbf{r}|Q) \;. \tag{2.31}$$

Hence we must have $\mathbf{G}_l(\hat{u}|Q)=0$ for $l=0,1,\ldots,l_0$.

In three dimensions, the coefficient $G_l^3(\hat{u}|Q)$ can be expressed in terms of the spherical harmonics $Y_{l,m}$ by

$$G_l^3(\hat{u}|Q)=\sum_{m=-l}^{l}a_{lm}Y_{l+1,m}(\hat{u})\int d\mathbf{r}|\mathbf{r}|^l Y_{l,m}(\hat{r})c(\mathbf{r}|Q), \qquad \hat{r}=\frac{\mathbf{r}}{|\mathbf{r}|} \;, \tag{2.32}$$

where a_{lm} are nonzero constants.[6] Since $\hat{u}$ is arbitrary, and the spherical harmonics are linearly independent, the (l,n) sum rules follow:

$$\int d\mathbf{r}\,|\mathbf{r}|^l Y_{l,m}(\hat{r})c(\mathbf{r}|Q)=0 \;, \qquad l=0,1,\ldots,l_0 \;. \tag{2.33}$$

One proceeds in the same way in two dimensions.

[5]This system has been extensively studied by Forrester (1984, 1986a, 1986b, 1988).

[6]See Appendix B in Martin and Gruber (1984).

In one dimension, however, the coefficients $G_l(\hat{u} \mid Q)$ are identically zero for $l>0$, since the force is constant; thus only the charge ($l=0$) sum rules can be derived. In fact, in spite of exponential clustering, the $l=1$ sum rule does not hold in the one-dimensional Coulomb system (see Sec. II.D).

In two and three dimensions, exponential decay implies an infinite number of sum rules: all multipoles are shielded. This is, in particular, true for the states described in cases (b) and (c) of Sec. II.A. In the sine-Gordon formalism used here, the sum rules follow from the fact that the Gaussian measure with covariance given by the inverse of the Coulomb potential (the Laplacian $-\Delta$) is formally invariant under translations by harmonic functions $\mathcal{Y}(\mathbf{r})$. Technically, one first approximates $\mathcal{Y}(\mathbf{r})$ by a smooth function with compact support; the resulting boundary terms do not contribute as a consequence of exponential clustering (Fontaine and Martin, 1984).

Let us write the sum rules more explicitly in some particular cases. The general charge sum rules reads

$$\int d\mathbf{r}\, c(\mathbf{r} \mid Q)=\int dq\, e_\alpha[\rho(q,Q)-\rho(q)\rho(Q)] + \left[\sum_{j=1}^{n} e_{\alpha_j}\right]\rho(Q)=0 \ . \tag{2.34}$$

When $Q=(\alpha,\mathbf{r})$ reduces to a single point, the higher-order sum rules are trivially verified because of spherical symmetry. The first nontrivial higher-order sum rule is the dipole sum rule when two particles are fixed:

$$\int d\mathbf{r}\, \mathbf{r} c(\mathbf{r} \mid q_1,q_2)=\int dq\, e_\alpha \mathbf{r}[\rho(q,q_1,q_2)-\rho(q)\rho(q_1,q_2)] +(e_{\alpha_1}\mathbf{r}_1+e_{\alpha_2}\mathbf{r}_2)\rho(q_1,q_2)=0 \ . \tag{2.35}$$

In the homogeneous three-dimensional OCP, the l-sum rules imply the following relations between the two- and three-point functions $g_2(\mathbf{r})=\rho^{-2}\rho(\mathbf{r},0)$ and $g_3(\mathbf{r}_1,\mathbf{r}_2)=\rho^{-3}\rho(\mathbf{r}_1,\mathbf{r}_2,0)$:

$$\rho\int d\mathbf{r}_2 \,|\mathbf{r}_2|^l P_l(\vartheta)[g_3(\mathbf{r}_1,\mathbf{r}_2)-g_2(\mathbf{r}_1)] = -|\mathbf{r}_1|^l g_2(\mathbf{r}_1), \quad l\geq 1 \ , \tag{2.36}$$

where $P_l(\vartheta)$ is the lth-order Legendre polynomial and ϑ the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$. Approximation schemes for closing the BGY hierarchy and computing the structure function of the OCP should be consistent with the constraints (2.36). In this respect it is interesting to observe that the Totsuji-Ichimaru convolution approximation (Totsuji and Ichimaru, 1973) has this property.

D. Second-moment conditions

1. Stillinger-Lovett second-moment condition

The charge sum rule, which holds under the condition of integrable clustering, can be interpreted as the shielding of test particles of the same species as those which constitute the system itself.

The situation is, however, not the same when we introduce test charges that are different from the system's charges: they may be shielded or not according to the plasma or dielectric nature of the phase (see the discussion following Proposition 2.3). We say that the system has the complete shielding property if any external charge distribution is screened by the system's charges. If this is the case, the structure function $S(\mathbf{r})$ has to satisfy the additional constraint (1.29), since this relation was precisely shown to be a consequence of the shielding of an infinitesimal charge in the linear-response theory. In fact, the second-moment condition (1.29) can also be derived directly from the equilibrium equations, as the multipolar sum rules, when the correlations have a sufficiently fast spatial decay. This is the content of Proposition 2.3 (Martin and Gruber, 1983).

Proposition 2.3. If the charge and dipole sum rules (2.34) and (2.35) are verified for $n=1,2$, and if

$$\int dq_1 \int dq_2 \,|\mathbf{r}_2|\,|\rho_T(q_1,q_2,q)| < \infty \ ,$$

then the second-moment condition (1.29) holds.

Proof. Setting $Q=\{q_1\}$ in Eq. (2.16), and using the first BGY equation

$$\beta^{-1}\nabla_1\rho(q_1)=\int dq\, \mathbf{F}(q_1,q)\rho_T(q_1,q)=0 \ ,$$

one can rewrite Eq. (2.16) as

$$\beta^{-1}\nabla_1\rho_T(q_1,q_2)=e_{\alpha_1}\rho(q_1)\mathbf{E}(\mathbf{r}_1 \mid q_2)+\int dq\, \mathbf{F}(q_1,q)[\rho_T(q_1,q_2,q)+(\delta_{q_2,q}+\delta_{q_2,q_1})\rho_T(q_1,q)] \ . \tag{2.37}$$

After multiplication by e_{α_2} and summation over α_2, and taking into account definitions (2.13), (1.20), (1.21), and (1.23), one gets

$$\beta^{-1}\nabla_1\left[\sum_{\alpha_2} e_{\alpha_2}\rho_T(q_1,q_2)\right]=e_{\alpha_1}\rho_{\alpha_1}\int d\mathbf{r}\, F(\mathbf{r}_1-\mathbf{r})S(\mathbf{r}-\mathbf{r}_2)+\int dq\, \mathbf{F}(q_1,q)c_T(\mathbf{r}_2 \mid q_1,q) \ . \tag{2.38}$$

The excess charge density

$$c_T(\mathbf{r}_2 \mid q_1,q)=\sum_{\alpha_2} e_{\alpha_2}[\rho_T(q_2,q_1,q)+(\delta_{q_2,q}+\delta_{q_2,q_1})\rho_T(q_1,q)] \tag{2.39}$$

differs from definition (1.21) only with respect to a truncation in the variables q_1 and q. It is easy to check that it also satisfies the charge and dipole sum rules. The same is true for the last term of Eq. (2.38) (here the joint integrability assumption on the three-point truncated function enters to allow the exchange of the $\mathbf{r}$ and $\mathbf{r}_2$ integrals). Multiplying Eq. (2.38) by $\mathbf{r}_2$, and integrating over $\mathbf{r}_2$, we are left with

$$\begin{aligned}\beta^{-1}\int d\mathbf{r}_2\mathbf{r}_2\cdot\nabla_1\left[\sum_{\alpha_2} e_{\alpha_2}\rho_T(q_1,q_2)\right]&=e_{\alpha_1}\rho_{\alpha_1}\int d\mathbf{r}_2\mathbf{r}_2\cdot\int d\mathbf{r}\,\mathbf{F}(\mathbf{r}_1-\mathbf{r})S(\mathbf{r}-\mathbf{r}_2)\ ,\\ \beta^{-1}\int d\mathbf{r}_2\mathbf{r}_2\cdot\nabla_2\left[\sum_{\alpha_2} e_{\alpha_2}\rho_T(q_1,q_2)\right]&=-e_{\alpha_1}\rho_{\alpha_1}\int d\mathbf{r}_2\mathbf{r}_2\cdot\nabla_2\int d\mathbf{r}\,\phi(\mathbf{r}_2-\mathbf{r}_1-\mathbf{r})S(\mathbf{r})\ .\end{aligned}\tag{2.40}$$

The second line of Eq. (2.40) results from translation and rotation invariance. After partial integration, and taking the charge sum rule into account, one finds (setting $\mathbf{r}_1=\mathbf{0}$)

$$\beta^{-1}e_{\alpha_1}\rho_{\alpha_1}\nu=e_{\alpha_1}\rho_{\alpha_1}\nu\int d\mathbf{r}_2\int d\mathbf{r}\,\phi(\mathbf{r}_2-\mathbf{r})S(\mathbf{r})\ . \tag{2.41}$$

This is equivalent to relations (1.27), (1.28), and (1.29) [if $\phi(\mathbf{r})=1/|\mathbf{r}|+\phi^{\mathrm{sr}}(\mathbf{r})$ has an integrable short-range regularization $\phi^{\mathrm{sr}}(\mathbf{r})$, the latter does not contribute, since then $\int d\mathbf{r}'\int d\mathbf{r}\,\phi^{\mathrm{sr}}(\mathbf{r}'-\mathbf{r})S(\mathbf{r})=\int d\mathbf{r}'\phi^{\mathrm{sr}}(\mathbf{r}')\int d\mathbf{r}\,S(\mathbf{r})=0$, by rule (1.24)]. The proof is the same in two dimensions.

The conditions of the proposition are obviously verified in the Debye screening regime [cases (b) and (c) of Sec. II.A], as well as for the two-dimensional OCP at $\Gamma=2$ [case (e)], implying the validity of the second-moment condition in these systems [in particular, this can be checked directly on the simple formula (2.18)].

One expects, however, that Eq. (1.29) fails [i.e., the second-moment differs from the universal value (1.29)] in the phases where arbitrary external charges are not screened. This can be shown to occur in two instances: in the Kosterlitz-Thouless phase (Kosterlitz and Thouless, 1973; Minnhagen, 1987) at sufficiently low activity and temperature, and in the one-dimensional Coulomb gas for all activities and temperatures.

2. Screening of external charges

In order to discuss the screening of external charges, it is convenient to introduce the correlation $\rho_{e_0}(\mathbf{r}_1,\mathbf{r}_2)$ of an external pair of charges $(e_0,-e_0)$ located in $\mathbf{r}_1$ and $\mathbf{r}_2$, defined by

$$\begin{aligned}\rho_{e_0}(\mathbf{r}_1,\mathbf{r}_2)&=\lim_{V\to\mathbb{R}^\nu}\frac{Z_V(\mathbf{r}_1,\mathbf{r}_2)}{Z_V}\\&=\exp[-\beta F^{\mathrm{ex}}(\mathbf{r}_1,\mathbf{r}_2)]\\&=\exp[\beta e_0^2\phi^{\mathrm{eff}}(\mathbf{r}_1,\mathbf{r}_2)]\ .\end{aligned}\tag{2.42}$$

The partition function $Z_V(\mathbf{r}_1,\mathbf{r}_2)$ (respectively, Z_V) refers to the fluid in the presence of (respectively, without) the pair $(e_0,-e_0)$. The quantity $F^{\mathrm{ex}}(\mathbf{r}_1,\mathbf{r}_2)=-e_0^2\phi^{\mathrm{eff}}(\mathbf{r}_1,\mathbf{r}_2)$, defined by Eq. (2.42), is the excess free energy when the pair $(e_0,-e_0)$ is immersed in the fluid. If the fluid particles are not capable of screening e_0 and $-e_0$, the effective potential $\phi^{\mathrm{eff}}(\mathbf{r}_1,\mathbf{r}_2)$ should behave as the Coulomb potential itself, i.e., $\phi^{\mathrm{eff}}(\mathbf{r}_1,\mathbf{r}_2)\approx-\ln|\mathbf{r}_1-\mathbf{r}_2|$ in two dimensions, or $\phi^{\mathrm{eff}}(x_1,x_2)\approx-|x_1-x_2|$ in one dimension. The absence of screening is therefore characterized by the divergence of the excess free energy, or by

$$\lim_{|\mathbf{r}_1-\mathbf{r}_2|\to\infty}\rho_{e_0}(\mathbf{r}_1,\mathbf{r}_2)=0,\quad \nu=1,2\ . \tag{2.43}$$

Fröhlich and Spencer (1981a) have been able to prove that in a two-dimensional charge-symmetric system of charges e and $-e$, the correlation (2.42) is bounded by

$$|\rho_{e_0}(\mathbf{r},\mathbf{0})|\le\frac{M}{(1+|\mathbf{r}|)^{\delta}} \tag{2.44}$$

for some positive constants M and δ, whenever e_0 is not an integer multiple of e, and the activity and temperature are small enough.[7] Loosely speaking, the fluid particles bind in pairs in the confining logarithmic potential: the system behaves rather as a gas of dipoles than as free charges, and it is known that a gas of dipoles does not screen external charges (Fröhlich and Spencer, 1981b). Moreover, it can be verified that the second-moment condition fails under the same conditions. The situation is similar in one dimension, where one has the estimate

$$|\rho_{e_0}(x,0)|\le M\exp(-\delta|x|) \tag{2.45}$$

for all activities and temperatures (Aizenman and Fröhlich, 1981), and the second-moment condition never holds (Aizenman and Martin, 1980).

In view of these results, it is natural to adopt the validity or the failure of the second-moment condition as a criterion for discriminating between a plasma or a dielectric phase of the Coulomb gas. One must remember here that this criterion applies only to the bulk properties, and does not take into account the surface polarization effects. The relation between the (bulk) Stillinger-Lovett second-moment condition (1.29), and the dielectric susceptibility of a macroscopic body, will be discussed in Sec. III.G.

The main assumption of Proposition 2.3 is the validity

[7]In the proof of Eq. (2.44), the self-energy of the charges is included. The self-energy terms are finite because of the regularization provided by the use of a lattice configuration space.

of the dipole sum rule (2.35), which is true if the correlations cluster faster than $|\mathbf{r}|^{-(\nu+1)}$, $\nu\geq 2$ (Proposition 2.1). Proposition 2.3 puts an upper bound on the decay of the particle correlations in the two-dimensional Kosterlitz-Thouless phase: the three- or four-point functions (or both) cannot decay faster than $|\mathbf{r}|^{-3}$. For the one-dimensional gas (which has exponential clustering), Proposition 2.3 implies that the dipole sum rule (2.35) is always violated because of the dielectric nature of the phase.

Another piece of information that follows from Proposition 2.3 is the asymptotic behavior of the Ornstein-Zernike direct correlation function $C_0(\mathbf{r})$. In Fourier space, the direct correlation function $\tilde{C}_0(\mathbf{k})$ of the OCP is related to the structure factor by

$$\tilde{C}_0(\mathbf{k})=\frac{\tilde{S}(\mathbf{k})-\rho}{\rho\tilde{S}(\mathbf{k})} . \tag{2.46}$$

Inserting the sum rule (1.28) one gets

$$\tilde{C}_0(k)=-\beta\frac{2\pi(\nu-1)}{|\mathbf{k}|^2}+o\left[\frac{1}{|\mathbf{k}|^2}\right]$$
$$=-\beta\tilde{\phi}^c(\mathbf{k})+o\left[\frac{1}{|\mathbf{k}|^2}\right], \tag{2.47}$$

i.e., $\tilde{C}_0(\mathbf{k})$ behaves as the Coulomb potential itself as $|\mathbf{k}|\to 0$. This fact, commonly used in the integral-equations theory of fluids, appears here as a rigorous consequence of the BGY hierarchy when the hypotheses of Proposition 2.3 are fulfilled. The behavior (2.47) of the direct correlation function has been used as a starting point to establish the second-moment condition (Mitchell *et al.*, 1977).

3. Second moment of higher-order correlations

a. One-component plasma

Combining various sum rules, it is possible to obtain simple second-moment sum rules for higher-order correlations. We give some examples in the OCP. With definition (1.23), the Stillinger-Lovett condition can also be written as

$$\int d\mathbf{r}\,|\mathbf{r}|^2\rho_T(\mathbf{r},\mathbf{0})=-\frac{3}{2\pi\beta e^2}\quad(\nu=3) . \tag{2.48}$$

In combination with the charge sum rule $\int d\mathbf{r}_2\rho_T(\mathbf{r}_1,\mathbf{r}_2,\mathbf{0})=-2\rho_T(\mathbf{r}_1,\mathbf{0})$, this leads to the following relation for the three-point function:

$$\int d\mathbf{r}_2\int d\mathbf{r}_1\,|\mathbf{r}_1|^2\rho_T(\mathbf{r}_1,\mathbf{r}_2,\mathbf{0})=\frac{3}{\pi\beta e^2} . \tag{2.49}$$

Using the dipole sum rule $\int d\mathbf{r}_2\mathbf{r}_2\rho_T(\mathbf{r}_1,\mathbf{r}_2,\mathbf{0}) =-\mathbf{r}_1\rho_T(\mathbf{r}_1,\mathbf{0})$, one also obtains from Eq. (2.48)

$$\int d\mathbf{r}_2\int d\mathbf{r}_1\mathbf{r}_1\cdot\mathbf{r}_2\rho_T(\mathbf{r}_1,\mathbf{r}_2,\mathbf{0})=\frac{3}{2\pi\beta e^2} . \tag{2.50}$$

More generally, one finds the analog of Eq. (2.49) for a fully truncated n-point function

$$\int d\mathbf{r}_{n-1}\cdots\int d\mathbf{r}_2\int d\mathbf{r}_1\,|\mathbf{r}_1|^2\rho_T(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{n-1},\mathbf{0})$$
$$=(-1)^{n-1}(n-1)!\frac{3}{2\pi\beta e^2} . \tag{2.51}$$

These rules have appropriate generalizations to multicomponent systems. They can also be understood as consistency relations imposed by the screening of an external charge when one goes beyond the linear term in the response theory.

More interesting are partial second-moment relations when only one variable is integrated out. The latter are specific to the jellium, and involve partial derivatives of the correlation functions with respect to the density

$$\int d\mathbf{r}_1\,|\mathbf{r}_1|^2\rho_T(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{n-1},\mathbf{0})$$
$$=-\left[\sum_{j=2}^{n-1}|\mathbf{r}_j|^2\right]\rho_T(\mathbf{r}_2,\ldots,\mathbf{r}_{n-1},\mathbf{0})$$
$$-\frac{3}{2\pi\beta e^2}\frac{\partial}{\partial\rho}\rho_T(\mathbf{r}_2,\ldots,\mathbf{r}_{n-1},\mathbf{0}) . \tag{2.52}$$

The compatibility between Eqs. (2.51) and (2.52) is easily checked. These relations for arbitrary n have been derived independently by Alastuey (1988) and Vieillefosse and Brajon (1988): they follow, for instance, from a study of the small-wave-number behavior of generalized Ornstein-Zernike equations for n-point functions. The case $n=3$ appears in Vieillefosse (1985).

b. Multicomponent jellium

We consider a mixture of s point charges e_α, $\alpha=1,2,\ldots s$, of equal sign, embedded in a neutralizing background. The overall neutrality is satisfied, but the particle density $\rho=\sum_{\alpha=1}^{s}\rho_\alpha$ is no longer proportional to the charge density when $s>1$. The statistical ensemble can be parametrized in several ways. A convenient parametrization is given by the inverse temperature β, the background charge density c_b, and $s-1$ activities $z_2,\ldots,z_s$, which are used to fix the $s-1$ densities $\rho_2,\ldots,\rho_s$. Then the density of species 1 is determined from the neutrality relation

$$\rho_1=-\frac{1}{e_1}\left[c_b+\sum_{\alpha=2}^{s}e_\alpha\rho_\alpha\right] . \tag{2.53}$$

In this setting, the following partial sum rules have been derived (Suttorp and Van Wonderen, 1987):

$$\sum_{\alpha_2}\int d\mathbf{r}_2\rho_T(\alpha_1,\mathbf{0},\alpha_2,\mathbf{r}_2)=\frac{2}{3}\beta\frac{\partial\rho_{\alpha_1}}{\partial\beta}+2c_b\frac{\partial\rho_{\alpha_1}}{\partial c_b}+\rho_{\alpha_1} , \tag{2.54}$$

$$\sum_{\alpha_2}e_{\alpha_2}\int d\mathbf{r}_2\,|\mathbf{r}_2|^2\rho_T(\alpha_1,\mathbf{0},\alpha_2,\mathbf{r}_2)=\frac{3}{2\pi\beta}\frac{\partial\rho_{\alpha_1}}{\partial c_b} . \tag{2.55}$$

When these equations are summed over α_1 with the factors e_{α_1} and the neutrality (2.53) is used, one recovers the usual charge sum rule for Eq. (2.54), and the Stillinger-Lovett second moment for Eq. (2.55), as one should.

The same authors also give sum rules for the three-point functions that generalize Eqs. (2.49) and (2.50) to the multicomponent jellium, in particular,

$$\sum_{\alpha_2\alpha_3} e_{\alpha_2}e_{\alpha_3}\int d\mathbf{r}_1\int d\mathbf{r}_3\,|\mathbf{r}_3|^2\rho_T(\alpha_1,\mathbf{r}_1,\alpha_2,0,\alpha_3,\mathbf{r}_3) = -\frac{3}{\pi\beta}e_{\alpha_1}\frac{\partial\rho_{\alpha_1}}{\partial c_b}\ . \tag{2.56}$$

One obviously recovers Eq. (2.49) when only one species is present.

4. Fourth moment

It has been known for a long time that the fourth moment of the structure function of the OCP is related to the isothermal compressibility χ_T (compressibility sum rule, Pines and Nozières, 1966; Vieillefosse and Hansen, 1975; Baus, 1978)

$$\int d\mathbf{r}\,|\mathbf{r}|^4 S(\mathbf{r}) = -\frac{15}{2\pi^2}\frac{1}{\rho e^2\beta\chi_T}\ , \tag{2.57}$$

or, equivalently,

$$\tilde{S}(\mathbf{k}) = \frac{1}{4\pi\beta}|\mathbf{k}|^2 - \frac{1}{16\pi^2\rho e^2\beta\chi_T}|\mathbf{k}|^4 + o(|\mathbf{k}|^4)\ . \tag{2.58}$$

Recently, Vieillefosse (1985) has provided an exact derivation of the compressibility rule (2.57) from the microscopic equilibrium equations, again taking into account the dipole sum rule (2.35) and various identities between the correlation functions. The same result has been obtained by Suttorp and Cohen (1985). In these works, the small-wave-number behavior of the fluctuations of other quantities of interest (such as the energy and pressure density) is also determined. In a multicomponent jellium, sum rules for the fourth moment of the pair correlation function can be established (Van Beijeren and Felderhof, 1979; Suttorp and Van Wonderen, 1987), as well as various fluctuation formulas (Van Wonderen and Suttorp, 1987).

E. Charge fluctuations

1. Moments of the charge-charge correlations

It has already been explained in the Introduction that the mean-square charge fluctuations in the bulk are strongly reduced as a consequence of neutrality. These fluctuations are related to the first moment of the structure function. Using the spherical symmetry of $S(\mathbf{r})$, Eq. (1.33) has the equivalent form

$$\lim_{|\Lambda|\to\infty}\frac{\langle C_\Lambda^2\rangle}{|\partial\Lambda|} = -a_\nu\int d\mathbf{r}\,|\mathbf{r}|\,S(\mathbf{r}) \equiv K > 0\ ,$$
$$a_1 = 1,\quad a_2 = \frac{1}{\pi},\quad a_3 = \tfrac{1}{4}\ . \tag{2.59}$$

Equation (2.59) holds when $S(\mathbf{r})$ has an integrable first moment, and satisfies the charge sum rule (1.24). Moreover, the result (2.59) is independent of the shape of the regions Λ. It is the same for spheres (van Beijeren and Felderhof, 1979), and more generally for a sequence of dilatations of any fixed domain Λ_0 (Martin and Yalçin, 1980).

The moments of the charge-charge correlations

$$m_k = \int d\mathbf{r}\,|\mathbf{r}|^k G(\mathbf{r})\ ,$$
$$G(\mathbf{r}) = \sum_{\alpha_1\alpha_2} e_{\alpha_1}e_{\alpha_2}\rho_T(\alpha_1,\mathbf{r},\alpha_2,0)\ , \tag{2.60}$$

always have a definite sign for $k=0,1,2$. Since $G(\mathbf{r}) = S(\mathbf{r}) - \delta(\mathbf{r})\sum_\alpha e_\alpha^2\rho_\alpha$ [Eq. (1.23)], Eqs. (1.24), (1.29), and (2.59) imply that its first moments are negative:

$$m_0 = -\sum_\alpha e_\alpha^2\rho_\alpha\ ,$$
$$m_1 = -\frac{K}{a_\nu}\ ,$$
$$m_2 = -\frac{\nu}{\pi(\nu-1)\beta},\quad \nu=2,3\ . \tag{2.61}$$

The negativity of these moments reflects the fact that the screening cloud of a charge is mainly made of charges of the opposite sign, and $G(\mathbf{r})$ has to be mostly negative. In solvable models [cases (a) and (d) of Sec. II.A], one finds that $G(\mathbf{r})$ is even pointwise negative. However, this will not be the case in general: when the particles have repulsive cores and the density is sufficiently high, $G(\mathbf{r})$ is expected to have oscillations at short distances.

2. Charge correlations in adjacent regions

It is also interesting to compute the correlations of the charge in two different subregions Λ_1 and Λ_2 (Lebowitz, 1983):

$$\langle C_{\Lambda_1}C_{\Lambda_2}\rangle = \int_{\Lambda_1}d\mathbf{r}_1\int_{\Lambda_2}d\mathbf{r}_2 S(\mathbf{r}_1-\mathbf{r}_2) = \int d\mathbf{r}\,S(\mathbf{r})\gamma_{\Lambda_1\Lambda_2}(\mathbf{r})\ . \tag{2.62}$$

Here $\chi_{\Lambda_i}(\mathbf{r})$ are the characteristic functions of Λ_i, $i=1,2$, and

$$\gamma_{\Lambda_1\Lambda_2}(\mathbf{r}) = \int d\mathbf{r}'\chi_{\Lambda_1}(\mathbf{r}+\mathbf{r}')\chi_{\Lambda_2}(\mathbf{r}')$$

is the volume of the intersection of Λ_1 with the $\mathbf{r}$-translate of Λ_2. Considering, for instance, two adjacent cubes centered at $(0,0\cdots0)$ and $(L,0\cdots0)$, one has, for L large enough and $\mathbf{r}=(r^1,\ldots,r^\nu)$,

$$\gamma_{\Lambda_1\Lambda_2}(\mathbf{r})=\begin{cases}0, & r^1\geq 0 \text{ or } r^1\leq -2L,\\ |r^1|L^{\nu-1}+O(L^{\nu-2}), & -L\leq |r^1|\leq 0,\\ (2L-|r^1|)L^{\nu-1}+O(L^{\nu-2}), & -2L\leq |r^1|\leq -L.\end{cases} \tag{2.63}$$

If $S(\mathbf{r})$ has an integrable first moment, one finds from expansion (2.63) that

$$\lim_{L\to\infty}\frac{\langle C_{\Lambda_1}C_{\Lambda_2}\rangle}{2\nu L^{\nu-1}}=\frac{1}{4\nu}\int d\mathbf{r}\,|r^1|\,S(\mathbf{r})$$
$$=-\frac{1}{2\nu}K<0\ . \tag{2.64}$$

Only the domain $-L\leq r^1\leq 0$ contributes to the limit, and $\langle C_{\Lambda_1}C_{\Lambda_2}\rangle$ is proportional to the common surface area of the two cubes. The negativity (2.64) of the correlations of adjacent regions again reflects the fact that the system behaves as if built of neutral entities. The charge fluctuations in Λ_1 are due to the neutral clusters of charges that intersect the surface between Λ_1 and Λ_2. An increase of the positive charge in Λ_1 necessarily results in an increase of the negative charge in Λ_2. In the Debye screening regime, the asymptotic statements (2.59) and (2.64) will hold approximately whenever the diameter L of adjoining regions is large compared to the Debye length (1.5).

3. A central limit theorem in dimension $\nu=2,3$

One can expect that the full probability distribution of the appropriately scaled charge random variables $\hat{C}_\Lambda=|\partial\Lambda|^{-1/2}C_\Lambda$ has a limit as $|\Lambda|\to\infty$. This is indeed the case: under suitable clustering assumptions, the limiting distribution is Gaussian in two and three dimensions (Martin and Yalçin, 1980; Lebowitz, 1983).

More generally, let the space $\mathbb{R}^\nu=U_j\Lambda_j$ be divided into disjoint cubes of volume L^ν centered on a simple cubic lattice, and let $\hat{C}_{\Lambda_j}=(2\nu L^{\nu-1})^{-1/2}C_{\Lambda_j}$ be the appropriately normalized charge in Λ_j. Then, as stated in the next proposition, these random variables are jointly Gaussian, with covariance given by the finite difference Laplacian Δ_{ij} on $\mathbb{Z}^\nu$, $\nu=2,3$.

Proposition 2.4. Assume that

(i) $\int d\mathbf{r}_2\cdots\int d\mathbf{r}_n\,|\rho_T(\alpha_1,\mathbf{0},\alpha_2,\mathbf{r}_2,\ldots,\alpha_n,\mathbf{r}_n)|<\infty$ ($\mathcal{L}^1$ clustering) ;

(ii) $\int d\mathbf{r}_2\cdots\int d\mathbf{r}_n\,|\mathbf{r}_2|\,|\rho_T(\alpha_1,\mathbf{0},\alpha_2,\mathbf{r}_2,\ldots,\alpha_n,\mathbf{r}_n)|<\infty$, for $n=2,3$;

(iii) the $(0,n)$ charge sum rules hold for $n=1,2,3$.

Then the joint distribution of the $\hat{C}_{\Lambda_j}$ is Gaussian as $L\to\infty$, with covariance

$$d_{ij}=\lim_{L\to\infty}\langle\hat{C}_{\Lambda_i}\hat{C}_{\Lambda_j}\rangle$$
$$=K\left[\delta_{i,j}-\frac{1}{2\nu}\delta_{|i-j|,1}\right]=-\frac{K}{2\nu}\Delta_{ij}\ . \tag{2.65}$$

Proof. To obtain the covariance d_{ij}, one verifies that nonadjacent cubes are not correlated:

$$\lim_{L\to\infty}\langle\hat{C}_{\Lambda_i}\hat{C}_{\Lambda_j}\rangle=0,\quad |i-j|\geq 2L\ . \tag{2.66}$$

The combination of Eqs. (2.59), (2.64), and (2.66) leads to Eq. (2.65) of the covariance.

If one denotes the generating function for the probability distribution of the charge $\hat{C}_\Lambda$ by $g_\Lambda(y)=\langle\exp(iy\hat{C}_\Lambda)\rangle$, one likes to show that $g_\Lambda(y)$ converges to the Gaussian $\exp(-y^2K)$ as $L\to\infty$ (for simplicity only a single charge variable is considered here). Using the cumulant expansion

$$\ln\langle\exp(iy\hat{C}_\Lambda)\rangle=\sum_{n=1}^{\infty}\frac{(iy)^n}{n!}M_n(\hat{C}_\Lambda)\ , \tag{2.67}$$

$$\begin{aligned}&M_1(\hat{C}_\Lambda)=\langle\hat{C}_\Lambda\rangle=0\ ,\\ &M_2(\hat{C}_\Lambda)=\langle\hat{C}_\Lambda^2\rangle-\langle\hat{C}_\Lambda\rangle^2\ ,\\ &M_3(\hat{C}_\Lambda)=\langle\hat{C}_\Lambda^3\rangle-3\langle\hat{C}_\Lambda^2\rangle\langle\hat{C}_\Lambda\rangle+2\langle\hat{C}_\Lambda\rangle^3\ ,\end{aligned} \tag{2.68}$$

This amounts to showing that all cumulants $M_n(\hat{C}_\Lambda)$, $n\geq 3$, vanish as $L\to\infty$. The nth-order cumulant can be represented as an integral over truncated correlation functions $\rho_T(q_1|\cdots|q_n)$, which include the contribution of coincident points

$$M_n(\hat{C}_\Lambda)=\frac{1}{(2\nu L^{\nu-1})^{n/2}}\int_\Lambda dq_1\cdots\int_\Lambda dq_n e_{\alpha_1}\cdots e_{\alpha_n}\rho_T(q_1|\cdots|q_n)\ , \tag{2.69}$$

$$\rho_T(q_1|q_2)=\rho_T(q_1,q_2)+\delta_{q_1,q_2}\rho(q_1)\ ,$$

$$\rho_T(q_1\mid q_2\mid q_3)=\rho_T(q_1,q_2,q_3)+\delta_{q_1,q_2}\rho_T(q_1,q_3)+\delta_{q_1,q_3}\rho_T(q_1,q_2)+\delta_{q_2,q_3}\rho_T(q_1,q_2)+\delta_{q_1,q_2}\delta_{q_2,q_3}\rho(q_1)\ , \tag{2.70}$$

$\ldots$.

One easily sees that the charge sum rule (2.34) is equivalent for the $\rho_T(q_1\mid\cdots\mid q_n)$ to

$$\int dq_1 e_{\alpha_1}\rho_T(q_1\mid q_2\mid\cdots\mid q_n)=0\ . \tag{2.71}$$

The $\mathcal{L}^1$-clustering assumption, and the translation invariance, imply that the integrals (2.69) are of the order of L^ν, i.e., $M_n(\hat{C}_\Lambda)=O(L^{\nu-n/2(\nu-1)})$. Therefore, $M_n(\hat{C}_\Lambda)$ vanishes as $L\to\infty$ when $n>3$ in three dimensions, and $n>4$ in two dimensions. Let us now estimate $M_3(\hat{C}_\Lambda)$ in three dimensions. Using the charge sum rule in the form of Eq. (2.71), one has

$$\begin{aligned}M_3(\hat{C}_\Lambda)&=\frac{1}{6^{3/2}L^3}\int_{\mathbb{R}^3\setminus\Lambda}dq_1\int_\Lambda dq_2\int_\Lambda dq_3 e_{\alpha_1}e_{\alpha_2}e_{\alpha_3}\rho_T(q_1\mid q_2\mid q_3)\\&=\frac{1}{6^{3/2}L^3}\int_{\mathbb{R}^3\setminus\Lambda}d\mathbf{r}_1\int_\Lambda d\mathbf{r}_2 h(\mathbf{r}_1-\mathbf{r}_2)\ ,\end{aligned} \tag{2.72}$$

where we have set

$$h(\mathbf{r}_1-\mathbf{r}_2)=\int dq_3\sum_{\alpha_1\alpha_2}e_{\alpha_1}e_{\alpha_2}e_{\alpha_3}\rho_T(\alpha_1,\mathbf{r}_1\mid\alpha_2,\mathbf{r}_2\mid\alpha_3,\mathbf{r}_3)\ . \tag{2.73}$$

Under assumption (ii), the integral (2.72) with $\mathbf{r}_2$ in Λ and $\mathbf{r}_1$ in the complement of Λ is on the order of the surface L^2, and thus the quantity (2.72) vanishes as $L\to\infty$. The proof in two dimensions and for the joint distribution of the $\hat{C}_j$ is similar.

In the one-dimensional system, there is no scaling $[\,|\partial\Lambda|=0(1)]$, and the charge variable C_Λ has a discrete range. In this case, all the cumulants are different from zero in the limit $L\to\infty$, and the distribution of C_Λ converges (weakly) to a discrete one. An explicit example of such a distribution can be obtained for the charge-symmetric model $(e,-e)$. Here the limiting distribution is expressed in terms of the Fourier coefficients of the fundamental solution of the Mathieu equation (Martin and Yalçin, 1980).

F. Potential and field fluctuations

1. General considerations

For particles with short-range interactions (for instance, with a finite range d), the potential at $\mathbf{r}$ is a local quantity, namely, it depends only on the part of the particle configuration that is in a sphere of radius d around $\mathbf{r}$. Then the potential and force fluctuations in a finite spatial region Λ in the bulk are well defined, since they depend only on the configuration of particles in the vicinity of Λ. Regions separated by large distances (larger than $2d$) do not influence each other directly.

The situation is very different in charged systems, where the potential at $\mathbf{r}$ due to a particle configuration is formally given by

$$\Psi(\mathbf{r})=\int d\mathbf{r}'\phi(\mathbf{r}-\mathbf{r}')C(\mathbf{r}')\ . \tag{2.74}$$

Here there is no conceivable way in which distant regions would be decoupled for arbitrary configurations. The potential at $\mathbf{r}$ is genuinely nonlocal, and particles far away will always contribute to the fluctuations at $\mathbf{r}$. It is therefore of interest to know if these fluctuations are well behaved, and how to compute them. The problem is also of practical importance: a knowledge of the distribution of the electric field, usually referred to as the microfield, is needed to determine the shape of spectral lines emitted by a neutral or partially ionized atom in a plasma.

Let us first investigate the possible behavior of the potential fluctuations in the thermodynamic limit, with the help of an argument due to Alastuey and Jancovici (1984). The potential fluctuations in a finite system of volume V are given by

$$\begin{aligned}W_V(\mathbf{r}_1,\mathbf{r}_2)&=\langle[\Psi(\mathbf{r}_1)-\langle\Psi(\mathbf{r}_1)\rangle_V][\Psi(\mathbf{r}_2)-\langle\Psi(\mathbf{r}_2)\rangle_V]\rangle_V\\&=\int_V d\mathbf{r}_1'\int_V d\mathbf{r}_2'\phi(\mathbf{r}_1-\mathbf{r}_1')\phi(\mathbf{r}_2-\mathbf{r}_2')S_V(\mathbf{r}_1'\mid\mathbf{r}_2')\ ,\end{aligned} \tag{2.75}$$

where $S_V(\mathbf{r}_1\mid\mathbf{r}_2)$ is the charge-charge correlation function in the finite system.[8] We choose for V a sphere (disk) of radius R_0, and consider the potential $\int_V d\mathbf{r}_2'\phi(\mathbf{r}_2-\mathbf{r}_2')S_V(\mathbf{r}_1'\mid\mathbf{r}_2')$ at $\mathbf{r}_2$, due to the charge distribution $S_V(\mathbf{r}_1'\mid\mathbf{r}_2')$ for fixed $\mathbf{r}_1'$. Although the global neutrality in the finite system implies

[8]The average potential $\langle\Psi\rangle=\lim_{V\to\mathbb{R}^\nu}\langle\Psi(\mathbf{r})\rangle_V$ can be different from zero even in a homogeneous state, because electric layers will be formed near the boundaries of the finite system. The potential in the bulk will be constant, and remains nonzero as the boundaries recede to infinity. An example is given by Alastuey and Jancovici (1984).

$$\int_V d\mathbf{r}_2' S_V(\mathbf{r}_1' \mid \mathbf{r}_2') = 0 , \tag{2.76}$$

this charge distribution will, in general, have a nonvanishing dipole moment:

$$\int_V d\mathbf{r}_2' \mathbf{r}_2' S_V(\mathbf{r}_1' \mid \mathbf{r}_2') = O(1) \tag{2.77}$$

due to charge layers at the boundary of the sphere (or the disk). The potential at the origin $\mathbf{r}_1 = \mathbf{0}$ due to this charge distribution is therefore of order

$$\int_V d\mathbf{r}_2' \phi(\mathbf{r}_2') S_V(\mathbf{r}_1' \mid \mathbf{r}_2') = \begin{cases} O\left[\dfrac{1}{R_0^2}\right], & \nu = 3, \\ O\left[\dfrac{1}{R_0}\right], & \nu = 2. \end{cases} \tag{2.78}$$

We estimate the order of magnitude of the potential fluctuations $W_V(\mathbf{0},\mathbf{0})$ at the origin as follows. If $\mathbf{r}_1'$ is in the vicinity of the boundary in the integral (2.75) one has $\phi(\mathbf{r}_1') \simeq 1/R_0 (\nu=3)$, $\phi(\mathbf{r}_1') \simeq -\ln R_0 (\nu=2)$. With the estimate (2.78), the contribution to $W_V(\mathbf{0},\mathbf{0})$ of a shell of volume $R_0^{\nu-1}$ near the boundary in the $\mathbf{r}_1'$ integral (2.75) is therefore of order $1/R_0$ in three dimensions, but diverges as $\ln R_0$ in two dimensions. We therefore expect that, when $\mathbf{r}_1$ and $\mathbf{r}_2$ are fixed in the bulk, $W_V(\mathbf{r}_1,\mathbf{r}_2)$ remains bounded as $R_0 \to \infty$ in three dimensions, but diverges in two dimensions.

2. Potential fluctuations in three dimensions

We concentrate now on the three-dimensional case, and shall assume that the potential fluctuations (2.75) have a translation-invariant thermodynamic limit

$$W(\mathbf{r}_1 - \mathbf{r}_2) = \lim_{V \to \mathbb{R}^3} W_V(\mathbf{r}_1, \mathbf{r}_2) . \tag{2.79}$$

Our main point is that whenever the limit (2.79) exists, $W(\mathbf{r})$ can as well be computed as the limit of averages of strictly local functions in the infinitely extended state.

For this, it is convenient to distinguish first between the contributions to the potential (2.74) due to the particles located in the neighborhood of $\mathbf{r}$ and the particles distant from $\mathbf{r}$. We split the potential into a local part $\Psi_R^{\text{in}}(\mathbf{r})$ due to the particles inside a sphere $\Sigma_R(\mathbf{r})$ of radius R centered at $\mathbf{r}$, and a global outside part $\Psi_R^{\text{out}}(\mathbf{r})$ due to the particles in the exterior of this sphere:

$$\Psi(\mathbf{r}) = \Psi_R^{\text{in}}(\mathbf{r}) + \Psi_R^{\text{out}}(\mathbf{r}) , \tag{2.80}$$

with

$$\Psi_R^{\text{in}}(\mathbf{r}) = \int_{\Sigma_R(\mathbf{r})} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} C(\mathbf{r}') , \tag{2.81}$$

$$\Psi_R^{\text{out}}(\mathbf{r}) = \int_{\mathbb{R}^3 \setminus \Sigma_R(\mathbf{r})} \frac{1}{|\mathbf{r} - \mathbf{r}'|} C(\mathbf{r}') . \tag{2.82}$$

We introduce moreover the spatial average of the total potential on this sphere

$$\overline{\Psi}_R(\mathbf{r}) = \frac{1}{|\Sigma_R|} \int_{\Sigma_R(\mathbf{r})} d\mathbf{r}' \Psi(\mathbf{r}'), \quad |\Sigma_R| = \frac{4\pi R^3}{3} . \tag{2.83}$$

Then the electrostatic formula

$$\int_{\Sigma_R(\mathbf{r})} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} = \begin{cases} \dfrac{4\pi R^3}{3} \dfrac{1}{|\mathbf{r}|}, & |\mathbf{r}| \geq R, \\ -\dfrac{2\pi}{3} |\mathbf{r}|^2 + 2\pi R^2, & |\mathbf{r}| \leq R, \end{cases} \tag{2.84}$$

yields the identity

$$\Psi_R^{\text{out}}(\mathbf{r}) = -\tilde{\Psi}_R(\mathbf{r}) + \overline{\Psi}_R(\mathbf{r}) , \tag{2.85}$$

with

$$\tilde{\Psi}_R(\mathbf{r}) = \int_{\Sigma_R(\mathbf{r})} d\mathbf{r}' \left[-\frac{1}{2R^3} |\mathbf{r}' - \mathbf{r}|^2 + \frac{3}{2R} \right] C(\mathbf{r}') . \tag{2.86}$$

Then one has (Lebowitz and Martin, 1984) the following proposition.

Proposition 2.5. (i) Assume that the limit (2.79) exists, and $\lim_{|\mathbf{r}| \to \infty} W(\mathbf{r}) = 0$; then the potential fluctuations can be computed locally in the infinite state by

$$W(\mathbf{r}_1 - \mathbf{r}_2) = \lim_{R \to \infty} \langle [\Psi_R(\mathbf{r}_1) - \langle \Psi_R(\mathbf{r}_1) \rangle] \times [\Psi_R(\mathbf{r}_2) - \langle \Psi_R(\mathbf{r}_2) \rangle] \rangle , \tag{2.87}$$

where the local function $\Psi_R(\mathbf{r}) = \Psi_R^{\text{in}}(\mathbf{r}) - \tilde{\Psi}_R(\mathbf{r})$ is given by definitions (2.81) and (2.86).

(ii) Moreover, if $\int d\mathbf{r} |\mathbf{r}| \, |\rho_T(\alpha_1, \mathbf{r}, \alpha_2, \mathbf{0})| < \infty$, and the (0,1) charge sum rule holds, $W(\mathbf{r})$ is given by the following equations:

$$\begin{aligned} W(\mathbf{r}) &= -2\pi \int d\mathbf{r}' |\mathbf{r} + \mathbf{r}'| S(\mathbf{r}') \\ &= \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left[\int d\mathbf{r}'' \frac{S(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \right] \\ &= \frac{2}{\pi} \int d\mathbf{k} \, e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\tilde{S}(\mathbf{k})}{|\mathbf{k}|^4} , \end{aligned} \tag{2.88}$$

and has the asymptotic behavior

$$W(\mathbf{r}) = \frac{1}{|\mathbf{r}|} \left[-\frac{2\pi}{3} \int d\mathbf{r}' |\mathbf{r}'|^2 S(\mathbf{r}') \right] + o\left[\frac{1}{|\mathbf{r}|} \right] . \tag{2.89}$$

Proof. Part (i) of the proposition results from the fact that the spatially averaged potential $\overline{\Psi}_R(\mathbf{r})$ does not contribute to the fluctuations. Indeed, the existence of the limit (2.79) implies that, for each fixed R,

$$\lim_{V\to\mathbb{R}^3}\langle[\overline{\Psi}_R(r)-\langle\overline{\Psi}_R(\mathbf{r})\rangle_V]^2\rangle_V$$
$$=\frac{1}{|\Sigma_R|^2}\int_{\Sigma_R(\mathbf{r})}d\mathbf{r}_1\int_{\Sigma_R(\mathbf{r})}d\mathbf{r}_2 W(\mathbf{r}_1-\mathbf{r}_2)$$
$$=\left[\frac{3}{4\pi}\right]^3\int_{\Sigma_1(0)}d\mathbf{r}_1\int_{\Sigma_1(0)}dr_2\, W[R(\mathbf{r}_1-\mathbf{r}_2)]\;,$$

and this quantity tends to zero as $R\to\infty$ if $\lim_{|\mathbf{r}|\to\infty}W(\mathbf{r})=0$. The first equation (2.88) is obtained by a direct calculation of the limit (2.87), with the help of definitions (2.81) and (2.86). Notice that the second formula (2.88) is the formal limit of Eq. (2.75), where the integrations have to be performed in the indicated order. The last equation (2.88) results from the convolution theorem for Fourier transforms.

To obtain the asymptotic behavior (2.89), we use the charge sum rule and the spherical symmetry to write

$$W(\mathbf{r})=-2\pi\int d\mathbf{r}'\left[|\mathbf{r}+\mathbf{r}'|-|\mathbf{r}|-\frac{\mathbf{r}'\cdot\mathbf{r}}{|\mathbf{r}|}\right]S(\mathbf{r}')$$
$$=-\frac{\pi}{|\mathbf{r}|}\sum_{i,j}^{3}\left[\delta_{i,j}-\frac{r^ir^j}{|\mathbf{r}|^2}\right]\int d\mathbf{r}'r'^ir'^jS(\mathbf{r}')$$
$$+o\left[\frac{1}{|\mathbf{r}|}\right]\,. \tag{2.90}$$

Since

$$\int d\mathbf{r}'r'^ir'^jS(\mathbf{r}')=\tfrac{1}{3}\delta_{i,j}\int d\mathbf{r}'\,|\mathbf{r}'|^2S(\mathbf{r}')\;,$$

the result (2.89) follows.

We see that the decay of the potential fluctuations is always slow, even if the clustering is exponentially fast. Moreover, when the second-moment relation (1.29) holds, the asymptotic behavior of $W(\mathbf{r})$ is $\beta^{-1}1/|\mathbf{r}|$, i.e., universal, and independent of the short-range part of the interaction.

Part (i) of the proposition shows that the contribution $\Psi_R^{\text{out}}(\mathbf{r})$ of the particles at infinity to the fluctuations can be calculated from the local function $-\widetilde{\Psi}_R(\mathbf{r})$, and the decomposition (2.80) provides a natural distinction between the contribution of the nearby particles and those far away. The complete probability distribution of $\Psi_R^{\text{out}}(\mathbf{r})$ can be determined by the same method as in Proposition 2.4. If the state has the property of $\mathcal{L}^1$ clustering, the random variables $\Psi_R^{\text{out}}(\mathbf{r})$ are jointly Gaussian as $R\to\infty$, with covariance

$$W^{\text{out}}(\mathbf{r})=-\pi\int d\mathbf{r}'\,|\mathbf{r}+\mathbf{r}'|\,S(\mathbf{r}')\,. \tag{2.91}$$

It is interesting to remark that the contribution $W^{\text{out}}(\mathbf{r})$ to the fluctuations of the particles at "infinity" is not negligible: it is just half of the total fluctuations (2.88).

3. Electric field fluctuations in three dimensions

The electric field fluctuations can be treated in the same way, replacing $\Psi(\mathbf{r})$ everywhere by $\mathbf{E}(\mathbf{r})=-\nabla\Psi(\mathbf{r})$. One finds the formula for the tensor $e^{ij}(\mathbf{r})=\langle E^i(\mathbf{r})E^j(\mathbf{0})\rangle$ of the electric field fluctuations (Lebowitz and Martin, 1984)

$$e^{ij}(\mathbf{r})=-\frac{\partial^2}{\partial r^i\partial r^j}W(\mathbf{r})=2\pi\int d\mathbf{r}'\frac{1}{|\mathbf{r}+\mathbf{r}'|}\left[\delta_{i,j}-\frac{(r+r')^i(r+r')^j}{|\mathbf{r}+\mathbf{r}'|^2}\right]S(\mathbf{r}')=\frac{2}{\pi}\int d\mathbf{k}\,e^{i\mathbf{k}\cdot\mathbf{r}}\frac{k^ik^j}{|\mathbf{k}|^4}\widetilde{S}(\mathbf{k})\;, \tag{2.92}$$

with the asymptotic behavior

$$e^{ij}(\mathbf{r})=\left[\frac{\delta_{i,j}-3\hat{r}^i\hat{r}^j}{|\mathbf{r}|^3}\right]\left[-\frac{2\pi}{3}\int d\mathbf{r}'\,|\mathbf{r}'|^2S(\mathbf{r}')\right]+o\left[\frac{1}{|\mathbf{r}|^3}\right]=\frac{1}{\beta}\left[\frac{\delta_{i,j}-3\hat{r}^i\hat{r}^j}{|\mathbf{r}|^3}\right]+o\left[\frac{1}{|\mathbf{r}|^3}\right],\quad \hat{r}=\frac{\mathbf{r}}{|\mathbf{r}|}\,. \tag{2.93}$$

The second equality follows from the second-moment condition (1.29). The off-diagonal part of $e^{ij}(\mathbf{r})$ always has a slow decay of dipolar type. However, the trace

$$\sum_{j=1}^{3}e^{jj}(\mathbf{r})=4\pi\int d\mathbf{r}'\frac{1}{|\mathbf{r}-\mathbf{r}'|}S(\mathbf{r}') \tag{2.94}$$

decays faster than any inverse power if $S(\mathbf{r})$ has that property [$S(\mathbf{r})$ satisfies the charge sum rule (1.24)].

Equations (2.88) and (2.92) refer to the fluctuations of electric quantities at a point $\mathbf{r}$ in space. It is also important to know in various physical situations the effects of the field fluctuations on a charged particle of type α_0 at $\mathbf{r}_0$ in the system. The previous results can be extended to this case by computing the potential and force fluctuations in the state $\langle\cdots\rangle_0$, with correlations $\rho_0(q_0,q_1,\ldots,q_n)/\rho(q_0)$ conditioned by the presence of a particle of type α_0 at $\mathbf{r}_0$.

We consider a general system of charged particles interacting with the locally regularized Coulomb force $\mathbf{F}(q_1,q_2)$. Using the BGY equation it is not hard to show that the correlations of the force at q_0 in the state $\langle\cdots\rangle_0$ involve only the two-point function

$$\langle F^i(q_0)F^j(q_0)\rangle_0=\frac{1}{\beta\rho(q_0)}\int dq\,F^i(q,q_0)(\nabla^j\rho_T)(q,q_0)\,. \tag{2.95}$$

This gives, in particular, after an integration by parts,

$$\sum_{j=1}^{3}\langle[F^j(q_0)]^2\rangle_0=-\frac{1}{\beta\rho(q_0)}\int dq(\nabla\cdot\mathbf{F})(q,q_0)\rho_T(q,q_0)\,. \tag{2.96}$$

It is, in general, not possible to suppress the regularization of the force in Eqs. (2.95) or (2.96) because of the loss of thermodynamic stability, except in the case of a jellium with all the particles having charges of the same sign. In the latter case, we can deal with point particles (no collapse) and the force

$$F(q,q_0)=-e_{\alpha_0}e_\alpha\nabla\frac{1}{|\mathbf{r}-\mathbf{r}_0|}=e_{\alpha_0}\mathbf{E}(\mathbf{r}_0)$$

is proportional to the electric field at q_0. Then, using the Poisson equation in Eq. (2.96), one obtains the following simple fluctuation formula for the electric field [with $q_0=(\alpha_0,\mathbf{0})$]:

$$\sum_{j=1}^{3}\langle |E^j(\mathbf{0})|^2\rangle_0=\frac{4\pi}{\beta\rho_{\alpha_0}e_{\alpha_0}}\sum_\alpha e_\alpha\rho_T(\alpha,\mathbf{0},\alpha_0,\mathbf{0})$$
$$=\frac{4\pi}{\beta}\left|\frac{c_b}{e_{\alpha_0}}\right| . \tag{2.97}$$

The last equation follows from the neutrality, and the fact that the correlation $\rho(\alpha,\mathbf{r},\alpha_0,\mathbf{r}_0)$ vanishes at coincident points because of the repulsive interaction between charges of the same sign. This exact value of the second moment of the field has been used by Iglesias, Lebowitz, and McGowan (1983) to compute the microfield distribution approximately.

4. Potential and field fluctuations in two dimensions

As noted at the beginning of this section, the two-dimensional potential fluctuations diverge with the size of the system. However, Alastuey and Jancovici (1984) have shown that the fluctuations of the potential difference

$$\Psi(\mathbf{r}_1)-\Psi(\mathbf{r}_2)=-\int d\mathbf{r}(\ln|\mathbf{r}_1-\mathbf{r}|-\ln|\mathbf{r}_2-\mathbf{r}|)C(\mathbf{r})$$

at two points $\mathbf{r}_1$ and $\mathbf{r}_2$ exist:

$$W(\mathbf{r}_1-\mathbf{r}_2)=\lim_{V\to\mathbb{R}^2}\langle[\Psi(\mathbf{r}_1)-\Psi(\mathbf{r}_2)-\langle\Psi(\mathbf{r}_1)-\Psi(\mathbf{r}_2)\rangle_V]^2\rangle_V , \tag{2.98}$$

and are given by formulas analogous to Eq. (2.88):

$$W(\mathbf{r})=\int d\mathbf{r}'(\ln|\mathbf{r}-\mathbf{r}'|-\ln|\mathbf{r}'|)\left[\int d\mathbf{r}''(\ln|\mathbf{r}-\mathbf{r}''|-\ln|\mathbf{r}''|)S(\mathbf{r}'-\mathbf{r}'')\right]=2\int d\mathbf{k}(1-e^{i\mathbf{k}\cdot\mathbf{r}})\frac{S(\mathbf{k})}{|\mathbf{k}|^4} . \tag{2.99}$$

The electric field fluctuations $e^{ij}(\mathbf{r})$ are expressed in Fourier representation by the same equation (2.92), with the factor $2/\pi$ suppressed. Both $W(\mathbf{r})$ and $e^{ij}(\mathbf{r})$ do not have a fast decay:

$$W(\mathbf{r})=\frac{2}{\beta}\ln|\mathbf{r}|+o(\ln|\mathbf{r}|) , \tag{2.100}$$

$$e^{ij}(\mathbf{r})=\frac{1}{\beta}\left[\frac{\delta_{i,j}-2\hat{r}^i\hat{r}^j}{|\mathbf{r}|^2}\right]+o\left[\frac{1}{|\mathbf{r}|^2}\right] , \tag{2.101}$$

where the second-moment condition has been taken into account. All these properties of two-dimensional fluctuations can be checked explicitly in the two-dimensional OCP at $\Gamma=2$ (Alastuey and Jancovici, 1984).

5. Electric field fluctuations in one dimension

In the neutral one-dimensional Coulomb gas, the configurations of the electric field are particularly simple:

$$E(x)=\sum_{j=1}^{N}e_{\alpha_j}\operatorname{sgn}(x-x_j)+E_0 ,$$
$$\operatorname{sgn}x=\begin{cases}1, & x>0,\\ -1, & x<0,\end{cases}\qquad \sum_{j=1}^{N}e_{\alpha_j}=0 . \tag{2.102}$$

They are piecewise constant functions with discrete jumps $2e_{\alpha_j}$ at the positions x_j of the charges. If one thinks of x as a "time parameter," one can identify the configurations (2.102) with those of a certain random process. It has been recognized by Lenard (1963) that, in the infinite-volume limit, this process is Markovian, translation-invariant, and has the exponential clustering property. The constant E_0 in Eq. (2.102) is a constant external field due to charges at the boundaries. An interesting point is that the states obtained in the thermodynamic limit for different values of E_0, corresponding to boundary charges that are not multiples of the e_α, are distinct (Aizenman and Martin, 1980). In these states, the average electric field $\langle E\rangle$ in the bulk does not vanish, and the system shows a dielectric behavior. This is again a consequence of the fact that the charges form dipoles bound by the confining potential $-|x|$. An external field induces a nonzero polarization of these dipoles in the bulk.

G. Mixture of ions and dipoles

The sum rules can be generalized to classical fluids where neutral molecules with multipoles are present, in addition to pure charges. If the densities of mobile charges are not zero, it is expected that the screening properties remain the same (i.e., of Debye type) as in a fluid consisting only of charges (Hoye and Stell, 1978).

The most commonly studied model is a system of ions interacting with a dipolar solvent (civilized-model electrolyte). It can be characterized as follows. The particles of species α carry either a charge e_α or a dipole moment of strength d_α. We set $d_\alpha=0$ (respectively, $e_\alpha=0$) if the species α is an ion (respectively, a dipole). For a solvent particle, we introduce the abbreviated notation $q=(\alpha,\mathbf{r},\boldsymbol{\omega})$, where $\mathbf{r}$ and $\boldsymbol{\omega}(|\boldsymbol{\omega}|=1)$ denote, respectively, the position of the particle, and the orientation of its dipole moment $\boldsymbol{\mu}_\alpha(\boldsymbol{\omega})=d_\alpha\boldsymbol{\omega}$. We normalize the angular integration over the angles of the dipole to 1, and set

$$\int dq=\int d\mathbf{r}\int d\boldsymbol{\omega}\sum_\alpha . \tag{2.103}$$

With this notation the BGY hierarchy (2.10) keeps the same form, with the Coulomb force (2.5) replaced by the Coulomb and dipole force

$$\mathbf{F}(q_1,q_2)=[e_{\alpha_1}+\boldsymbol{\mu}_{\alpha_1}(\boldsymbol{\omega}_1)\cdot\boldsymbol{\nabla}_1]\times[e_{\alpha_2}+\boldsymbol{\mu}_{\alpha_2}(\boldsymbol{\omega}_2)\cdot\boldsymbol{\nabla}_2]\mathbf{F}(\mathbf{r}_1-\mathbf{r}_2) . \tag{2.104}$$

Then, Proposition 2.2 holds: under the same clustering hypothesis, the multipole moment tensor of order l due to the excess particle density $\rho(q\,|\,q_1,\ldots,q_n)$ vanishes (Blum *et al.*, 1982):[9]

$$\int dq\;\tau_l(q)\rho(q\,|\,q_1,\ldots,q_n)=0 . \tag{2.105}$$

For the lowest orders, the tensors $\tau(q)$ are

$$\tau_0(q)=e_\alpha\quad(\text{charge}) , \tag{2.106}$$

$$\tau_1^i(q)=e_\alpha r^i+\mu_\alpha^i(\boldsymbol{\omega})\quad(\text{dipole}) , \tag{2.107}$$

$$\tau_2^{ij}(q)=e_\alpha r^i r^j+\tfrac{1}{2}[\mu_\alpha^i(\boldsymbol{\omega})r^j+\mu_\alpha^j(\boldsymbol{\omega})r^i]-\frac{1}{\nu}[e_\alpha|\mathbf{r}|^2+\boldsymbol{\mu}_\alpha(\boldsymbol{\omega})\cdot\mathbf{r}]\delta_{i,j}\quad(\text{quadrupole}) . \tag{2.108}$$

As an explicit example we write the dipole sum rule for the two-point function:

$$\int d\mathbf{r}\int d\boldsymbol{\omega}\sum_\alpha[e_\alpha\mathbf{r}+\boldsymbol{\mu}_\alpha(\boldsymbol{\omega})]\rho_T(\alpha,\mathbf{r},\boldsymbol{\omega},\alpha_1,\mathbf{r}_1,\boldsymbol{\omega}_1)=-[e_{\alpha_1}\mathbf{r}_1+\boldsymbol{\mu}_{\alpha_1}(\boldsymbol{\omega}_1)]\rho_{\alpha_1} , \tag{2.109}$$

which holds for each choice of the orientation $\boldsymbol{\omega}_1$ of the dipole at $\mathbf{r}_1$. The extension to the case where the fluid has molecules with permanent multipoles of higher order is straightforward. For instance, permanent quadrupoles will contribute to the formation of the quadrupole tensor (2.108), and so on.

If one assumes that the system screens arbitrary external charges, the Stillinger-Lovett condition has the following generalization for a dipolar solvent (Carnie and Chan, 1981a; Martin and Gruber, 1983):

$$\beta\int d\mathbf{r}'\int d\mathbf{r}\frac{1}{|\mathbf{r}'-\mathbf{r}|}[S(\mathbf{r})-\boldsymbol{\nabla}\cdot\mathbf{P}(\mathbf{r})]=1 , \tag{2.110}$$

or, equivalently,

$$\frac{\beta}{\nu}\int d\mathbf{r}\,|\mathbf{r}|^2[S(\mathbf{r})-\boldsymbol{\nabla}\cdot\mathbf{P}(\mathbf{r})]=-\frac{1}{\pi(\nu-1)},\quad \nu=2,3 . \tag{2.111}$$

In Eqs. (2.110) and (2.111), $S(\mathbf{r})$ is the charge-charge correlation function

$$S(\mathbf{r})=\sum_{\alpha_1\alpha_2}\int d\boldsymbol{\omega}_1\int d\boldsymbol{\omega}_2 e_{\alpha_1}e_{\alpha_2}\rho_T(\alpha_1,\mathbf{r},\boldsymbol{\omega}_1\,|\,\alpha_2,\mathbf{0},\boldsymbol{\omega}_2) , \tag{2.112}$$

and $\mathbf{P}(\mathbf{r})$ the charge-dipole correlation function

$$\mathbf{P}(\mathbf{r})=\sum_{\alpha_1\alpha_2}\int d\boldsymbol{\omega}_1\int d\boldsymbol{\omega}_2 e_{\alpha_1}\boldsymbol{\mu}_{\alpha_2}(\boldsymbol{\omega}_2)\rho_T(\alpha_1,\mathbf{r},\boldsymbol{\omega}_1\,|\,\alpha_2,\mathbf{0},\boldsymbol{\omega}_2) . \tag{2.113}$$

One should note that the screening is less effective if the ions have a structure and themselves carry dipoles (i.e., e_α and d_α both different from zero). A perturbative calculation shows that the decay of the correlations is now algebraic (as $|r|^{-(\nu+1)}$ for the dipole-dipole correlations). The screening of the charge still holds [Eq. (2.105) for $l=0$, and Eqs. (2.110) and (2.111)], but the higher-order rules (2.105) are no longer true. Because of their own dipolar structure, the ions can no longer be arranged in the screening clouds to compensate for any multipole.[10]

Finally, we recall that a gas of pure dipoles ($e_\alpha=0,\alpha=1,\ldots,s$) does not screen. It can be shown (Fröhlich and Spencer, 1981b) that the truncated correlation function of two infinitesimal external dipoles cannot decay integrably fast. The dipole-dipole correlations in a gas of pure dipoles must also have a weak decay. Indeed, if the decay of the dipole-dipole correlations is faster than $|\mathbf{r}|^{-(\nu+1)}(\nu\geq 2)$, the dipole sum rule (2.109) (with $e_\alpha=0$) would hold according to Proposition 2.1. Hence the dielectric bulk part of the susceptibility tensor

$$\chi^{ij}=\int d\mathbf{r}_1\sum_{\alpha_1\alpha_2}\int d\boldsymbol{\omega}_1\int d\boldsymbol{\omega}_2\mu_{\alpha_1}^i(\boldsymbol{\omega}_1)\mu_{\alpha_2}^j(\boldsymbol{\omega}_2)\rho_T\times(\alpha_1,\mathbf{r}_1,\boldsymbol{\omega}_1\,|\,\alpha_2,\mathbf{0},\boldsymbol{\omega}_2) \tag{2.114}$$

would vanish. This is in contradiction to the physical property that a pure dipole gas behaves as a dielectric, and should have a nonzero polarization in the bulk. One expects that the dipole-dipole correlations decay as $|r|^{-\nu}$, i.e., as the dipole-dipole potential itself (Stell, 1977).

[9]The excess particle $\rho(q\,|\,q_1,\ldots,q_n)$ is defined as in Eq. (1.20), with $\delta_{q_1,q_1}=\delta_{\alpha_1,\alpha_2}\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(\boldsymbol{\omega}_1-\boldsymbol{\omega}_2)$.

[10]One encounters an analogous situation in a quantum-mechanical plasma (Sec. V.B).

III. INHOMOGENEOUS FLUIDS

A. Introduction

In this section we review screening properties and sum rules in charged fluids at thermal equilibrium that are not invariant by translations. The cause of the inhomogeneities is external, for instance, the presence of walls, of external charge distributions and applied field, or of additional forces which are not of an electric nature. With the exception of Sec. III.F we shall not be concerned with inhomogeneous states that result from a spontaneous breaking of translation invariance, such as ionic crystals. Typical physical situations that we have in mind are electrolyte solutions in the vicinity of an electrode, metallic interfaces, or plasmas confined in varied geometries.

One first has to make a distinction between two classes of systems, the semi-infinite and the strictly finite ones. By semi-infinite systems we mean fluids which may be restricted to a domain D by appropriate walls, but D is not bounded, and extends to infinity at least in one direction. Examples are plasmas in a slab or in a half-space bounded by impenetrable walls. The correlation functions of a semi-infinite system are obtained by a thermodynamic limit, in which all boundaries except those delimiting D are sent to infinity. In finite systems the fluid is confined in a bounded region of space and described by the usual finite-volume correlation functions.

In semi-infinite systems, some form of local neutrality will be true on a microscopic scale: no macroscopic excess of charge can be built, since charge can always escape to infinity. Semi-infinite systems are suitable for the investigation of the microscopic structure of density profiles and correlations in the vicinity of an inhomogeneity. On the other hand, it is only for finite-volume systems that the surface polarization effects are fully taken into account, and the findings can be compared with the predictions of the electrostatics of macroscopic bodies. This will be discussed in Sec. III.G.

The inhomogeneous fluid that we consider here will always be assumed to be in a plasma phase. In other words, the thermodynamic parameters are such that the bulk correlations of the same fluid (obtained by removing the finite-distance boundaries and the external disturbances) have an exponential decay, and all the related properties typical for a plasma phase (Secs. I.C and I.D). This precaution is necessary: one knows from numerical evidence that the two-dimensional Coulomb gas in the periodic field of a static infinite ionic lattice undergoes a transition, at sufficiently low temperatures, from a plasma phase to localized phase, where electrons are bound to the ions (Clérouin and Hansen, 1985; Clérouin, Hansen, and Piller, 1987a, 1987b). This very interesting phase of an inhomogeneous Coulomb system is the equivalent of the Kosterlitz-Thouless phase of the two-component Coulomb gas (Alastuey, Cornu, and Jancovici, 1988). It is currently under investigation and will not be discussed here.

A remarkable point is that, even in the plasma phase, the correlations of the nonuniform fluid can exhibit a slow (nonexponential) decay. Specifically, along a plane insulating wall, the pair correlation decays only as $|\mathbf{r}|^{-\nu}$ $(\nu=2,3)$. The origin of this slow decay has to be asymmetry effects in the screening cloud of a particle sitting near the wall. This screening cloud can only consist of arrangements of particles lying in the half-space where the fluid is confined, since no mobile charges are available at the wall and behind it. As a consequence of this constraint, the particle plus its screening cloud has a nonvanishing dipole moment. Then, a slow decay of the pair correlation can be inferred from the general theorem that a fast decay of the correlations in every direction would imply the vanishing of all electrical moments (Proposition 3.1). The situation is expected to be different in a conducting interface, where mobile charges always surround a particle and can succeed in building a screening cloud without multipoles (although not necessarily spherically symmetric).

B. Semi-infinite systems

1. General features

The rigorous results on three-dimensional inhomogeneous fluids are still scarce: we quote the work of Federbush and Kennedy (1985) on surface properties in the Debye screening regime. On the other hand, many investigations on the effects of inhomogeneities have been performed in the two-dimensional OCP at $\Gamma=2$; they will be mentioned below.

We shall admit here that the correlations of the semi-infinite system also obey the BGY hierarchy obtained by formally taking the thermodynamic limit of the corresponding finite-volume system. If $c^{\text{ext}}(\mathbf{r})$ denotes the distribution of all external charges (localized in D or at the boundaries of D), the electric field (2.7) has to be replaced by

$$\mathbf{E}_V(\mathbf{r})=\int_V d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\left[\sum_\alpha e_\alpha\rho_V(\alpha,\mathbf{r}')+c^{\text{ext}}(\mathbf{r}')\right]$$
$$=\mathbf{E}_V^{\text{sys}}(\mathbf{r})+\mathbf{E}_V^{\text{ext}}(\mathbf{r}) , \tag{3.1}$$

i.e., the field due to all charges (system's charges and external charges). Assuming that the correlations have a limit as $V\to D$, $\mathbf{E}_V(\mathbf{r})$ converges to $\mathbf{E}(\mathbf{r})$, the electric field at $\mathbf{r}$ in the semi-infinite system, which is now, in general, different from zero. This entails the following modifications of Eq. (2.10) and (2.16): $\sum_{j=2}^n \mathbf{F}(q_1,q_j)$ has to be replaced by $\sum_{j=2}^n \mathbf{F}(q_1,q_j)+e_{\alpha_1}\mathbf{E}(\mathbf{r}_1)$, and the space integral has to be carried over the region D. Equation (2.16) becomes

$$\beta^{-1}\nabla_1\rho_T(q_1,Q)=e_{\alpha_1}\rho(q_1)\mathbf{E}(\mathbf{r}_1\,|\,Q)+\left[e_{\alpha_1}\mathbf{E}(\mathbf{r}_1)+\sum_{j=2}^{n}\mathbf{F}(q_1,q_j)\right]\rho_T(q_1,Q)+\int_D dq\,\mathbf{F}(q_1,q)\rho_T(q_1,q,Q)\ . \tag{3.2}$$

This form of the equation holds when the dielectric constant of the external medium is set equal to one, so no image forces have to be taken into account in Eq. (3.2). Then we have the analog of Proposition 2.2.

Proposition 3.1. If the correlations satisfy Eq. (3.2) with the same cluster conditions (i) as in Proposition 2.2 and (ii) D contains an open ν-dimensional cone in which the asymptotic densities of the charged particles do not all vanish, then the (l,n) sum rules hold for $l \le l_0, n \le n_0$.

The proof is the same as that of Proposition 2.2. The additional assumption (ii) enters in the derivation of the multipolar sum rules (2.33) from Eq. (2.32) by using the freedom to vary the unit vector $\hat{u}$ in an open set.[11] This is where one explicitly uses the fact that D is semi-infinite.

Here, the proposition is conditional: the multipolar sum rules are true only if the correlations have good decay properties in all directions in D. In particular, if it is known that, for some reason, a screening cloud carries a nonzero multipole moment, one infers from the proposition that the decay must be algebraic, at least in one direction.

When the decay is faster than any inverse power in all directions (a case that is expected to occur when the medium is everywhere conducting in infinite space), the simplest set of nontrivial sum rules is that all multipoles of the charge-charge correlations vanish:[12]

$$\int d\mathbf{r}\,\mathcal{Y}_l(\mathbf{r})S(\mathbf{r}\,|\,\mathbf{r}')=0\ . \tag{3.3}$$

An example of this situation has been given by Jancovici (1982b) in the two-dimensional OCP at $\Gamma=2$, and by Alastuey and Lebowitz (1984) for a class of inhomogeneous background densities in the same model.

2. The Carnie-Chan sum rule

The screening of an infinitesimal charge leads again to Eq. (1.26),

$$\beta\int_D d\mathbf{r}'\int_D d\mathbf{r}\frac{1}{|\mathbf{r}|}S(\mathbf{r}\,|\,\mathbf{r}')=1\ , \tag{3.4}$$

which was derived in the Introduction by a linear-response argument; the argument applies as well when the system is semi-infinite and there are no image forces. The sum rule (3.4) is the Carnie and Chan generalization to nonuniform fluids of the second-moment Stillinger-Lovett condition (Carnie and Chan, 1981a; Carnie, 1983).

Equation (3.4) can also be seen to be a consequence of the equilibrium equations. A derivation, which is an extension of that of Sec. II.D, can be found in the Appendix. It applies to two different classes of inhomogeneous plasmas: (i) asymptotically uniform plasmas; (ii) infinite jellium systems with periodic density. The first class (i) is characterized by densities that are asymptotically constant in (almost) all directions, i.e.,

$$\lim_{|\mathbf{r}|\to\infty}\rho(\alpha,|\mathbf{r}|,\Omega)=\rho_\alpha(\Omega)\ , \tag{3.5}$$

where Ω are the angles of $\mathbf{r}$. One expects, in a plasma phase, that the convergence to bulk quantities occurs on a microscopic scale (on the order of the Debye length) when one goes away from the inhomogeneity. In this situation, the correlations will converge sufficiently fast, when all arguments tend to infinity in the fixed direction Ω, to those of a uniform system with densities $\rho_\alpha(\Omega)$. Typical examples are treated in Secs. III.C–III.E. An infinite periodic jellium [class (ii)] constitutes an elementary model for an electron gas in the periodic field of an ionic lattice. At a sufficiently high temperature, the electrons are delocalized, and behave as a perfectly conducting fluid. This will be briefly discussed in Sec. III.F.

Some remarks on Eq. (3.4) are in order. Even if $S(\mathbf{r}\,|\,\mathbf{r}')$ has good decay properties, the integrals over $\mathbf{r}$ and $\mathbf{r}'$ cannot be permuted: if this were possible, one would obtain zero by the charge sum rule (1.24), instead of $1\neq 0$. Thus some care has to be exercised when applying the sum rule (3.4) to specific geometries.

The strict Coulomb potential can be modified in the sum rule (3.4) to $1/|\mathbf{r}|+\phi^{\mathrm{sr}}(\mathbf{r})$, where $\phi^{\mathrm{sr}}(\mathbf{r})$ is any integrable short-range potential. This short-range part does not contribute, since now integrals can be exchanged, and the charge sum rule applies.

The slightly more general relation

$$\beta\int_D d\mathbf{r}'\int_D d\mathbf{r}\frac{1}{|\mathbf{r}-\mathbf{r}_0|}S(\mathbf{r}\,|\,\mathbf{r}')=1\ , \tag{3.6}$$

where $\mathbf{r}_0$ is an arbitrary point, is equivalent to rule (3.4). Indeed, taking the Laplacian of the left-hand side of Eq. (3.6) with respect to $\mathbf{r}_0$, one finds with the Poisson equation (2.2) and charge sum rules (1.24) that

$$\nabla^2_{\mathbf{r}_0}\int_D d\mathbf{r}'\int_D d\mathbf{r}\frac{1}{|\mathbf{r}-\mathbf{r}_0|}S(\mathbf{r}\,|\,\mathbf{r}')$$
$$=-4\pi\int_D d\mathbf{r}'S(\mathbf{r}_0\,|\,\mathbf{r}')=0\ . \tag{3.7}$$

Thus the left-hand side of Eq. (3.6) is a harmonic (bound-

[11]Assumption (ii) is really used for the (l,n) sum rules with $l\ge 1$. The charge sum rule can be derived whenever D extends to infinity in at least one direction (as in an infinite cylinder).

[12]Of course, Eq. (3.3) is trivial for $l\ge 1$ by rotational invariance in the homogeneous plasma.

ed) function of $\mathbf{r}_0$ on the whole of $\mathbb{R}^3$; it is therefore constant with respect to $\mathbf{r}_0$.

In an inhomogeneous plasma with good decay properties (faster than algebraic), the system's charges screen not only any external charge distribution, but also all its multipoles. This leads to a nontrivial generalization of the Carnie-Chan form (Jancovici, 1986)

$$\beta \int d\mathbf{r}' \mathcal{Y}_l(\mathbf{r}') \int d\mathbf{r} \frac{1}{|\mathbf{r}-\mathbf{r}_0|} S(\mathbf{r} \mid \mathbf{r}') = \mathcal{Y}_l(\mathbf{r}_0) \ . \quad (3.8)$$

The multipole sum rules (3.8) have the same relation with the screening of external distributions as do rules (3.3) with respect to the screening of the system's charges. Using Eq. (3.3), it is easily verified that the LHS of Eq. (3.8) is harmonic.

C. Insulating plane wall

1. A dipole sum rule

We consider a charged fluid confined in the half-space $x \geq 0$ by a plane wall located at $x=0$, and we write $\mathbf{r}=(x,\mathbf{y})$, where $\mathbf{y}$ stands for the components parallel to the wall. We first show under very reasonable conditions that $S(\mathbf{r} \mid \mathbf{r}')$ carries a nonvanishing dipole moment by establishing the dipole sum rule

$$2\pi(\nu-1)\beta \int_0^\infty dx' \int_0^\infty dx \int d\mathbf{y}\, x S(x,\mathbf{y} \mid x') = -1 \ , \quad \nu=2,3 \ . \quad (3.9)$$

Because of invariance under translations along the plane and rotations around the x direction,

$$S(\mathbf{r} \mid \mathbf{r}') = S(x, \mathbf{y}-\mathbf{y}' \mid x') = S(x \mid x', \mathbf{y}'-\mathbf{y})$$

is only a function of the length $|\mathbf{y}-\mathbf{y}'|$. As x and x' become large, $S(\mathbf{r} \mid \mathbf{r}')$ approaches a fully translation-invariant function $S^b(\mathbf{r} \mid \mathbf{r}') = S^b(\mathbf{r}-\mathbf{r}')$, the bulk charge correlations for the same value of the temperature and densities. We assume that this convergence occurs on a microscopic scale, so that the following joint integral is finite:

$$\int_0^\infty dx' \int_0^\infty dx \int d\mathbf{y}\, |x| \ |S(x,\mathbf{y} \mid x') - S^b(x-x',\mathbf{y})| < \infty \ . \quad (3.10)$$

Adding and subtracting the same bulk quantity we can write

$$\begin{aligned}\int_0^\infty dx' \int_0^\infty dx \int d\mathbf{y}\, x S(x,\mathbf{y} \mid x') &= \int_0^\infty dx' \int_0^\infty dx \int d\mathbf{y}\, x [S(x,\mathbf{y} \mid x') - S^b(x-x',\mathbf{y})] \\ &\quad + \int_0^\infty dx' \int_0^\infty dx \int d\mathbf{y}\, x S^b(x-x',\mathbf{y}) \\ &= -\int_0^\infty dx \int_0^\infty dx'\, x \int d\mathbf{y}\, S^b(x-x',\mathbf{y}) + \int_0^\infty dx' \int_0^\infty dx\, x \int d\mathbf{y}\, S^b(x-x',\mathbf{y}) \ . \end{aligned} \quad (3.11)$$

This result follows from the permutation of the x and x' integrals in the first term of the second member of Eq. (3.11) [this is allowed under condition (3.10)]. Then, the integral over the correlation function of the semi-infinite system gives zero because of electroneutrality:

$$\int_0^\infty dx' \int d\mathbf{y}\, S(x,\mathbf{y} \mid x') = \int_0^\infty dx' \int d\mathbf{y}\, S(x \mid x',\mathbf{y}) = 0 \ . \quad (3.12)$$

Using the translation and rotation invariance of the bulk function, the quantity (3.11) is also equal to

$$\int_0^\infty dx' \int_0^\infty dx (x-x') \int d\mathbf{y}\, S^b(x-x',\mathbf{y}) = \frac{1}{2} \int_{-\infty}^{\infty} dx \int d\mathbf{y}\, x^2 S^b(x,\mathbf{y}) = -\frac{1}{2\pi(\nu-1)\beta} \ , \quad (3.13)$$

where the last equality is the second-moment condition (1.29), and this leads to the sum rule (3.9). This sum rule was derived by Carnie (1983) using a different method [see the remark following Eq. (3.35) below].

Obviously, the dipole sum rule (3.3) for $l=1$ cannot hold in this semi-infinite system, and we must conclude that $S(x,\mathbf{y} \mid x')$ cannot have a fast decay in all directions (according to Proposition 3.1, it must be slower than $|\mathbf{r}|^{-(\nu+1)}$ in some direction). Since there are good decay properties in the bulk, the weak clustering should be along the wall.

2. Long-range correlations along the wall

More detailed information on this slow decay can be obtained from a closer inspection of the Carnie-Chan sum rule (3.4). We consider the two-dimensional Fourier transforms of $S(x,\mathbf{y} \mid x')$ and $S^b(x-x',\mathbf{y})$ ($\nu=3$):

$$\begin{aligned}\tilde{S}(x,\mathbf{k} \mid x') &= \int d\mathbf{y}\, e^{i\mathbf{k}\cdot\mathbf{y}} S(x,\mathbf{y} \mid x') \ , \\ \tilde{S}^b(x-x',\mathbf{k}) &= \int d\mathbf{y}\, e^{i\mathbf{k}\cdot\mathbf{y}} S^b(x-x',\mathbf{y}) \ , \end{aligned} \quad (3.14)$$

and we like to determine the small $\mathbf{k}$ behavior of

$$\int_0^\infty dx' \int_0^\infty dx [\tilde{S}(x,\mathbf{k} \mid x') - \tilde{S}^b(x-x',\mathbf{k})] \equiv a(\mathbf{k}) + b(\mathbf{k}) + c(\mathbf{k}) \ , \quad (3.15)$$

where we have set

$$a(\mathbf{k})=\int_0^\infty dx'\int_0^\infty dx\, e^{-|\mathbf{k}|x}\tilde{S}(x,\mathbf{k}\,|\,x')\ , \tag{3.16}$$

$$b(\mathbf{k})=-\int_0^\infty dx'\int_0^\infty dx\,(e^{-|\mathbf{k}|x}-1)\times[\tilde{S}(x,\mathbf{k}\,|\,x')-\tilde{S}^{\,b}(x-x',\mathbf{k})]\ , \tag{3.17}$$

$$c(\mathbf{k})=-\int_0^\infty dx'\int_0^\infty dx\, e^{-|\mathbf{k}|x}\tilde{S}^{\,b}(x-x',\mathbf{k})\ . \tag{3.18}$$

The bulk function has been subtracted out in Eq. (3.15) to form an absolutely convergent integral according to assumption (3.10). Introducing the two-dimensional partial Fourier transform of the Coulomb potential

$$\frac{1}{(x^2+|\mathbf{y}|^2)^{1/2}}=\frac{1}{2\pi}\int d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{y}}\frac{e^{-|\mathbf{k}|x}}{|\mathbf{k}|}\ , \tag{3.19}$$

the Carnie-Chan relation (3.4) becomes

$$\frac{\beta}{2\pi}\int d\mathbf{k}\int d\mathbf{y}'\int_0^\infty dx'\int_0^\infty dx\frac{e^{-|\mathbf{k}|x}}{|\mathbf{k}|}\int d\mathbf{y}\, e^{i\mathbf{k}\cdot\mathbf{y}}S(x,\mathbf{y}-\mathbf{y}'\,|\,x')=\lim_{|\mathbf{k}|\to 0}\frac{2\pi\beta}{|\mathbf{k}|}\int_0^\infty dx'\int_0^\infty dx\, e^{-|\mathbf{k}|x}\tilde{S}(x,\mathbf{k}\,|\,x')=1\ , \tag{3.20}$$

and thus

$$a(\mathbf{k})=\frac{|\mathbf{k}|}{2\pi\beta}+o(\mathbf{k})\ . \tag{3.21}$$

Under assumption (3.10) we are allowed to expand $b(\mathbf{k})$ under the integral sign. Then the sum rule (3.9) implies

$$\begin{aligned} b(\mathbf{k})&=|\mathbf{k}|\left[\int_0^\infty dx'\int_0^\infty dx\, x[\tilde{S}(x,0\,|\,x')-\tilde{S}^{\,b}(x-x',0)]\right]+o(|\mathbf{k}|)\\ &=-\frac{|\mathbf{k}|}{4\pi\beta}-|\mathbf{k}|\int_0^\infty dx'\int_0^\infty dx\, x\tilde{S}^{\,b}(x-x',0)+o(|\mathbf{k}|)\ . \end{aligned} \tag{3.22}$$

Finally, one finds that [$\tilde{S}^{\,b}(x-x',\mathbf{k})$ has no linear contribution in $\mathbf{k}$ by symmetry]

$$\begin{aligned} c(\mathbf{k})&=-\int_0^\infty dx'\int_0^\infty dx\,\tilde{S}^{\,b}(x-x',0)+|\mathbf{k}|\int_0^\infty dx'\int_0^\infty dx\, x\tilde{S}^{\,b}(x-x',0)+o(|\mathbf{k}|)\\ &=\tfrac{1}{2}\int d\mathbf{r}\,|x|\,S^b(\mathbf{r})+|\mathbf{k}|\int_0^\infty dx'\int_0^\infty dx\, x\tilde{S}^{\,b}(x-x',0)+o(|\mathbf{k}|)\ . \end{aligned} \tag{3.23}$$

Collecting Eqs. (3.21), (3.22), and (3.23) in Eq. (3.15) leads to the sum rule

$$\int_0^\infty dx'\int_0^\infty dx[\tilde{S}(x,\mathbf{k}\,|\,x')-\tilde{S}^{\,b}(x-x',\mathbf{k})]=\tfrac{1}{2}\int d\mathbf{r}\,|x|\,S^b(\mathbf{r})+\frac{|\mathbf{k}|}{4\pi\beta}+o(|\mathbf{k}|)\ . \tag{3.24}$$

The singularity at $\mathbf{k}=0$ implies a slow decay along the wall. Since the Fourier transform of $|\mathbf{k}|$ is $-1/2\pi|\mathbf{y}|^3$, Eq. (3.24) implies the asymptotic behavior in space:

$$\int_0^\infty dx'\int_0^\infty dx[S(x,\mathbf{y}\,|\,x')-S^b(x-x',\mathbf{y})]\simeq-\frac{1}{8\pi^2\beta}\frac{1}{|\mathbf{y}|^3},\quad |\mathbf{y}|\to\infty\ , \tag{3.25}$$

provided that there are no other singularities for real values of $\mathbf{k}$ different from zero causing a still weaker decay. We expect that this long-range correlation is a specific surface feature, to which the bulk term in Eq. (3.25) does not contribute. If one assumes an asymptotic behavior of the form

$$S(x,\mathbf{y}\,|\,x')\simeq\frac{f(x,x')}{|\mathbf{y}|^3},\quad |\mathbf{y}|\to\infty\ , \tag{3.26}$$

$f(x,x')$ obeys the sum rule

$$\int_0^\infty dx'\int_0^\infty dx\, f(x,x')=-\frac{1}{8\pi^2\beta}\ . \tag{3.27}$$

In two dimensions one must replace $-1/8\pi^2\beta|\mathbf{y}|^3$ by $-1/2\pi^2\beta|\mathbf{y}|^2$ in Eq. (3.25). The sum rule (3.27) was obtained by Jancovici (1982b) from a direct linear-response argument. Its validity, as well as that of the asymptotic form (3.26), can be explicitly checked in the two-dimensional OCP at $\Gamma=2$ (Jancovici, 1982a). Federbush and Kennedy (1985) give a rigorous bound on the fall-off along the surface, of the form $C\cdot|\mathbf{y}|^{-(3-\varepsilon)}$, $\varepsilon>0$ ($\nu=3$). The derivation of Eqs. (3.9) and (3.25) presented here uses the same methods as in Jancovici, Lebowitz, and Martin (1985).

3. Image forces

We consider the case where the half-space $x<0$ is filled with a material that has a dielectric constant ε_w different from 1. A particle of charge e_α at the point $\mathbf{r}=(x,\mathbf{y})$ has an electrical image of charge $(1-\varepsilon_w)/(1+\varepsilon_w)e_\alpha=\Delta e_\alpha$ at the point $\bar{\mathbf{r}}=(-x,\mathbf{y})$. One must now include the effect of the images in Eq. (3.2), replacing $\mathbf{F}(q_1,q)$ by

$$\mathbf{F}_\Delta(q_1,q)=e_{\alpha_1}e_\alpha[\mathbf{F}(\mathbf{r}_1-\mathbf{r})+\Delta\mathbf{F}(\mathbf{r}_1-\bar{\mathbf{r}})]\ ,$$

$$\Delta=\frac{1-\varepsilon_w}{1+\varepsilon_w}\ , \tag{3.28}$$

i.e., the force exerted on a charge e_{α_1} at $\mathbf{r}_1$ by another charge e_α at $\mathbf{r}$ and its image at $\bar{\mathbf{r}}$. The electric field (2.13) produced by the excess charge density can be written as

$$\mathbf{E}_\Delta(\mathbf{r}_1 \mid Q) = \int d\mathbf{r}[\mathbf{F}(\mathbf{r}_1-\mathbf{r})+\Delta\mathbf{F}(\mathbf{r}_1-\bar{\mathbf{r}})]c(\mathbf{r} \mid Q)$$
$$= \int d\mathbf{r}\, \mathbf{F}(\mathbf{r}_1-\mathbf{r})c_\Delta(\mathbf{r} \mid Q) \;, \qquad (3.29)$$

where

$$c_\Delta(\mathbf{r} \mid Q) = c(\mathbf{r} \mid Q) + \Delta c(\bar{\mathbf{r}} \mid Q) \qquad (3.30)$$

is the excess charge density due to the system's particles and their images. In Eq. (3.29) the correlation functions have been defined to be identically zero when one or several arguments lie in the half-plane $x<0$, and the integral extends over the whole space. With this, the conditional Proposition 3.1 can be phrased in the same terms: the multipole moments of $c_\Delta(\mathbf{r} \mid Q)$ vanish if the clustering is fast in all directions. This implies, with definition (3.30), that

$$\int d\mathbf{r}\, \mathcal{Y}(\mathbf{r})c_\Delta(\mathbf{r} \mid Q) = (1\pm\Delta)\int d\mathbf{r}\, \mathcal{Y}^{\pm}(\mathbf{r})c(\mathbf{r} \mid Q) = 0 \;. \qquad (3.31)$$

The result holds with the upper sign when the harmonic polynomial $\mathcal{Y}(\mathbf{r})=\mathcal{Y}^{+}(\mathbf{r})$ is even under reflection with respect to the plane $x=0$, and with the lower sign when $\mathcal{Y}(\mathbf{r})=\mathcal{Y}(\bar{\mathbf{r}})$ is odd under this reflection $[\mathcal{Y}^{\pm}(x,\mathbf{y})=\pm\mathcal{Y}^{\pm}(-x,\mathbf{y})]$. If $\Delta\neq\pm1$, one finds again that all multipoles must vanish under the assumption of faster-than-algebraic decay.

For the whole range of positive and finite values of $\varepsilon_w(\Delta\neq\pm1)$, the surface properties of the fluid are the same as for $\varepsilon_w=1$. The dipole sum rule (3.9) holds, and is not affected by ε_w: this should be clear from its derivation, which involves a comparison with quantities pertaining to the bulk only. There is still a slow decay along the wall, the only difference being that the right-hand sides of Eqs. (3.25) and (3.27) must be multiplied by ε_w (Jancovici, 1982b).

The extreme case $\varepsilon_w=0$ $(\Delta=1)$ is also of interest: it mimics a situation where the fluid has an effective dielectric constant much larger than ε_w. Here, the electroneutrality sum rule is true by Eq. (3.31), but nothing can be concluded about the odd multipole moments of the excess charge density, in particular, on the x component of its dipole. Therefore, the sum rule (3.9), which can still be derived in the same manner, is no longer in contradiction with a good decay parallel to the wall. Also, the long tail in Eq. (3.25) (which is now multiplied by $\varepsilon_w=0$) disappears. This leads to the conjecture that, in this limiting case, the decay of the charge-charge correlations is faster than any inverse power in all directions. It turns out that the two-dimensional OCP at $\Gamma=2$ is solvable when $\varepsilon_w=0$ (Smith, 1982). One indeed verifies in this model that the sum rule (3.9) holds, the decay along the wall is exponentially fast (with damped oscillations), and all even-multipole moments of the excess charge density vanish, in conformity with Eq. (3.31) (Jancovici, 1982b).

4. Charged wall

We let the plane wall at $x=0$ be charged by a uniform surface charge density σ, creating an electrical field $E_0=2\pi(\nu-1)\sigma$, and ε_w is finite.[13] In addition to Eqs. (3.9) and (3.25), there are a number of other sum rules that can be seen to be a consequence of the screening of the plate by fluid layers of opposite charge. These sum rules, which we state here, have been checked in the two-dimensional OCP at $\Gamma=2$ (Jancovici, 1981b, 1982b; Smith, 1981).

The simplest case is the perfect screening of the plate by unit of surface. By symmetry, the particle densities depend only on x, and the integrated charge density profile satisfies

$$\int_0^\infty dx \left[\sum_\alpha e_\alpha \rho(\alpha,x)+c_b\right] = -\sigma \;. \qquad (3.32)$$

In the Debye regime the screening is expected to take place over a microscopic distance (as shown in the models).

The contact theorem relates the bulk pressure p to the particle densities at the wall. For a Coulomb gas $(c_b=0)$ in the presence of a charged hard wall without image forces $(\varepsilon_w=1)$, it takes the form (Henderson and Blum, 1978; Henderson, Blum, and Lebowitz, 1979)

$$p=\beta^{-1}\sum_\alpha \rho(\alpha,\mathbf{0})-\pi(\nu-1)\sigma^2 \;. \qquad (3.33)$$

If the particle α has a hard core of diameter d_α, the corresponding density must be taken at the point of contact $d_\alpha/2$. In a jellium system one must add to Eq. (3.33) a quantity involving the potential difference $\delta\phi$ across the surface layer (Choquard, Favre, and Gruber, 1980; Totsuji, 1981). For the OCP, the relation reads $(\varepsilon_w=1)$

$$p=\beta^{-1}\rho(\mathbf{0})-\pi(\nu-1)\sigma^2-c_b\delta\phi \;,$$
$$\delta\phi=2\pi(\nu-1)\int_0^\infty dx\, x\,[e\rho(x)+c_b] \;. \qquad (3.34)$$

In Eq. (3.34) the pressure p is defined (in the thermodynamic limit) as minus the derivative of the free energy with respect to the volume, while keeping the system globally neutral.[14] In the presence of image forces $(\varepsilon_w\neq1)$, there is still an additional term in Eqs. (3.33) and (3.34) that depends on ε_w and on the two-point correlation (Carnie and Chan, 1981b; Jancovici, 1982b).

There is a sum rule that relates the dipole moment of the excess charge carried by a particle $q=(\alpha,\mathbf{r})$ to the variation of its density $\rho(q)$ with respect to the external

[13]A second electrode carrying a surface charge $-\sigma$ is located at $x=+\infty$.

[14]Namely, for N charges in a volume V, $c_b=-Ne/V$ is also subject to the volume change.

electrical field $E_0=2\pi(\nu-1)\sigma$ (Blum *et al.*, 1981):

$$\frac{\partial}{\partial E_0}\rho(q)=\beta\int_{x_1\geq 0}d\mathbf{r}_1 x_1 c(\mathbf{r}_1\mid q)$$
$$=\beta\int_{x_1\geq 0}dq_1 e_{\alpha_1}(x_1-x)\rho_T(q_1,q)\ . \qquad (3.35)$$

The second equality follows from definition (1.21) and the charge sum rule. This relation can be considered to be a more detailed statement than the dipole sum rule (3.9). Indeed, differentiating Eq. (3.32) with respect to σ, and inserting Eq. (3.35), leads immediately to the result (3.9).

We can deduce from Eqs. (3.35) and (3.33) a constraint on the truncated functions when a particle is at the wall. Since the bulk pressure is independent of σ, differentiating Eq. (3.33) with respect to σ gives

$$\sum_\alpha \frac{\partial}{\partial\sigma}\rho(\alpha,\mathbf{0})=2\pi(\nu-1)\beta\sigma\ , \qquad (3.36)$$

and, inserting Eq. (3.35),

$$\sum_\alpha \int_{x_1\geq 0}dq_1 e_{\alpha_1}x_1\rho_T(\alpha_1,\mathbf{r}_1,\alpha,\mathbf{0})=\sigma\ . \qquad (3.37)$$

This holds when $c_b=0$. In particular, it is interesting to see that when $\sigma=0$, the dipoles of the screening clouds of positive and negative charges at the wall compensate each other exactly. The analogous relation for a jellium system includes an additional contribution due to the background, and can be found in Blum *et al.* (1983).

Finally, Rosinberg, Lebowitz, and Blum (1986) have presented a solvable model of localized adsorption at the wall. Here the wall acquires a surface charge by adsorption of ions: the effect of an absorptive site is represented by an effective attractive δ-function potential.

D. Other geometries

The implications of the Carnie-Chan relation (3.4) can be worked out for plasmas confined in varied geometries (Jancovici, Lebowitz, and Martin, 1985). In the cases described below, the walls are always insulating, with dielectric constant $\varepsilon_w=1$.

We first consider a slab of thickness a. With the same notation as for the plane wall, the two-dimensional Fourier transform of $S(x,\mathbf{y}\mid x')$ along the slab faces (located at $x=0$ and $x=a$) satisfies Eq. (3.20), the only difference being that the x and x' integrals extend on the thickness of the slab a. No subtraction is needed here and the equivalent of the behaviors (3.24) and (3.25) are

$$\int_0^a dx'\int_0^a dx\ \tilde{S}(x,\mathbf{k}\mid x')=\frac{|\mathbf{k}|}{2\pi\beta}+o(|\mathbf{k}|)\ , \qquad (3.38)$$

$$\int_0^a dx'\int_0^a dx\ S(x,\mathbf{y}\mid x')=-\frac{1}{4\pi^2\beta}\frac{1}{|\mathbf{y}|^3}\ ,$$
$$|\mathbf{y}|\to\infty\ . \qquad (3.39)$$

This decay is typical for a bidimensional electron film interacting with the three-dimensional Coulomb potential. The strip geometry is studied in detail by Forrester and Smith (1982), Forrester, Jancovici, and Smith (1983), and Choquard, Forrester, and Smith (1983).

We consider next a fluid confined in a cylinder with a cross section of arbitrary shape Σ. The z axis is along the cylinder and we write $\mathbf{r}=(\mathbf{R},z)$, where $\mathbf{R}$ stands for the components of $\mathbf{r}$ perpendicular to the cylinder axis. In terms of the one-dimensional Fourier transform

$$\tilde{S}(\mathbf{R},k\mid\mathbf{R}')=\int_{-\infty}^{\infty}dz\ e^{ikz}S(\mathbf{R},z\mid\mathbf{R}')\ , \qquad (3.40)$$

Eq. (3.4) becomes

$$-\lim_{|\mathbf{k}|\to 0}2\beta\ln|k|\int_\Sigma d\mathbf{R}'\int_\Sigma d\mathbf{R}\,\tilde{S}(\mathbf{R},k\mid\mathbf{R}')=1\ , \qquad (3.41)$$

where we have used the small-k behavior of the partial Fourier transform

$$\int_{-\infty}^{\infty}dz\ e^{ikz}\frac{1}{\sqrt{z^2+|\mathbf{R}|^2}}=2K_0(k\,|\mathbf{R}|)$$
$$\simeq-2\ln(|k|\,|\mathbf{R}|)\ ,$$
$$|k|\to 0\ . \qquad (3.42)$$

This leads to the asymptotic behavior along the cylinder axis

$$\int_\Sigma d\mathbf{R}'\int_\Sigma d\mathbf{R}\,S(\mathbf{R},z\mid\mathbf{R}')\simeq-\frac{1}{4\beta|z|(\ln|z|)^2}\ ,$$
$$|z|\to\infty\ . \qquad (3.43)$$

Because of this slow decay only the charge sum rule holds in the cylinder, and the higher-order multipoles of the excess charge density are not defined (see Jancovici and Artru, 1983, where the cases $\varepsilon_w\neq 1$ are also discussed). As in the plane wall case, the expressions (3.39) and (3.43) are the leading asymptotic terms provided that the Fourier transform of S has no singularities for real $\mathbf{k}$ ($\mathbf{k}\neq 0$) which may give rise to longer oscillating tails.

The properties of a plasma in a wedge (formed by two half-planes intersecting along the z axis, with an angle ϑ) have been investigated by Jancovici, Lebowitz, and Martin (1985), and Choquard, Piller, Rentsch and Vieillefosse (1988). The results are not yet conclusive. In the first work, one assumes that the infinitely extended integrals on $\mathbf{R}$ and $\mathbf{R}'$ are convergent after appropriate substractions of bulk and plane wall contributions, and one finds a decay in the z direction ($0<\vartheta<\pi$) similar to that of the cylinder, Eq. (3.43). In the second work; a Debye-Hückel type of approximation leads to a power-law decay, where the power depends on the angle ϑ of the wedge.

E. Interface between two conducting media

1. The two-densities OCP

A plane interface at $x=0$, between two charged fluids, can be represented by a OCP with a background $c_b(\mathbf{r})=c_b(x)$ [$\mathbf{r}=(x,\mathbf{y})$] having two different (asymptotic) densities in the half-spaces $x>0$ and $x<0$:

$$\lim_{x\to\infty} c_b(x)=c_b^+, \quad \lim_{x\to-\infty} c_b(x)=c_b^- . \tag{3.44}$$

The system is uniform in the directions $\mathbf{y}$ parallel to the interface, and asymptotically neutral as $x\to\pm\infty$. The charged particles adjust their density to interpolate between c_b^+ and c_b^-. Examples of this system have been provided in the two-dimensional OCP at $\Gamma=2$. Jancovici (1984) has considered a background that is a step function at $x=0$. Blum (1984) has treated the case of a metal-metal junction or semiconductor junction, where the interface between the two different media is separated by a charged gap. A class of smoothly varying backgrounds satisfying Eq. (3.44) is introduced by Alastuey and Lebowitz (1984). It is found in these models (and also by weak coupling calculations) that the correlations decay faster than any inverse power in all directions, including those parallel to the interface, and various sum rules given below can be explicitly checked. In this situation, according to the general theorems, all multipole sum rules are true, as well as the Carnie-Chan relation (3.4) and its generalization (3.8). We now discuss some forms of the sum rules that are specific to the geometry of the interface.

One has first the overall neutrality of the charge-density profile:

$$\int_{-\infty}^{\infty} dx\, c(x)=0, \quad c(x)=e\rho(x)+c_b . \tag{3.45}$$

The electrostatic potential [determined by $\Delta\phi(x)=-2\pi(\nu-1)c(x)$, $\nu=2,3$] verifies the electrochemical balance equation (Ballone, Senatore, and Tosi, 1981a, 1981b; Rosinberg, Badiali, and Goodisman, 1983)

$$\begin{aligned}&\mu(\rho^+)-\mu(\rho^-)+e[\phi(\infty)-\phi(-\infty)]=0 ,\\ &\rho^\pm=\left|\frac{c_b^\pm}{e}\right| ,\end{aligned} \tag{3.46}$$

where $\mu(\rho)$ is the chemical potential in the bulk phase of density ρ, and

$$\phi(\infty)-\phi(-\infty)=2\pi(\nu-1)\int_{-\infty}^{\infty} dx\, xc(x) \tag{3.47}$$

is the potential drop across the interface.

The fluid obeys two dipole sum rules analogous to Eq. (3.9) in the half-spaces $x>0$ and $x<0$:

$$\begin{aligned}&2\pi(\nu-1)\beta\int_{-\infty}^{\infty} dx'\int_{x\geq 0} d\mathbf{r}\, xS(\mathbf{r}\mid\mathbf{r}')=-1 ,\\ &2\pi(\nu-1)\beta\int_{-\infty}^{\infty} dx'\int_{x\leq 0} d\mathbf{r}\, xS(\mathbf{r}\mid\mathbf{r}')=1 .\end{aligned} \tag{3.48}$$

They can be derived, as was Eq. (3.9), by a comparison as $x\to\infty$ (respectively, $x\to-\infty$), with a uniform OCP of density ρ^+ (respectively, ρ^-). Notice that the two equations (3.48), once added, are compatible with the usual dipole sum rule (3.3) for $l=1$.

It is interesting to remark that two additional dipole sum rules are true at a conducting interface, and are not equivalent to Eq. (3.48):

$$\begin{aligned}&2\pi(\nu-1)\beta\int_{-\infty}^{\infty} dx'x'\int_{x\geq 0} d\mathbf{r}\, S(\mathbf{r}\mid\mathbf{r}')=1 ,\\ &2\pi(\nu-1)\beta\int_{-\infty}^{\infty} dx'x'\int_{x\leq 0} d\mathbf{r}\, S(\mathbf{r}\mid\mathbf{r}')=-1 .\end{aligned} \tag{3.49}$$

One gets the first Eq. (3.49) by adding and subtracting the same bulk quantity, with the function $S^+(\mathbf{r}-\mathbf{r}')$ corresponding to the density ρ^+

$$\int_{-\infty}^{\infty} dx'x'\int_{x\geq 0} d\mathbf{r}\, S(\mathbf{r}\mid\mathbf{r}')=\int_{-\infty}^{\infty} dx'x'\int_{x\geq 0} d\mathbf{r}[S(\mathbf{r}\mid\mathbf{r}')-S^+(\mathbf{r}-\mathbf{r}')]+\int_{-\infty}^{\infty} dx'x'\int_{x\geq 0} d\mathbf{r}\, S^+(\mathbf{r}-\mathbf{r}') . \tag{3.50}$$

Since $S(\mathbf{r}\mid\mathbf{r}')$ approaches $S^+(\mathbf{r}-\mathbf{r}')$ as both x and x' are large [see assumption (3.10)], we can interchange the integrals in the first term of Eq. (3.50). Then this term vanishes because of the usual dipole sum rule, which holds for $S(\mathbf{r}\mid\mathbf{r}')$ and $S^+(\mathbf{r}-\mathbf{r}')$. The second term of Eq. (3.50) is easily seen to be equal to

$$-\tfrac{1}{2}\int d\mathbf{r}\, x^2S^+(\mathbf{r})=\frac{1}{2\pi(\nu-1)\beta}$$

by the bulk second-moment condition (1.29). This gives the first Eq. (3.49); the second one is established in the same way. Equations (3.49) are also a consequence of the sum rule (3.8), when one specializes it to $l=1$ and to the geometry of the interface (Jancovici, 1986).

2. Metallic wall

A metallic interface is also obtained if one considers a fluid in the half-space $x\geq 0$ in contact with an ideal conductor plane wall at $x=0$ ($\varepsilon_w=\infty$). The correlations are expected to have a decay faster than any inverse power law in all directions. This has been verified in the two-dimensional OCP at $\Gamma=2$ by Forrester (1986), where sum rules reported below can also be checked.[15] Here the situation is as follows. According to the discussion of the image forces of Sec. III.C, when $\varepsilon_w=\infty$ (i.e., $\Delta=-1$)

[15]The fast decay is also supported by weak coupling theories (Onsager and Samaras, 1934; Alastuey, 1983).

only the odd multipoles of the system's excess charge density have to vanish. In particular, the $l=0$ charge sum rule (3.3) is not valid here. This implies that, disregarding the image charges, the screening cloud of a particle near the wall is not complete. Electroneutrality is only recovered if the images are taken into account in the screening process.

However, since the usual dipole $l=1$ sum rule (3.3) holds, it is possible to derive, as before, the equivalent of the rule (3.49):

$$2\pi(\nu-1)\beta\int_0^\infty dx'x'\int_{x\geq 0} d\mathbf{r}\, S(\mathbf{r}\,|\,\mathbf{r}')=1\ , \tag{3.51}$$

but one should note that Eq. (3.9) is no longer true.

As far as the overall neutrality is concerned, it is only satisfied by the charge density of the fluid and its image[16]

$$\begin{aligned} &\int_{-\infty}^{\infty} dx\, c_\Delta(x)=0\ ,\\ &c_\Delta=c(x)-c(-x)\ ,\\ &c(x)=\sum_\alpha e_\alpha\rho(\alpha,x)+c_b\ . \end{aligned}\tag{3.52}$$

In fact, the region of the fluid close to the conducting wall (the double electric layer) may carry a nonvanishing surface charge given by

$$\sigma=\int_0^\infty dx\, c(x)\ . \tag{3.53}$$

This surface charge can be prescribed and considered as an external parameter in the system. Instead of σ, it is convenient to choose, as an independent parameter, the potential drop $\delta\phi$ across the double electric layer. This potential drop can be simply expressed in terms of the dipole of the charge density:

$$\delta\phi=\phi(\infty)-\phi(0)=2\pi(\nu-1)\int_0^\infty dx\, xc(x)\ . \tag{3.54}$$

Then one can establish a sum rule that relates the total excess charge density carried by a particle $q=(\alpha,\mathbf{r})$ to the variation of its density $\rho(q)$ with respect to $\delta\phi$ (Forrester, 1985; Jancovici, 1986):

$$\frac{\partial}{\partial(\delta\phi)}\rho(q)=\beta\int_{x_1\geq 0} d\mathbf{r}_1 c(\mathbf{r}_1\,|\,q)\ . \tag{3.55}$$

This is the analog, for a conducting wall, of Eq. (3.35) which was for the insulating charged wall. If one differentiates Eq. (3.54) with respect to $\delta\phi$, and inserts Eq. (3.55), one recovers the rule (3.51).

Two limiting cases of the two-densities OCP (3.44) are of interest. In the first case, one lets the background density c_b^- tend to infinity in the half-space $x<0$. Since the Debye length $\lambda^-=[2\pi(\nu-1)\beta e^2 c_b^-]^{-1/2}$ will vanish in the region $x<0$, this region is expected to behave as a perfectly conducting medium. This will produce the effect of a metallic wall for the fluid particles in the region $x>0$, provided that they are prevented from moving across the interface. One introduces a model (the ideally polarizable interface) where an impermeable membrane is set up between the two media (Rosinberg and Blum, 1984). Then it is possible to show, in the two-dimensional OCP at $\Gamma=2$, that the infinite density limit $c_b^-\to\infty$ indeed corresponds to the metallic wall boundary for the fluid in the region $x>0$ (Alastuey *et al.*, 1985).

In the second case one lets the density c_b^- tend to zero in the half-space $x<0$: the fluid particles have a permeable boundary at $x=0$ through which they can evaporate, but there is no neutralizing background for $x<0$ (Ballone, Senatore, and Tosi, 1981b). One shows that the particle density tends to zero only as $|x|^{-2}(\nu=3)$ as $x\to-\infty$. The overall neutrality is satisfied:

$$e\int_{-\infty}^0 dx\,\rho(x)+\int_0^\infty dx[e\rho(x)+c_b^+]=0\ . \tag{3.56}$$

The truncated correlation $\rho_T(x,x',\mathbf{y})$ has an algebraic decay as $x\to-\infty$ ($x',\mathbf{y}$ fixed) or as $\mathbf{y}\to\infty$ (x,x' fixed), which is sufficient to ensure that the charge and the dipole sum rule hold for the excess charge density, but the higher-order multipoles are not defined. Thus the screening in this permeable boundary is more efficient than in an insulating hard wall, but not as strong as in a metallic interface (Alastuey and Lebowitz, 1984; Jancovici, 1984).

F. WLMB Equations and long-range order

1. The WLMB equations

In addition to the equilibrium equations (3.2), there is another set of exact relations between the correlations that proves useful for the study of inhomogeneous fluids. They are a generalization, to charged systems, of a set of equations, the WLMB (Wertheim, Lovett, Mou, and Buff) equations, that these authors have derived for neutral systems (Lovett, Mou, and Buff, 1976; Wertheim, 1976). The peculiarity of the WLMB equations is that they do not explicitly involve the intermolecular forces. They apply to semi-infinite systems, and relate the gradient of the density to an integral of the external force over the pair correlation function, plus a surface contribution of the finite-distance boundaries ∂D of the system:

$$\begin{aligned}\beta^{-1}\nabla_1\rho(q_1)=e_{\alpha_1}\mathbf{E}^{\text{ext}}(\mathbf{r}_1)\rho(q_1)+\int_D dq\, e_\alpha \mathbf{E}^{\text{ext}}(\mathbf{r})\rho_T(q,q_1)\\ -\beta^{-1}\int_{\partial D} d\mathbf{s}\,\rho_T(q,q_1)\ .\end{aligned}\tag{3.57}$$

In Eq. (3.57), $\mathbf{E}^{\text{ext}}(\mathbf{r}_1)$ is the part of the electric field (3.1) at $\mathbf{r}_1$ (when $V\to D$) that is due only to the external charge distribution (thus disregarding the system's charges), and $\int_{\partial D} d\mathbf{s}$ means integration over the surface ∂D and summation over the species α.

The WLMB equation can be deduced from the equilibrium equations (3.2) in a few lines. Integrating both members of Eq. (3.2) over the region D one gets (with $Q=\{q_2\}$)

[16]One defines $c(x)=0$ for $x<0$, since the wall is assumed to be impermeable to the fluid particles.

$$\beta^{-1}\int_{\partial D} d\mathbf{s}_1\rho_T(q_1,q_2) = \int_D dq_1\rho(q_1)e_{\alpha_1}\mathbf{E}(\mathbf{r}_1\mid q_2) + \int_D dq_1[e_{\alpha_1}\mathbf{E}(\mathbf{r}_1)+\mathbf{F}(q_1,q_2)]\rho_T(q_1,q_2) , \quad (3.58)$$

since the joint integral

$$\int dq_1\int dq_2\mathbf{F}(q_1,q_2)\rho_T(q_1,q_2,q)=0 \quad (3.59)$$

vanishes as a consequence of the antisymmetry of the force $\mathbf{F}(q_1,q)=-\mathbf{F}(q,q_1)$. Using the definitions (2.13) and (1.21) of $\mathbf{E}(\mathbf{r}_1\mid q_2)$ and of the excess charge density, the first term on the RHS of Eq. (3.58) can be written as

$$\begin{aligned}\int_D dq_1\rho(q_1)e_{\alpha_1}\mathbf{E}(\mathbf{r}_1\mid q_2)&=\int_D dq_1\rho(q_1)\int_D dq\,\mathbf{F}(q_1,q)\rho_T(q\mid q_2)\\ &=-\int_D dq\int_D dq_1\mathbf{F}(q,q_1)\rho(q_1)\rho_T(q\mid q_2)\\ &=-\int_D dq\,e_\alpha\mathbf{E}^{\rm sys}(\mathbf{r})\rho_T(q\mid q_2)\\ &=-\int_D dq\,e_\alpha[\mathbf{E}(\mathbf{r})-\mathbf{E}^{\rm ext}(\mathbf{r})][\rho_T(q,q_2)+\delta_{q,q_2}\rho(q_2)] .\end{aligned} \quad (3.60)$$

To obtain Eq. (3.60), one interchanges the q and q_1 integrals, and notices that

$$\int_D dq_1\mathbf{F}(q,q_1)\rho(q_1)=e_\alpha\int_D d\mathbf{r}_1\mathbf{F}(\mathbf{r}-\mathbf{r}_1)\sum_{\alpha_1}e_{\alpha_1}\rho(\alpha_1,\mathbf{r}_1)=e_\alpha\mathbf{E}^{\rm sys}(\mathbf{r}) , \quad (3.61)$$

where $E^{\rm sys}(\mathbf{r})$ is the part of the total electric field at $\mathbf{r}$ that is due to the system's charges only [see Eq. (3.1)]. When Eq. (3.60) is inserted into Eq. (3.58) one finds

$$\beta^{-1}\int_{\partial D} d\mathbf{s}_1\rho_T(q_1,q_2)=e_{\alpha_2}\mathbf{E}^{\rm ext}(\mathbf{r}_2)\rho(q_2)+\int_D dq\,e_\alpha\mathbf{E}^{\rm ext}(\mathbf{r})\rho_T(q,q_2)-e_{\alpha_2}\mathbf{E}(\mathbf{r}_2)\rho(q_2)-\int_D dq\,\mathbf{F}(q_2,q)\rho_T(q_2,q) . \quad (3.62)$$

The WLMB equation (3.57) results when one remarks that the combination of the last two terms of Eq. (3.62) equals $-\beta^{-1}\nabla_2\rho(q_2)$ by the first equation of the BGY hierarchy. In fact, Eq. (3.57) is a member of a WLMB hierarchy, which reads, for a general $Q=\{q_1,\ldots,q_n\}$,

$$\beta^{-1}\sum_{j=1}^n\nabla_j\rho(Q)=\sum_{j=1}^n e_{\alpha_j}\mathbf{E}^{\rm ext}(\mathbf{r}_j)\rho(Q)+\int_D dq\,e_\alpha\mathbf{E}^{\rm ext}(\mathbf{r})[\rho(q,Q)-\rho(q)\rho(Q)]-\beta^{-1}\int_{\partial D}d\mathbf{s}[\rho(q,Q)-\rho(q)\rho(Q)] . \quad (3.63)$$

The derivation (3.58)–(3.62) is formal, insofar as the convergence of integrals has to be discussed in relation with the cluster properties, and the exchange of integrals in Eq. (3.60) has to be justified. This can be done in a number of inhomogeneous situations under assumptions that are compatible with the findings of Sec. III.C (Blum *et al.*, 1983). We give some applications.

2. The charged wall

We consider again the case of a Coulomb fluid without background ($c_b=0$), in the vicinity of a plane wall at $x=0$ carrying a uniform charge density σ. Notation is the same as in Sec. III.C, and $\varepsilon_w=1$. Because of the uniform charge distribution on the electrodes, the external electric field $E^{\rm ext}=2\pi(\nu-1)\sigma$ is constant for $x>0$.[17] Taking into account the charge sum rule and the translation invariance along the wall, only the surface integral contributes in Eq. (3.57), and the WLMB equation simplifies to $[\mathbf{r}=(x,\mathbf{y})]$

$$\frac{\partial}{\partial x_1}\rho(\alpha_1,x_1)=\int d\mathbf{y}\sum_\alpha\rho_T(\alpha,\mathbf{y},\alpha_1,x_1) . \quad (3.64)$$

From there one can easily recover the sum rule (3.37). By integration one first obtains the charge density at x

$$\sum_{\alpha_1}e_{\alpha_1}\rho(\alpha_1,x) = -\int_x^\infty dx_1\int d\mathbf{y}_1\sum_{\alpha\alpha_1}e_{\alpha_1}\rho_T(\alpha_1,x_1,\mathbf{y}_1,\alpha,\mathbf{0}) . \quad (3.65)$$

Integrating again over x from 0 to ∞, the left-hand side of Eq. (3.65) yields $-\sigma$ by the electroneutrality rule (3.32), whereas the right-hand side gives the same expression as in Eq. (3.37), after an integration by parts.

3. Symmetry breaking and long-range order

Interesting information can be obtained, from the WLMB equations, on the conditions under which a crystalline phase may be formed. It is well known that the spontaneous breaking of a continuous group (e.g., the group of space translations) is accompanied by the occurrence of long-range order in the system, which manifests itself by a slow (nonexponential) decay of the corre-

[17] A second electrode carrying a surface charge $-\sigma$ is located at $x=+\infty$.

lations. This is due to the existence of excitations in the system (here, the phonons) which can have vanishingly small energies. It is therefore of interest to know what kind of decay of the correlations is expected in a phase of charged particles that spontaneously breaks the translation invariance. To this end one notes that when the system has no boundaries ($D=\mathbb{R}^\nu$), and no external disturbances are present [$\mathbf{E}^{\text{ext}}(\mathbf{r})=\mathbf{0}$], the WLMB hierarchy (3.63) formally reduces to

$$\sum_{j=1}^{n} \nabla_j \rho(q_1,\ldots,q_n)=0 , \qquad (3.66)$$

which means that all correlation functions are translation invariant. This assertion is, of course, subjected to the clustering assumptions that are needed to rigorously establish the WLMB equations. A precise statement is formulated in Proposition 3.2 below (Gruber and Martin, 1980b). A state is periodic if it is invariant under some discrete subgroup of the translations generated by ν independent vectors $\{\mathbf{e}_1,\ldots,\mathbf{e}_\nu\}$ (Bravais lattice), i.e.,

$$\rho(\alpha_1,\mathbf{r}_1,\ldots,\alpha_n,\mathbf{r}_n)=\rho(\alpha_1,\mathbf{r}_1+\mathbf{e}_j,\ldots,\alpha_n,\mathbf{r}_n+\mathbf{e}_j) , \quad j=1,\ldots,\nu . \qquad (3.67)$$

It is locally neutral if the charge of the (Wigner-Seitz) cell Δ associated with $\{\mathbf{e}_1,\ldots,\mathbf{e}_\nu\}$ is zero:

$$\int_\Delta d\mathbf{r}\left[\sum_\alpha e_\alpha \rho(\alpha,\mathbf{r})+c_b\right]=0 . \qquad (3.68)$$

Proposition 3.2. Assume that there are no external charges (except for a uniform background in jellium systems). Then, in dimension $\nu\geq 2$, any periodic and locally neutral state that satisfies the clustering conditions

$$|d^\eta \rho_T(q_1,\ldots q_n)|\leq M,\quad d=\sup_{i,j}|\mathbf{r}_i-\mathbf{r}_j|,\quad \eta>\nu+1 , \qquad (3.69)$$

$$\int dq_1\int dq_2\,|\rho_T(q_1,q_2,q_3,\ldots,q_n)|<\infty , \qquad (3.70)$$

is necessarily invariant under the full translation group.

Proof. In the derivation (3.58)–(3.62) of the WLMB equation, condition (3.70) ensures that the joint integral (3.59) is absolutely convergent (and thus vanishes). The exchange of integrals in Eq. (3.60) can be justified as follows. We first limit the $\mathbf{r}_1$ integral in Eq. (3.60) to a sphere of radius R. One has to show that the following limit

$$\int dq_1\int dq\,\mathbf{F}(q_1,q)\rho(q_1)\rho_T(q\,|\,q_2)=\lim_{R\to\infty}\int dq\left\{\int_{|\mathbf{r}_1|\leq R} d\mathbf{r}_1[\mathbf{F}(\mathbf{r}_1-\mathbf{r})-\mathbf{F}(\mathbf{r}_1)]\left[\sum_{\alpha_1} e_{\alpha_1}\rho(\alpha_1,\mathbf{r}_1)\right]\right\}e_\alpha \rho_T(q\,|\,q_2) \qquad (3.71)$$

exists, and gives the final expression (3.60). The subtracted term in large curly brackets has been introduced to improve the convergence of the $\mathbf{r}_1$ integral. It does not contribute to Eq. (3.71) because of the charge sum rule, which holds under assumption (3.69). Consider first the case where $c_b=0$. Then $\mathbf{E}^{\text{ext}}(\mathbf{r})=0$, and $\sum_{\alpha_1} e_{\alpha_1}\rho(\alpha_1,\mathbf{r}_1)=c(\mathbf{r}_1)$ is the total charge density. It is not difficult to show that if $c(\mathbf{r}_1)$ is periodic and locally neutral,

$$\lim_{R\to\infty}\int_{|\mathbf{r}_1|\leq R} d\mathbf{r}_1[\mathbf{F}(\mathbf{r}_1-\mathbf{r})-\mathbf{F}(\mathbf{r}_1)]c(\mathbf{r}_1) =\mathbf{E}^{\text{sys}}(\mathbf{r})=\mathbf{E}(\mathbf{r}) \qquad (3.72)$$

converges to the periodic electric field due to this charge density and the large brackets in Eq. (3.71) in $O(|\mathbf{r}|)$ uniformly with respect to R.[18] With assumption (3.69) the limit can be taken under the integral sign in Eq. (3.71) by dominated convergence. This establishes the validity of Eq. (3.57), which reduces in this case to $\nabla_1\rho(q_1)=0$. Thus the density is constant.

If $c_b\neq 0$, the system's charge density $\sum_{\alpha_1} e_{\alpha_1}\rho(\alpha_1,\mathbf{r}_1)=c(\mathbf{r}_1)-c_b$ differs from $c(\mathbf{r}_1)$ by the constant c_b. The contribution of the uniform background

$$\lim_{R\to\infty}\int_{|\mathbf{r}_1|\leq R} d\mathbf{r}_1[\mathbf{F}(\mathbf{r}_1-\mathbf{r})-\mathbf{F}(\mathbf{r}_1)]c_b=\frac{2\pi(\nu-1)}{\nu}c_b\mathbf{r} \qquad (3.73)$$

is linear in $\mathbf{r}$, and the limit $R\to\infty$ can be taken under the integral sign in Eq. (3.71) for the same reasons as above.[19] This gives

$$\beta^{-1}\nabla_1\rho(q_1)=\frac{2\pi(\nu-1)}{\nu}c_b \times\left[e_{\alpha_1}\mathbf{r}_1\rho(q_1)+\int dq\,e_\alpha \mathbf{r}\rho_T(q,q_1)\right] . \qquad (3.74)$$

The right-hand side of Eq. (3.74) is again equal to zero, because of the dipole sum rule that holds under condition (3.69). The same arguments apply to the higher-order correlations, leading to the translation invariance (3.66) in all cases.

One concludes from this analysis that the correlations in an ionic crystal cannot decay faster than $|\mathbf{r}|^{-(\nu+1)}$ in dimensions $\nu=2,3$. This lower bound is probably not optimal. In the two-dimensional OCP, it has been im-

[18]Lemma 2 in Gruber and Martin (1980b).

[19]The proof is not dependent on the choice of a sequence of spheres in Eq. (3.71). With a sequence of dilatations of an arbitrary fixed volume, one would always get a linear function of $\mathbf{r}$ in Eq. (3.73) and the conclusions are the same.

proved to $|\mathbf{r}|^{-2}$ with the help of a refined version of the Mermin argument (Martinelli and Merlini, 1984). In a two-dimensional OCP of electrons interacting with the $1/|\mathbf{r}|$ potential, it has been shown that crystalline order is destroyed by transverse long-wavelength phonons (Alastuey and Jancovici, 1981b).

If one includes the rotation group in the analysis, one obtains that the state is invariant under the full Euclidean group, if it clusters faster than $|\mathbf{r}|^{-(\nu+2)}$ for $\nu=2,3$ (Gruber, Martin, and Oguey, 1982).

4. Periodic jellia

a. The one-dimensional OCP with uniform background

The one-dimensional OCP of point charges e, with a uniform background c_b, has the remarkable property of yielding states that are nontrivially periodic for all temperatures, yet exponentially clustering (Kunz, 1974). The occurrence of the period $a=ec_b^{-1}$ is easily understood in the ground state, where the minimal electrostatic energy is obtained by locating the charges equidistant, each of them neutralizing a background segment of length ec_b^{-1}. The point is that there is only one longitudinal excitation mode that does not vanish in the long-wavelength limit (but equals the plasmon frequency $2e^2\rho/m$). For lack of low-energy excitations, the order is not destroyed by thermal fluctuations.

Since the electric field due to the background is $E^{\mathrm{ext}}(x)=2xc_b$, the one-dimensional OCP obeys the nontrivial WLMB equations (3.63)

$$\beta^{-1}\sum_{j=1}^{n}\frac{\partial}{\partial x_j}\rho(x_1,\ldots,x_n)=2c_b\int dx\, xc(x\mid x_1,\ldots,x_n)\;, \qquad (3.75)$$

where $c(x\mid x_1,\ldots,x_n)$ is the excess charge density (1.21). This shows that the dipole sum rule (2.35) does not hold, a situation that is possible in one dimension, even if there is exponential clustering (see the remark after Proposition 2.2). However, if one introduces the averaged correlations on a cell Δ ($|\Delta|=a$)

$$\bar{\rho}(x_1,\ldots,x_n)=\frac{1}{a}\int_\Delta dx\,\rho(x_1+x,\ldots,x_n+x)\;,$$

one deduces immediately, from Eq. (3.75) and the charge sum rule, that the averaged excess density obeys the dipole sum rule

$$\int dx\, x\bar{c}(x\mid x_1,\ldots,x_n)=0\;. \qquad (3.76)$$

With the help of Eq. (3.76), it is not hard to prove that the averaged structure function $\bar{S}(x)$ verifies the Stillinger-Lovett second-moment condition (1.29). The one-dimensional OCP, although periodic, is in the plasma phase for all temperatures.

The several-component one-dimensional jellium, with charges e_α that are multiple integers of a common charge, is also solvable (Lugrin and Martin, 1982). The state is a periodic plasma phase with period $a=ec_b^{-1}$, where e is the greatest common divisor of the charges e_α.

b. Two- and three-dimensional OCP with periodic background

At high temperatures, the two- or three-dimensional OCP with uniform background is in a translation-invariant plasma phase that satisfies all sum rules [case (c) of Sec. II.A]. If the background charge density $c_b(\mathbf{r})$ is nontrivially periodic (representing the effect of a ionic lattice), one expects that, at sufficiently high temperatures, the electrons still form a fluid plasma phase (although not homogeneous), and that the correlations have a fast decay. In this case the dipole sum rule holds according to Proposition 3.1, and this periodic OCP verifies the second-moment condition (Appendix). Moreover, it satisfies the WLMB equations (3.63)

$$\beta^{-1}\sum_{j=1}^{n}\nabla_j\rho(\mathbf{r}_1,\ldots,\mathbf{r}_n)=\int d\mathbf{r}\,\mathbf{E}^{\mathrm{ext}}(\mathbf{r})c(\mathbf{r}\mid\mathbf{r}_1,\ldots,\mathbf{r}_n)\;, \qquad (3.77)$$

where $\mathbf{E}^{\mathrm{ext}}(\mathbf{r})$ is the periodic electric field due to the background density $c_b(\mathbf{r})$. An example of this situation has been provided by Alastuey and Lebowitz (1984) in the two-dimensional OCP at $\Gamma=2$, with a background density $c_b(x)=c_b(x+na)$ (n integer), which is constant in the y direction and periodic in the x direction with period a. Cornu and Jancovici (1988) and Cornu, Jancovici, and Blum (1988) have been able to solve the fully periodic case $c_b(x,y)=c_b(x+na,y+mb)$ (n,m integers). The state is a plasma, and the correlations have a fast decay. As indicated in Sec. III.A, this two-dimensional system has a transition to a dielectric low-temperature phase with localized electrons.

G. Finite systems

By a finite system we mean a fluid in thermal equilibrium, confined in a finite domain V by impermeable walls. The particle configurations in V are assumed to have a fixed total charge $\int_V d\mathbf{r}\, C(\mathbf{r})=C_V$.[20] The surrounding medium may have a dielectric constant ε_w different from that of empty space ($\varepsilon_w\neq 1$).

The finite-volume structure function

$$S_V(\mathbf{r}\mid\mathbf{r}')=\langle C(\mathbf{r})C(\mathbf{r}')\rangle_V-\langle C(\mathbf{r})\rangle_V\langle C(\mathbf{r}')\rangle_V \qquad (3.78)$$

obviously verifies the relation

[20]The statistical ensemble is canonical with respect to the charge (no global charge fluctuations), but it may be canonical or grand canonical with respect to the particle numbers.

$$\int_V d\mathbf{r}\, S_V(\mathbf{r}\,|\,\mathbf{r}')=\int_V d\mathbf{r}' S_V(\mathbf{r}\,|\,\mathbf{r}')=0 \ . \tag{3.79}$$

Here this sum rule is not informative: it only reflects the fact that the total charge of the fluid in V is fixed, but it is not related to any kind of local screening properties. In general, no higher-order simple multipole sum rules exist in the finite system, because of surface polarization and shape-dependence effects.

1. The susceptibility tensor

Useful information on the behavior of the finite system can be obtained more conveniently from the study of the polarization fluctuations (the dielectric susceptibility tensor) defined by

$$\chi_V^{ij}=\frac{\beta}{V}[\langle P^i P^j\rangle_V-\langle P^i\rangle_V\langle P^j\rangle_V] \ , \tag{3.80}$$

where

$$P^i=\int_V dr\, r^i C(\mathbf{r}), \quad i=1,\ldots,\nu \tag{3.81}$$

is the total polarization in the system. In linear-response theory, and when the external space is empty ($\varepsilon_w=1$), the tensor χ_V relates the average polarization to a constant external applied field $\mathbf{E}_0$:

$$\langle P^i\rangle_V=\sum_{j=1}^{\nu}\chi_V^{ij}E_0^j \ . \tag{3.82}$$

According to the above definitions, using Eq. (3.79) and the formula

$$r_1^i r_2^j=-\tfrac{1}{2}(r_1^i-r_2^j)^2+\tfrac{1}{2}[(r_1^i)^2+(r_2^j)^2] \ , \tag{3.83}$$

the tensor χ_V can be written in two different, but equivalent, forms:

$$\begin{aligned}\chi_V^{ij}&=\frac{\beta}{V}\int_V d\mathbf{r}_1\int_V d\mathbf{r}_2 r_1^i r_2^j S_V(\mathbf{r}_1\,|\,\mathbf{r}_2)\\ &=-\frac{\beta}{2V}\int_V d\mathbf{r}_1\int_V d\mathbf{r}_2(r_1^i-r_2^j)^2 S_V(\mathbf{r}_1\,|\,\mathbf{r}_2) \ .\end{aligned} \tag{3.84}$$

The second expression (3.84) is like a second-moment formula. On the grounds that $S_V(\mathbf{r}\,|\,\mathbf{r}')$ converges as $V\to\mathbb{R}^\nu$ to the homogeneous bulk function $S(\mathbf{r}-\mathbf{r}')$, one may be tempted to conclude formally that the limit of the diagonal components $\chi_V^i=\chi_V^{ii}$ are equal to

$$-\frac{\beta}{2}\int d\mathbf{r}\,|\,r^i\,|^2 S(\mathbf{r})=\frac{1}{2\pi(\nu-1)}, \quad i=1,\ldots,\nu \ ,$$

by the bulk second-moment condition (1.29). This is not the case: the dielectric susceptibility embodies surface effects, and its limit is shape dependent.

The correct value of the dielectric susceptibility is predicted by the findings of macroscopic electrostatics for homogeneously polarizable systems. Here, one considers only elliptic ($\nu=2$) and ellipsoidal ($\nu=3$) domains, with the limiting situations, the strip ($\nu=2$), the slab, and the cylinder ($\nu=3$). With each of these domains is associated a dilatation-invariant quantity, the depolarization tensor T_V, generally defined by[21]

$$\begin{aligned}&T_V^{ij}=-\frac{1}{2\pi(\nu-1)}\int_V d\mathbf{r}\frac{\partial^2}{\partial r^i\partial r^j}\phi^c(\mathbf{r}) \ ,\\ &\sum_{i=1}^{\nu}T_V^{ii}=1 \ ,\end{aligned} \tag{3.85}$$

where $\phi^c(\mathbf{r})$ is the Coulomb potential. In the reference frame defined by the axis of the ellipsoid, both tensors χ_V and T_V are diagonal, with diagonal elements χ_V^i and T_V^i, $i=1,\ldots,\nu$. Then, in the case where there are no image forces ($\varepsilon_w=1$), electrostatics give the following relation between the dielectric constant ε of the fluid and the components of the dielectric susceptibility (Choquard, Piller, and Rentsch, 1985):

$$\varepsilon=\frac{1+2\pi(\nu-1)(1-T_V^i)\chi_V^i}{1-2\pi(\nu-1)T_V^i\chi_V^i}, \quad i=1,\ldots,\nu \ . \tag{3.86}$$

One concludes from Eq. (3.86) that in the plasma (or perfectly conducting) phase characterized by $\varepsilon=\infty$, one must have

$$\chi_V^i=\frac{1}{2\pi(\nu-1)T_V^i} \ . \tag{3.87}$$

This has to be contrasted with the bulk second-moment value $[2\pi(\nu-1)]^{-1}$.

Let us examine some special cases. For a sphere or disk, the depolarization tensor is isotropic, with $T_{\text{sphere}}^i=1/\nu$, thus giving

$$\chi_{\text{sphere}}^i=\frac{\nu}{2\pi(\nu-1)}, \quad i=1,\ldots,\nu \ . \tag{3.88}$$

For a slab or strip perpendicular to the x axis, in the $(x,\mathbf{y})$ frame ($\mathbf{y}$ labeling the directions parallel to the slab), the diagonal elements of the tensor T_V are $T_{\text{slab}}^x=1$, $T_{\text{slab}}^y=0$. This leads to

$$\chi_{\text{slab}}^x=\frac{1}{2\pi(\nu-1)}, \quad \chi_{\text{slab}}^y=\infty \ . \tag{3.89}$$

In a statistical-mechanical calculation, the susceptibility tensor has to be identified with the polarization fluctuations in the infinite-volume limit, defined by the dilatation of the fundamental elliptic or ellipsoidal domain.

[21]For elliptic or ellipsoidal domains the depolarization tensor

$$T_V^{ij}(\mathbf{r}_1)=-\frac{1}{2\pi(\nu-1)}\int_V d\mathbf{r}\frac{\partial^2}{\partial r^i\partial r^j}\phi^c(\mathbf{r}-\mathbf{r}_1) \ ,$$

calculated at an arbitrary point $\mathbf{r}_1$ in V, has the fundamental property of being independent of this point $\mathbf{r}_1$ in V, and thus it depends only on the shape of V. For more general domains one would need a more elaborate formulation in terms of local quantities.

Then the predictions (3.88) and (3.89) can be confirmed by explicit calculations in the two-dimensional OCP at $\Gamma=2$ (Choquard, Piller, and Rentsch, 1985, 1986). These authors show that, for a sequence of disks of radius R, the diagonal elements of the tensor $\chi_{R,\text{disk}}$ approach the value $1/\pi$ (3.88) as $R\to\infty$. Similarly, for a strip obtained as the limit of an ellipse by first letting the large y axis tend to infinity, the x component of the susceptibility approaches the value $1/2\pi$ given by the electrostatic result (3.89). Finite-size corrections can also be calculated. The discrepancy with the Stillinger-Lovett value has to be attributed to the long-range correlations along the boundaries, combined with the effect of the unbounded polarization observable (3.81).[22] The weak decay as $|\mathbf{y}|^{-\nu}$ along the slab or the strip, displayed in Sec. III.C, obviously implies the divergence (3.89) of the parallel components χ^{y}_{strip} in the infinite-volume limit. In the case of the disk, the bulk and surface contributions to $\chi^{i}_{R,\text{disk}}$ can be appropriately disentangled. The bulk contribution tends to $1/2\pi$, as it should; the surface contribution also approaches $1/2\pi$ as a consequence of the weak decay at the boundary, so that their sum is in agreement with Eq. (3.88). It is pleasing to see how the peculiar statistical-mechanical effects induced by the walls in charged systems are needed for a complete agreement with the laws of macroscopic electrostatics.

2. Image forces

We describe, finally, the case where the surrounding medium has a dielectric constant $\varepsilon_w\neq 1$ (always in elliptic or ellipsoidal domains). The inclusion of the image forces leads to the following modification of Eq. (3.86) (Choquard, Piller, Rentsch, and Viellefosse, 1988):

$$\varepsilon=\frac{\varepsilon_w+(1-\varepsilon_w)T_V^i+2\pi(\nu-1)\varepsilon_w(1-T_V^i)\chi_V^i(\varepsilon_w)}{\varepsilon_w+(1-\varepsilon_w)T_V^i-2\pi(\nu-1)T_V^i\chi_V^i(\varepsilon_w)}\;. \tag{3.90}$$

In this formula, the components $\chi_V^i(\varepsilon_w)$ must be identified with the polarization fluctuations (3.80), with image forces taken into account in the statistical ensemble.

To discuss the implications of the plasma condition $\varepsilon=\infty$, one treats the cases $0<\varepsilon_w<\infty$, $\varepsilon_w=\infty$, and $\varepsilon_w=0$ separately. If $0<\varepsilon_w<\infty$, the plasma condition implies the vanishing of the denominator of Eq. (3.90):

$$\chi_V^i(\varepsilon_w)=\frac{T_V^i+\varepsilon_w(1-T_V^i)}{2\pi(\nu-1)T_V^i}\;. \tag{3.91}$$

[22]In this respect, it is interesting to see that when the particles are confined at the surface of a sphere, i.e., a finite two-dimensional OCP without boundaries, one recovers the Stillinger-Lovett value for the susceptibility.

An inspection of Eq. (3.90) shows that the formula is also true in the limiting cases $T_V^i=1$ or $T_V^i=0$. In particular, for a slab perpendicular to the x axis, one finds the same result (3.89).

If the walls are perfectly conducting ($\varepsilon_w=\infty$), Eq. (3.90) reduces to

$$\begin{aligned}\varepsilon&=\frac{(1-T_V^i)[1+2\pi(\nu-1)\chi_V^i(\infty)]}{1-T_V^i}\\&=1+2\pi(\nu-1)\chi_V^i(\infty),\quad T_V^i\neq 1\;.\end{aligned} \tag{3.92}$$

The value $T_V^i=1$ is only obtained for an infinitely extended slab (strip). On the grounds that the dielectric constant of the external medium is fixed before taking the infinite-volume limit, Eq. (3.92) is extended to the limit $T_V^i\to 1$. One concludes from Eq. (3.92) that, in a metallic medium, the plasma condition $\varepsilon=\infty$ implies the divergence of all components of the susceptibility

$$\chi_V^i(\infty)=\infty,\quad i=1,\ldots,\nu\;. \tag{3.93}$$

Here, in a canonical finite system with metallic boundaries, this divergence must be attributed to residual correlations across the whole system, which are due to the charge conservation constraint, and would vanish in the limit of infinite volume.

In the extreme case, $\varepsilon_w=0$, Eq. (3.90) gives

$$\begin{aligned}\varepsilon&=\frac{T_V^i}{T_V^i[1-2\pi(\nu-1)\chi_V^i(0)]}\\&=\frac{1}{1-2\pi(\nu-1)\chi_V^i(0)},\quad T_V^i\neq 0\;.\end{aligned} \tag{3.94}$$

The value $T_V^i=0$ can be obtained in an infinite slab (strip) or cylinder. For the same reasons as before, one extends Eq. (3.94) to the limit $T_V^i\to 0$. One finds the interesting fact that when the fluid is in the plasma phase, all components of the susceptibility have the Stillinger-Lovett value

$$\chi_V^i(0)=\frac{1}{2\pi(\nu-1)},\quad i=1,\ldots,\nu\;, \tag{3.95}$$

and this holds for the whole class of ellipsoidal domains considered here. This absence of surface effects in the susceptibility must be related to the fast decay of the correlations along the walls, which is expected when $\varepsilon_w=0$ (Sec. III.C). One concludes that the choice $\varepsilon_w=0$ (which corresponds to defining the potential with Neumann conditions at the boundary of V) minimizes the surface effects, an observation that may be useful for numerical simulations. The mechanisms that are at the origin of the behaviors (3.91), (3.93), and (3.95) can be studied in detail in the framework of a Debye-Hückel approximation (Choquard, Piller, Rentsch, and Vieillefosse, 1988).

IV. TIME-DISPLACED CORRELATIONS

A. Introduction

We have seen in the preceding sections that the static correlations of a charged fluid are subjected to a variety of constraints that can be traced back to the long range of the Coulomb potential. The dynamics of a charged fluid also exhibits several particular properties: in the presence of any charge inbalance due to external causes, the system will tend to restore the neutrality. However, the charge clouds involved in this dynamical process will, in general, carry multipoles, as a consequence of inertia effects and interparticle collisions. For this reason one does not expect that the time-dependent correlations show exponential clustering in space, even in the range of thermodynamic parameters characteristic for a plasma phase. Only a limited number of sum rules will remain true.

In this section we consider a classical OCP of particles of mass m and charge e. The OCP has the special feature, not present in multicomponent systems, that the electric current is proportional to the total momentum (with a factor e/m). The dynamics of the latter is not sensitive to collisions, and follows simple macroscopic laws. This implies some exact sum rules specific to the OCP, which are described below. The dynamical properties of multicomponent systems are more complex and, except for the electroneutrality, apparently no other simple exact sum rules are known for them.

1. Definitions

A quantity of particular interest, which enters in the linear-response theory, is the position and velocity correlations of the charge at times 0 and t (the generalized structure function), defined

$$S(\mathbf{r},\mathbf{v},t\mid\mathbf{r}',\mathbf{v}')=e^2[\langle N(\mathbf{r},\mathbf{v},t)N(\mathbf{r}',\mathbf{v}',0)\rangle-\langle N(\mathbf{r},\mathbf{v},t)\rangle\langle N(\mathbf{r}',\mathbf{v}',0)\rangle] . \tag{4.1}$$

In this definition,

$$N(\mathbf{r},\mathbf{v},t)=\sum_j \delta[\mathbf{r}-\mathbf{r}_j(t)]\delta[\mathbf{v}-\mathbf{v}_j(t)] \tag{4.2}$$

is the microscopic phase-space particle density at time t, where $[\mathbf{r}_j(t),\mathbf{v}_j(t)]$ are the position and velocity of the jth particle under the time evolution, and $\langle\cdots\rangle$ is the thermal average on the initial conditions $[\mathbf{r}_j(0),\mathbf{v}_j(0)]$. Integration over the velocity variables yields the usual time-dependent structure function

$$S(\mathbf{r},t\mid\mathbf{r}')=\int d\mathbf{v}\int d\mathbf{v}' S(\mathbf{r},\mathbf{v},t\mid\mathbf{r}',\mathbf{v}') . \tag{4.3}$$

In the following we simply suppress velocity arguments in the correlation functions when they have been integrated out.

More generally we introduce the correlation functions $\rho(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}';\ldots;t\mid U)$ between a set of particles with positions and velocities $\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}';\ldots$ at time t, and another set of particles $U=(\mathbf{r}_1,\mathbf{v}_1;\mathbf{r}_2,\mathbf{v}_2;\ldots;\mathbf{r}_n,\mathbf{v}_n)$ at time $t=0$, given by

$$\rho(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}';\ldots;t\mid U)=\langle[N(\mathbf{r},\mathbf{v},t)N(\mathbf{r}',\mathbf{v}',t)\cdots]_{\mathrm{nc}}[N(\mathbf{r}_1,\mathbf{v}_1,0)\cdots N(\mathbf{r}_n\mathbf{v}_n,0)]_{\mathrm{nc}}\rangle . \tag{4.4}$$

The notation $[\cdots]_{\mathrm{nc}}$ means that the contributions of coincident points in the two groups $(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}';\ldots)$ and $(\mathbf{r}_1,\mathbf{v}_1;\mathbf{r}_2,\mathbf{v}_2;\ldots)$ are not included. When the set U is empty, the correlations (4.4) are time independent, and reduce to the equilibrium correlations with a factorized Maxwellian distribution of the velocities

$$\rho(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}';\ldots)=\varphi(\mathbf{v})\varphi(\mathbf{v}')\cdots\rho(\mathbf{r},\mathbf{r}',\ldots),\quad \varphi(\mathbf{v})=\left[\frac{\beta m}{2\pi}\right]^{3/2}\exp\left[-\beta\frac{m\,|\mathbf{v}|^2}{2}\right] . \tag{4.5}$$

Note that the fact that the equilibrium state is stationary implies the relation

$$\rho(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}';\ldots;t\mid\mathbf{r}_1,\mathbf{v}_1;\mathbf{r}_2,\mathbf{v}_2;\ldots)=\rho(\mathbf{r}_1,\mathbf{v}_1;\mathbf{r}_2,\mathbf{v}_2;\ldots;-t\mid\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}';\ldots) . \tag{4.6}$$

In terms of these correlations, the generalized structure function (4.1) reads

$$S(\mathbf{r},\mathbf{v},t\mid\mathbf{r}',\mathbf{v}')=e^2[\rho(\mathbf{r},\mathbf{v},t\mid\mathbf{r}',\mathbf{v}')-\rho(\mathbf{r},\mathbf{v})\rho(\mathbf{r}',\mathbf{v}')]=e^2\rho_T(\mathbf{r},\mathbf{v},t\mid\mathbf{r}',\mathbf{v}') . \tag{4.7}$$

The quantity

$$c(\mathbf{r},t\mid U)=e\int d\mathbf{v}[\rho(\mathbf{r},\mathbf{v},t\mid U)-\rho(\mathbf{r},\mathbf{v})\rho(U)]=e\int d\mathbf{v}\,\rho_T(\mathbf{r},\mathbf{v},t\mid U) \tag{4.8}$$

is the time-dependent generalization of the static excess charge density (1.21), and one has

$$c(\mathbf{r},0\mid U)=\left[\prod_{j=1}^{n}\varphi(\mathbf{v}_j)\right]c(\mathbf{r}\mid\mathbf{r}_1,\ldots,\mathbf{r}_n) . \tag{4.9}$$

2. Dynamical equations

Definitions (4.1) and (4.4) are formal in an infinitely extended system, since there is no proof at the moment of the existence of the dynamics in the thermodynamic limit, except for the one-dimensional Coulomb gas (Marchioro and Pulvirenti, 1982). Throughout this section we shall admit that the correlations (4.4) are well defined in an infinite or semi-infinite system, and that their dynamics is governed by the well-known BBGKY hierarchy (Balescu, 1963; Ichimaru, 1973). For a OCP with a (possibly inhomogeneous) background density $c_b(\mathbf{r})$, the first equation of the hierarchy has the form

$$\frac{\partial}{\partial t}\rho(\mathbf{r},\mathbf{v},t \mid U)=-\mathbf{v}\cdot\nabla_r\rho(\mathbf{r},\mathbf{v},t \mid U)-\frac{e}{m}\mathbf{E}(\mathbf{r})\cdot\nabla_{\mathbf{v}}\rho(\mathbf{r},\mathbf{v},t \mid U) -\frac{e^2}{m}\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\cdot\nabla_{\mathbf{v}}[\rho(\mathbf{r},\mathbf{v};\mathbf{r}';t \mid U)-\rho(\mathbf{r}')\rho(\mathbf{r},\mathbf{v},t \mid U)] , \tag{4.10}$$

where $\mathbf{F}(\mathbf{r})=-\nabla\phi^c(\mathbf{r})$ is the Coulomb force (a local regularization is not needed in the OCP), and

$$\mathbf{E}(\mathbf{r})=\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')[e\rho(\mathbf{r}')+c_b(\mathbf{r}')] \tag{4.11}$$

is the static electric field due to the total charge density. When the particles are constrained to move in a semi-infinite domain D (in the sense of Sec. III.A) bounded by hard walls, the configuration integrals are restricted to D, and we supplement Eq. (4.10) (valid inside D) by the condition of elastic collisions at the walls, i.e.,

$$\rho(\mathbf{r},\mathbf{v},t \mid U)\,|_{\mathbf{r}\in\partial D}=\rho(\mathbf{r},\bar{\mathbf{v}},t \mid U)\,|_{\mathbf{r}\in\partial D} . \tag{4.12}$$

$\bar{\mathbf{v}}$ is the velocity of an elastically reflected particle at $\mathbf{r}$ on the boundary ∂D, with incident velocity $\mathbf{v}$. Here the dielectric constant of the walls is set equal to one.

As in the static case, it is convenient to rewrite Eq. (4.10) in terms of the truncated correlations and of the electric field

$$\mathbf{E}(\mathbf{r},t \mid U)=\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')c(\mathbf{r}',t \mid U) \tag{4.13}$$

generated by the excess charge density at time t [cf. Eq. (2.13)]. The truncated correlations with respect to the particles $(\mathbf{r},\mathbf{v})$, $(\mathbf{r}',\mathbf{v}')$, and the set U are defined as in Eqs. (2.14) and (2.15). Then Eq. (4.10) becomes

$$\frac{\partial}{\partial t}\rho_T(\mathbf{r},\mathbf{v},t \mid U)=-\mathbf{v}\cdot\nabla_{\mathbf{r}}\rho_T(\mathbf{r},\mathbf{v},t \mid U)-\frac{e}{m}\mathbf{E}(\mathbf{r})\cdot\nabla_{\mathbf{v}}\rho(\mathbf{r},\mathbf{v},t \mid U)-\frac{e}{m}[\nabla_{\mathbf{v}}\rho(\mathbf{r},\mathbf{v})]\cdot\mathbf{E}(\mathbf{r},t \mid U) -\frac{e^2}{m}\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\cdot\nabla_{\mathbf{v}}\rho_T(\mathbf{r},\mathbf{v};\mathbf{r}';t \mid U) . \tag{4.14}$$

B. Bulk properties

For lack of any solvable model in dynamics, exact results have to rely on an analysis of the BBGKY hierarchy (taking now the existence of the thermodynamic limit for granted). For a homogeneous OCP with constant background c_b, the static field $\mathbf{E}(\mathbf{r})$ vanishes because of the local neutrality $e\rho+c_b=0$, and Eq. (4.14) becomes $[\rho(\mathbf{r},\mathbf{v})=\varphi(\mathbf{v})\rho]$

$$\frac{\partial}{\partial t}\rho_T(\mathbf{r},\mathbf{v},t \mid U)=-\mathbf{v}\cdot\nabla_{\mathbf{r}}\rho_T(\mathbf{r},\mathbf{v},t \mid U)+\beta e\rho\varphi(\mathbf{v})\mathbf{v}\cdot\mathbf{E}(\mathbf{r},t \mid U)-\frac{e^2}{m}\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\cdot\nabla_{\mathbf{v}}\rho_T(\mathbf{r},\mathbf{v};\mathbf{r}';t \mid U) . \tag{4.15}$$

An immediate piece of information which can be extracted from the dynamical equations is the value of the coefficients of the small-time expansion of the structure function

$$\tilde{S}(\mathbf{k},\mathbf{v},t \mid \mathbf{v}')=\sum_{n=0}^{\infty}\frac{t^n}{n!}a_n(\mathbf{k},\mathbf{v},\mathbf{v}') , \tag{4.16}$$

where $\tilde{S}(\mathbf{k},\mathbf{v},t \mid \mathbf{v}')$ is the spatial Fourier transform of the translation-invariant function (4.7). By successive iterations of Eq. (4.15), the coefficients $a_n(\mathbf{k},\mathbf{v},\mathbf{v}')$ are expressible in terms of the static correlations. The expressions have been obtained in the literature up to order 6, and we refer the reader to Sec. 4 of the review by Baus and Hansen (1980), and to Ichimaru (1973), for a discussion of this short-time behavior. In the sequel we address ourselves to the properties that are exact in the course at the time.

By integration over the velocities in Eq. (4.15) one gets the continuity equation[23]

$$\frac{\partial}{\partial t}\rho_T(\mathbf{r},t \mid U)+\nabla_{\mathbf{r}}\cdot\int d\mathbf{v}\,\mathbf{v}\rho_T(\mathbf{r},\mathbf{v},t \mid U)=0 , \tag{4.17}$$

which implies the conservation of the excess charge

[23]At time $t=0$ the velocity distribution is a Gaussian. One assumes here that this distribution remains sufficiently short-ranged at time t to ensure the existence of the average kinetic energy and the vanishing of the integral of gradient terms.

$$\frac{\partial}{\partial t}\int d\mathbf{r}\, c(\mathbf{r},t \mid U)=0 \; . \tag{4.18}$$

Since at $t=0$ the total static excess charge (4.9) vanishes, the same property remains true for all times and for arbitrary positions and velocities of the initial particles, i.e.,

$$\int d\mathbf{r}\, c(\mathbf{r},t \mid U)=0 \; . \tag{4.19}$$

This result holds, provided that there is no contribution from the integral of the gradient term in Eq. (4.17), e.g., if $\rho_T(\mathbf{r},\mathbf{v},t \mid U)$ decays faster than $|\mathbf{r}|^{-2}$ for fixed U. We shall assume this minimal cluster property in the following.

1. Spatial clustering compatible with the dynamical equations

As in the static case, the structure of the equations of motion has implications for the nature of the cluster properties (Alastuey and Martin, 1988). To discuss them, it is useful to also form a second time derivative with the help of Eqs. (4.15) and (4.17):

$$\frac{\partial^2}{\partial t^2}\rho_T(\mathbf{r},t \mid U)+\omega_p^2\rho_T(\mathbf{r},t \mid U)$$
$$=\int d\mathbf{v}(\mathbf{v}\cdot\nabla_{\mathbf{r}})^2\rho_T(\mathbf{r},\mathbf{v},t \mid U) \tag{4.20a}$$
$$-\frac{e^2}{m}\nabla_{\mathbf{r}}\cdot\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\rho_T(\mathbf{r},\mathbf{r}',t \mid U) \; . \tag{4.20b}$$

The second term of the left-hand side follows from the Poisson equation applied to the field (4.13), and $\omega_p=(4\pi e^2\rho/m)^{1/2}$ is the plasmon frequency.

The first observation is that the excess charge density (4.8) at time t, although globally neutral [see Eq. (4.19)], has, in general, a dipole moment different from zero, when the positions and velocities $U=(\mathbf{r}_1,\mathbf{v}_1;\ldots;\mathbf{r}_n,\mathbf{v}_n)$ of the particles at $t=0$ are specified; this will be explicitly exhibited by the sum rule (4.31) below. Hence the corresponding electric field (4.13) has a dipolar behavior:

$$\mathbf{E}(\mathbf{r},t \mid U)=-\frac{1}{|\mathbf{r}|^3}\int d\mathbf{r}'[\mathbf{r}'-3\hat{r}(\hat{r}\cdot\mathbf{r}')]c(\mathbf{r}',t \mid U) \; ,$$
$$|\mathbf{r}|\to\infty, \quad \hat{r}=\frac{\mathbf{r}}{|\mathbf{r}|} \; . \tag{4.21}$$

For the consistency of Eq. (4.15), it is necessary that some correlations also behave as $|\mathbf{r}|^{-3}$, $|\mathbf{r}|\to\infty$, and it is natural to assume that the general position and velocity correlations have an asymptotic development, starting with a $|\mathbf{r}|^{-3}$ term, as the particle at $\mathbf{r}$ is sent to infinity. We set, for instance,

$$\rho_T(\mathbf{r},\mathbf{v},t \mid U)=\frac{w_3(\hat{r},\mathbf{v},t \mid U)}{|\mathbf{r}|^3}+\frac{w_4(\hat{r},\mathbf{v},t \mid U)}{|\mathbf{r}|^4}$$
$$+\frac{w_5(\hat{r},\mathbf{v},t \mid U)}{|\mathbf{r}|^5}+\cdots \; , \tag{4.22}$$

as $|\mathbf{r}|\to\infty$ with U fixed. When this is inserted in Eq. (4.20) one sees that the term (4.20a) decays as $|\mathbf{r}|^{-5}$. The slowest-decaying contribution to the term (4.20b) comes from the integration region $\mathbf{r}'$ close to $\mathbf{r}$, as $|\mathbf{r}|\to\infty$. If $\mathbf{r}'$ remains in a bounded region, $\rho_T(\mathbf{r},\mathbf{r}',t \mid U)$ decays at least as $|\mathbf{r}|^{-3}$ according to the above assumption, and $\mathbf{F}(\mathbf{r}-\mathbf{r}')$ as $|\mathbf{r}|^{-2}$. Thus this contribution to the term (4.20b) is $O(|\mathbf{r}|^{-6})$. When the three distances between the points $\mathbf{r}$, $\mathbf{r}'$, and U tend to infinity, the decay is even faster, because of the very definition of the truncated function. If $\mathbf{r}'$ remains at a finite distance d from $\mathbf{r}$ in the integral (4.20b), and $\rho_T(\mathbf{r},\mathbf{r}',t \mid U)$ is assumed to decay as $|\mathbf{r}|^{-3}$, the integral

$$\int_{|\mathbf{r}-\mathbf{r}'|\le d} d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\rho_T(\mathbf{r},\mathbf{r}',t \mid U)$$
$$=\int_{|\mathbf{r}'|\le d} d\mathbf{r}'\mathbf{F}(\mathbf{r}')\rho_T(\mathbf{r},\mathbf{r}-\mathbf{r}',t \mid U)$$

will decay at least as $|\mathbf{r}|^{-4}$ because of the antisymmetry of the force;[24] hence, its gradient is $O(|\mathbf{r}|^{-5})$.

The result of this analysis is that both terms (4.20a) and (4.20b) decay at least as $|\mathbf{r}|^{-5}$. Therefore, the coefficients

$$w_k(\hat{r},t \mid U)=\int d\mathbf{v}\, w_k(\hat{r},\mathbf{v},t \mid U), \quad k=3,4 \; ,$$

of the development of $\rho_T(\mathbf{r},t \mid U)$ must satisfy the differential equation

$$\frac{d^2}{dt^2}w_k(\hat{r},t \mid U)+\omega_p^2 w_k(\hat{r},t \mid U)=0 \; .$$

In the situation of a plasma phase where the static correlations decay exponentially fast, the initial conditions are

$$w_k(\hat{r},0 \mid U)=0, \quad \left.\frac{d}{dt}w_k(\hat{r},t \mid U)\right|_{t=0}=0 \; ,$$

and thus $w_k(\hat{r},t \mid U)=0$, $k=3,4$, for all times. One concludes that the positional correlations of a charge with any set of particles U behaves as

$$\rho_T(\mathbf{r},t \mid U)=\frac{w_5(\hat{r},t \mid U)}{|\mathbf{r}|^5}+\frac{w_6(\hat{r},t \mid U)}{|\mathbf{r}|^6}+\cdots \; ,$$
$$|\mathbf{r}|\to\infty \; . \tag{4.23}$$

A similar analysis can be carried out for the structure function $S(\mathbf{r},t)=e^2\rho_T(\mathbf{r},t \mid 0)$. Specializing Eq. (4.20) to $U=(\mathbf{0},\mathbf{v}_1)$, and integrating over $\mathbf{v}_1$, gives

$$\frac{\partial^2}{\partial t^2}S(\mathbf{r},t)+\omega_p^2 S(\mathbf{r},t)$$
$$=e^2\int d\mathbf{v}(\mathbf{v}\cdot\nabla_{\mathbf{r}})^2\rho_T(\mathbf{r},\mathbf{v},t \mid \mathbf{0}) \tag{4.24a}$$
$$-\frac{e^4}{m}\nabla_{\mathbf{r}}\cdot\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\rho_T(\mathbf{r},\mathbf{r}',t \mid \mathbf{0}) \; . \tag{4.24b}$$

[24] If one assumes that

$$\rho_T(\mathbf{r},\mathbf{r}+\mathbf{r}',t \mid U)=|\mathbf{r}|^{-3}w(\mathbf{r}',t \mid U)+o(|\mathbf{r}|^{-3}) \; ,$$

the symmetry of ρ_T under the exchange of the particles implies $w(\mathbf{r}',t \mid U)=w(-\mathbf{r}',t \mid U)$.

Using the stationarity (4.6) and the translation invariance, the correlations occurring in terms (4.24a) and (4.24b) can be written in the form

$$\rho_T(\mathbf{r},\mathbf{v},t \mid 0)=\rho_T(-\mathbf{r},-t \mid 0,\mathbf{v}) , \tag{4.25}$$

$$\rho_T(\mathbf{r},\mathbf{r}',t \mid 0)=\rho_T(-\mathbf{r},-t \mid 0,\mathbf{r}-\mathbf{r}') . \tag{4.26}$$

According to the development (4.23), the correlation (4.25) behaves as $|\mathbf{r}|^{-5}$, hence term (4.24a) is $O(|\mathbf{r}|^{-7})$. The contribution of the bounded $\mathbf{r}'$ regions to term (4.24b) are again $O(|\mathbf{r}|^{-6})$. When $\mathbf{r}'$ remains at a finite distance from $\mathbf{r}$, the correlation (4.26) decays as $|\mathbf{r}|^{-5}$ because of result (4.23), and this contribution to the term (4.24b) is $O(|\mathbf{r}|^{-7})$. Since both terms (4.24a) and (4.24b) decay at least as $|\mathbf{r}|^{-6}$, one concludes as before that the structure function must have a bound of the form

$$|S(\mathbf{r},t)| \le \frac{M(t)}{|\mathbf{r}|^6} . \tag{4.27}$$

In contrast to the equilibrium situation (see Sec. I.B), it is not possible to pursue this analysis further to exclude a monotonous inverse-power-law decay of the correlations. In fact, a detailed study of the short-time expansion reveals that, at the order t^8, $(1/8!)(\partial^8/\partial t^8)S(\mathbf{r},t)|_{t=0}$ has the nontrivial inverse-power-law behavior $\frac{3}{4}(e^6\rho^2/m^4\beta^2)|\mathbf{r}|^{-10}$ (Alastuey and Martin, 1988). The lower orders t^k, $k<8$, have a fast decay, as a consequence of the strong static screening properties. In the course of the dynamics, the screening clouds acquire multipoles; the interplay of these multipoles with the dynamics eventually induces an algebraic decay of the structure function. Even if these arguments do not determine the exact asymptotic behavior of $S(\mathbf{r},t)$, they strongly indicate that there is no exponential regime in dynamics. In other words, the structure factor $\tilde{S}(\mathbf{k},t)$ [the Fourier transform of $S(\mathbf{r},t)$] is never analytic at $\mathbf{k}=0$ when $t\neq 0$. This is qualitatively different from the predictions of mean-field theory (the Vlasov approximation), which gives an analytic structure factor. In this respect, the effect of the three-point and higher-order correlations cannot be neglected. One should add that the latter conclusions are not particular to the OCP, but should also be valid for a multicomponent Coulomb gas.

2. Sum rules

a. Dipole sum rule and current-current fluctuations

From now on we adopt the viewpoint that the dynamical correlations are characterized by the asymptotic behaviors (4.22), (4.23), and (4.27). Then one can easily derive a sum rule for the dipole of the excess charge density. Multiplying Eq. (4.20) by $e\mathbf{r}$ and integrating gives simply

$$\frac{\partial^2}{\partial t^2}\int d\mathbf{r}\,\mathbf{r}c(\mathbf{r},t \mid U)+\omega_p^2\int d\mathbf{r}\,\mathbf{r}c(\mathbf{r},t \mid U)=0 . \tag{4.28}$$

After an integration by parts, terms (4.20a) and (4.20b) do not contribute to the first moment $[\int d\mathbf{r}\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\rho_T(\mathbf{r},\mathbf{r}',t \mid U)=0$ because of the antisymmetry of $\mathbf{F}(\mathbf{r}-\mathbf{r}')]$. Since the static correlations obey the dipole sum rule, one has

$$\int d\mathbf{r}\,\mathbf{r}c(\mathbf{r},0 \mid U)=0 , \tag{4.29}$$

and one computes easily from Eq. (4.17)

$$\left.\frac{\partial}{\partial t}\int d\mathbf{r}\,\mathbf{r}c(\mathbf{r},t \mid U)\right|_{t=0}=\left[e\sum_{j=1}^{n}\mathbf{v}_j\right]\rho(U) , \tag{4.30}$$

where $\rho(U)$ is the static correlation. With these initial conditions the solution of Eq. (4.28) is

$$\int d\mathbf{r}\,\mathbf{r}c(\mathbf{r},t \mid U)=\left[e\sum_{j=1}^{n}\mathbf{v}_j\right]\rho(U)\frac{1}{\omega_p}\sin\omega_p t , \tag{4.31}$$

showing that the dipole of the excess charge density (4.8) is different from zero when $t\neq 0$ (Jancovici, Lebowitz, and Martin, 1985).

One deduces from Eq. (4.15) the law of force

$$\begin{aligned}\frac{\partial}{\partial t}\int d\mathbf{v}\,\mathbf{v}\rho_T(\mathbf{r},\mathbf{v},t \mid U) &= \frac{e\rho}{m}\mathbf{E}(\mathbf{r},t \mid U)-\int d\mathbf{v}\,\mathbf{v}(\mathbf{v}\cdot\nabla_{\mathbf{r}})\rho_T(\mathbf{r},\mathbf{v},t \mid U)\\ &\quad+\frac{e^2}{m}\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\rho_T(\mathbf{r},\mathbf{r}',t \mid U) .\end{aligned} \tag{4.32}$$

According to our discussion of the cluster properties, the last two terms on the RHS of Eq. (4.32) decay faster than $|\mathbf{r}|^{-3}$. Therefore one concludes from Eqs. (4.21), (4.22), and (4.32) that the coefficient $\int d\mathbf{v}\,\mathbf{v}w_3(\hat{r},\mathbf{v},t \mid U)$ is determined by

$$\frac{\partial}{\partial t}\int d\mathbf{v}\,\mathbf{v}w_3(\hat{r},\mathbf{v},t \mid U) =-\frac{e\rho}{m}\int d\mathbf{r}'[\mathbf{r}'-3\hat{r}(\hat{r}\cdot\mathbf{r}')]c(\mathbf{r}',t \mid U) . \tag{4.33}$$

With the result (4.31), and the initial condition $\int d\mathbf{v}\,\mathbf{v}w_3(\hat{r},\mathbf{v},0 \mid U)=0$, this gives

$$\int d\mathbf{v}\,\mathbf{v}w_3(\hat{r},\mathbf{v},t \mid U)=\frac{1}{4\pi}(\cos\omega_p t-1)\left[\sum_{j=1}^{n}\mathbf{v}_j-3\hat{r}\left[\hat{r}\cdot\sum_{j=1}^{n}\mathbf{v}_j\right]\right]\rho(U) \tag{4.34}$$

a quantity that is, in general, different from zero for $t\neq 0$. As a particular case of the result (4.34) one finds the asymptotic behavior of the current-current correlations

$$\int d\mathbf{v}\int d\mathbf{v}_1 v^i v_1^j \rho_T(\mathbf{r},\mathbf{v},t\mid \mathbf{v}_1)\simeq \frac{\rho}{4\pi\beta m}(\cos\omega_p t-1)\left[\frac{\delta_{i,j}-3\hat{r}^i\hat{r}^j}{|\mathbf{r}|^3}\right],\quad |\mathbf{r}|\to\infty\ . \tag{4.35}$$

At order t^2 this formula agrees with the static fluctuations (2.93) of the electric field (with a factor ρ^2). This correspondence should be clear if one attributes the instantaneous velocity $d\mathbf{v}=(e/m)\mathbf{E}\,dt$ to the effect of the force due to the electric field.

When Eq. (4.31) is averaged over the Maxwellian distribution of initial velocities, one obtains that the usual dipole sum rule holds at all times when one specifies only the positions of the initial particles

$$\int d\mathbf{r}\,\mathbf{r}c(\mathbf{r},t\mid \mathbf{r}_1,\ldots,\mathbf{r}_n)=0\ . \tag{4.36}$$

The dipole sum rules (4.31) and (4.36) can be understood as follows: in the OCP, the dipole (4.31) is proportional to the center of mass at time t of the local perturbation initially at $\mathbf{r}_1,\ldots,\mathbf{r}_n$. Since the center of mass decouples from the relative coordinates it is only subjected to the harmonic force of the background. Thus it oscillates at frequency ω_p and remains constant if there is no initial velocity. The simple sum rules (4.31) and (4.36) are not true in multicomponent systems, because of inertia effects due to the different masses.

No higher-order multipole sum rules are satisfied by the time-dependent correlations of the OCP, as can be checked from the small-time expansions.

b. *Second moment*

Another sum rule plays a role in dynamics analogous to the Stillinger-Lovett second-moment condition. For a homogeneous OCP, it can be written in three equivalent forms as in the static case [see Eqs. (1.27), (1.28), and (1.29)]:

$$\begin{aligned}\beta\int d\mathbf{r}'\int d\mathbf{r}\frac{1}{|\mathbf{r}'-\mathbf{r}|}S(\mathbf{r},t) &= -\frac{2\pi\beta}{3}\int dr\,|\mathbf{r}|^2 S(\mathbf{r},t)\\ &=4\pi\beta\lim_{|\mathbf{k}|\to 0}\frac{\tilde{S}(\mathbf{k},t)}{|\mathbf{k}|^2}=\cos\omega_p t\ .\end{aligned} \tag{4.37}$$

This well-known long-wavelength sum rule can be obtained in several ways (see, for instance, Hansen, McDonald, and Pollock, 1975). In particular, it will appear as a special case of the derivation presented in Sec. IV.C in the framework of linear-response theory.

Let us show here that Eq. (4.37) follows immediately from the BBGKY equation (4.24). One multiplies it by $|\mathbf{r}|^2$ and integrates over space. After a partial integration, terms (4.24a) and (4.24b) become

$$2\int d\mathbf{v}\,|\mathbf{v}|^2\int d\mathbf{r}\,\rho_T(\mathbf{r},\mathbf{v},t\mid 0) =2\int d\mathbf{v}\,|\mathbf{v}|^2\int d\mathbf{r}\,\rho_T(\mathbf{r},-t\mid 0,\mathbf{v})\ , \tag{4.38}$$

$$2\int d\mathbf{r}\,\mathbf{r}\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\rho_T(\mathbf{r},\mathbf{r}',t\mid 0) =2\int d\mathbf{r}'\mathbf{F}(\mathbf{r}')\int d\mathbf{r}\,\mathbf{r}\rho_T(\mathbf{r},-t\mid 0,\mathbf{r}')\ ,$$

where Eqs. (4.25) and (4.26) have been used. Both quantities vanish because of the charge sum rule (4.19) and the dipole sum rule (4.36). This provides an exact closure of the BBGKY equation (4.24) for the second moment, which reduces to the simple differential equation

$$\frac{\partial^2}{\partial t^2}\int d\mathbf{r}\,|\mathbf{r}|^2 S(\mathbf{r},t)+\omega_p^2\int d\mathbf{r}\,|\mathbf{r}|^2 S(\mathbf{r},t)=0\ . \tag{4.39}$$

Supplemented with the static second-moment value as initial condition, and $\partial/\partial t\int d\mathbf{r}\,|\mathbf{r}|^2S(\mathbf{r},t)\,|_{t=0}=0$, we find the result (4.37).

C. Semi-infinite systems

1. The time-dependent Carnie-Chan sum rule

We consider an inhomogeneous OCP belonging to class (i) of Sec. III.B, i.e., a OCP having a background density that is asymptotically constant in almost all directions Ω:

$$\lim_{|\mathbf{r}|\to\infty} c_b(|\mathbf{r}|,\Omega)=c_b(\Omega),\quad \mathbf{r}=(|\mathbf{r}|,\Omega)\ . \tag{4.40}$$

Because of neutrality, the same property (4.40) will be true for the particle density. It turns out that for this class of systems, there exists the following simple time-dependent generalization of the Carnie-Chan rule (3.4) (Jancovici, Lebowitz, and Martin, 1985; Lebowitz and Martin, 1985):

$$\beta\int_D d\mathbf{r}'\int_D d\mathbf{r}\frac{1}{|\mathbf{r}|}S(\mathbf{r},t\mid \mathbf{r}')=\cos\bar{\omega}_p t\ , \tag{4.41}$$

where $\bar{\omega}_p^2$ is given by the angular average of the squares of the asymptotic plasma frequencies

$$\begin{aligned}\bar{\omega}_p^2&=\frac{1}{4\pi}\int d\Omega\,\omega_p^2(\Omega)=\frac{e^2}{m}\int d\Omega\,\rho(\Omega)\ ,\\ \omega_p^2(\Omega)&=\frac{4\pi e^2\rho(\Omega)}{m}\ ,\\ \rho(\Omega)&=\lim_{|\mathbf{r}|\to\infty}\rho(|\mathbf{r}|,\Omega)\ .\end{aligned} \tag{4.42}$$

The pure $\cos\bar{\omega}_p t$ oscillation in Eq. (4.41) is due to the fact that, in a OCP satisfying property (4.40), the long-wavelength mode oscillates undamped with a single frequency $\bar{\omega}_p$. This feature does not extend to the electron gas in the periodic field of an (infinite) ionic lattice. In this case the plasmon mode is shifted and damped as a consequence of the coupling of the electrons to the ionic lattice (Alastuey and Hansen, 1986).

The sum rule (4.41) can be deduced from the BBGKY hierarchy in a manner analogous to that for the static case (Appendix). We give here an elementary derivation based on linear-response theory and the assumption that macroscopic electrodynamics is valid in the long-wavelength limit.

We consider the electric field $\mathbf{E}(\omega,\mathbf{r})$ due to an oscillating external charge in the plasma $e_0\exp(-i\omega t)$ located at the origin. The macroscopic equations can be written in the form

$$\nabla\cdot[\varepsilon(\omega,\mathbf{r})\mathbf{E}(\omega,\mathbf{r})]=4\pi e_0\delta(\mathbf{r}) ,$$

$$\varepsilon(\omega,\mathbf{r})=1-\frac{\omega_p^2(\mathbf{r})}{\omega^2} , \tag{4.43}$$

$$\omega_p^2(\mathbf{r})=\frac{4\pi e^2\rho(\mathbf{r})}{m} ,$$

where $\varepsilon(\omega,\mathbf{r})$ is a local dielectric function.

Assuming that the induced charge density decays sufficiently fast at large distances, the electric field is asymptotically radial:

$$\mathbf{E}(\omega,\mathbf{r})\simeq[e_0+C^{\mathrm{ind}}(\omega)]\frac{\hat{r}}{|\mathbf{r}|^2}, \quad |\mathbf{r}|\to\infty , \tag{4.44}$$

where $C^{\mathrm{ind}}(\omega)$ is the total net charge induced in the plasma by the external charge. Then, integrating Eq. (4.43) over a large sphere, and using Gauss's theorem, yields

$$R^2\int d\Omega\,\varepsilon(\omega,R,\Omega)\left[\frac{e_0+C^{\mathrm{ind}}(\omega)}{R^2}\right]=4\pi e_0 . \tag{4.45}$$

Letting $R\to\infty$ we obtain from Eq. (4.45), with the property (4.40),

$$C^{\mathrm{ind}}(\omega)=\frac{\bar{\omega}_p^2}{\omega^2-\bar{\omega}_p^2}e_0 . \tag{4.46}$$

Finally, we obtain from the fluctuation-dissipation theorem and Eq. (4.46) (ω being understood as having an infinitesimal positive imaginary part corresponding to switching on the perturbation adiabatically)

$$\begin{aligned}\mathrm{Im}C^{\mathrm{ind}}(\omega)&=-\pi\beta\omega\int d\mathbf{r}'\int d\mathbf{r}\frac{e_0}{|\mathbf{r}|}S(\mathbf{r},\omega\,|\,\mathbf{r}')\\&=-\pi\beta e_0\tfrac{1}{2}[\delta(\omega-\bar{\omega}_p)+\delta(\omega+\bar{\omega}_p)] ,\end{aligned} \tag{4.47}$$

which is equivalent to the sum rule (4.41) by Fourier transform. We describe some special cases (Jancovici, Lebowitz, and Martin, 1985).

2. Applications

a. Plane wall

The situation and the notation are the same as in Sec. III.C. The dielectric constant of the wall is taken to be equal to one. The dipole sum rule (3.9) is generalized to ($\nu=3$)

$$4\pi\beta\int_0^\infty dx'\int_0^\infty dx\int d\mathbf{y}\,xS(x,\mathbf{y},t\,|\,x')=-\cos\omega_p t , \tag{4.48}$$

where $\omega_p=(4\pi e^2\rho/m)^{1/2}$ is the bulk-plasmon frequency. Equation (4.48) can be established by the same arguments that led to result (3.13).

The dynamical structure function decays as $|\mathbf{y}|^{-\nu}$ along the wall. One first specializes Eq. (4.41) to the planar geometry as in Eq. (3.20) (in three dimensions)

$$\lim_{|\mathbf{k}|\to 0}\frac{2\pi\beta}{|\mathbf{k}|}\int_0^\infty dx'\int_0^\infty dx\,e^{-|\mathbf{k}|x}\tilde{S}(x,\mathbf{k},t\,|\,x')=\cos\bar{\omega}_p t . \tag{4.49}$$

Here the averaged frequency in Eq. (4.49) is the surface-plasmon mode $\bar{\omega}_p=\omega_p/\sqrt{2}$. Proceeding exactly along the same lines as Eqs. (3.15)–(3.24), one finds the equivalent of the long-wavelength behavior (3.24) and the spatial decay along the wall

$$\begin{aligned}&\int_0^\infty dx'\int_0^\infty dx[\tilde{S}(x,\mathbf{k},t\,|\,x')-\tilde{S}^{\,b}(x-x',\mathbf{k},t)]=\tfrac{1}{2}\int d\mathbf{r}\,|\,x\,|\,S^b(\mathbf{r},t)+\frac{|\mathbf{k}|}{4\pi\beta}\left[2\cos\left[\frac{\omega_p}{\sqrt{2}}t\right]-\cos\omega_p t\right]+o(|\mathbf{k}|) ,\\&\int_0^\infty dx'\int_0^\infty dx\,[S(x,\mathbf{y},t\,|\,x')-S^b(x-x',\mathbf{y},t)]\simeq-\frac{1}{|\mathbf{y}|^3}\frac{1}{8\pi^2\beta}\left[2\cos\left[\frac{\omega_p}{\sqrt{2}}t\right]-\cos\omega_p t\right], \quad |\mathbf{y}|\to\infty ,\end{aligned} \tag{4.50}$$

as well as the corresponding dynamical generalization of the sum rule (3.27).

If the wall has a dielectric constant $\varepsilon_w<\infty$, the sum rule (4.48) is not modified, but the time-dependent bracket in Eq. (4.50) has to be replaced by

$$[\cdots]\to\left[(1+\varepsilon_w)\cos\left[\frac{\omega_p}{\sqrt{1+\varepsilon_w}}t\right]-\cos\omega_p t\right] . \tag{4.51}$$

In the extreme case, $\varepsilon_w=0$, the long tail along the wall disappears. The sum rules (4.50) and (4.51) can be found in Jancovici (1985) as the classical limit of their quantum-mechanical analogs (see Sec. V.C).

b. Slab

Since $c_b(\mathbf{r})$ vanishes in all directions not parallel to the slab, one has $\bar{\omega}_p=0$. The right-hand side of Eq. (4.41) is time independent, and equal to the static value. This is because the slab behaves essentially as a two-dimensional electron gas, where the plasmon frequency vanishes as $|\mathbf{k}|^{1/2}$, $|\mathbf{k}|\to 0$. Thus the sum rules (3.38) and (3.39) remain valid over the course of time.

c. Cylinder

Here again $\bar{\omega}_p=0$, and the static result (3.43) holds for all times. This is due to the fact that the plasmon oscillation in an infinite cylinder goes to zero with $|\mathbf{k}|$ as $|\mathbf{k}|(\ln|\mathbf{k}|)^{1/2}$.

d. Two-densities OCP

The dipole sum rules (3.48) have the following time-dependent generalizations ($\nu=3$):

$$\begin{aligned} 4\pi\beta\int_{-\infty}^{\infty}dx'\int_{x\geq 0}d\mathbf{r}\, xS(\mathbf{r},t\mid\mathbf{r}')&=-\cos\omega_p^+t\ ,\\ 4\pi\beta\int_{-\infty}^{\infty}dx'\int_{x\leq 0}d\mathbf{r}\, xS(\mathbf{r},t\mid\mathbf{r}')&=\cos\omega_p^-t\ , \end{aligned} \tag{4.52}$$

where $\omega_p^{\pm}=(4\pi e^2\rho^{\pm}/m)^{1/2}$ are the frequencies associated with the asymptotic densities. Adding the two expressions (4.52) shows that the usual dipole sum rule is not satisfied in the interface when $t\neq 0$. As a consequence, there is a weak decay parallel to the interface when $t\neq 0$. The averaged frequency is now

$$\bar{\omega}_p=\left[\frac{\omega_p^{+2}+\omega_p^{-2}}{2}\right]^{1/2}=\left[\frac{2\pi e^2(\rho^++\rho^-)}{m}\right]^{1/2}, \tag{4.53}$$

and the sum rule (4.41) implies again that

$$\lim_{|\mathbf{k}|\to 0}\frac{2\pi\beta}{|\mathbf{k}|}\int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dx\, e^{-|\mathbf{k}|x}\tilde{S}(x,\mathbf{k},t\mid x')=\cos\bar{\omega}_p t\ . \tag{4.54}$$

To determine the long-wavelength behavior one subtracts out the bulk functions as $x\to\infty$ and $x\to-\infty$, setting

$$\begin{aligned} \tilde{S}^{\,b}(x,\mathbf{k},t\mid x')&=\theta(x)\tilde{S}^{\,+}(x-x',\mathbf{k},t)\\ &\quad+\theta(-x)\tilde{S}^{\,-}(x-x',\mathbf{k},t)\ ,\\ \theta(x)&=\begin{cases}1, & x>0\ ,\\ -1, & x<0\ ,\end{cases} \end{aligned} \tag{4.55}$$

where $\tilde{S}^{\,+}(x,\mathbf{k},t)$ $[\tilde{S}^{\,-}(x,\mathbf{k},t)]$ is the $\mathbf{y}$-Fourier transform (3.14) of the bulk function corresponding to the density ρ^+ (ρ^-). Using the sum rules (4.53) and (4.54), and proceeding as in Eqs. (3.15)–(3.24), one obtains

$$\begin{aligned} \int_{-\infty}^{\infty}dx'\int_{\infty}^{\infty}dx[\tilde{S}(x,\mathbf{k},t\mid x')-\tilde{S}^{\,b}(x,\mathbf{k},t\mid x')]&=\frac{|\mathbf{k}|}{4\pi\beta}\left[2\cos\left[\frac{\omega_p^{+2}+\omega_p^{-2}}{2}\right]^{1/2}t-\cos\omega_p^+t\right.\\ &\quad\left.-\cos\omega_p^-t\right]+o(|\mathbf{k}|)\ , \end{aligned} \tag{4.56}$$

which leads to the asymptotic form along the interface (Jancovici, 1985)

$$\int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dx[S(x,\mathbf{y},t\mid x')-S^b(x,\mathbf{y},t\mid x')]=-\frac{1}{|\mathbf{y}|^3}\frac{1}{8\pi^2\beta}\left[2\cos\left[\frac{\omega_p^{+2}+\omega_p^{-2}}{2}\right]^{1/2}t-\cos\omega_p^+t-\cos\omega_p^-t\right],\quad |\mathbf{y}|\to\infty\ . \tag{4.57}$$

This example clearly shows that the dynamical screening is less efficient: the strong static screening properties of the conducting interface are lost when $t\neq 0$.

D. Uniform magnetic field

When the classical OCP is submitted to a uniform magnetic field $\mathbf{B}$ its static properties are not altered, but its dynamical correlations present interesting new features, which we summarize here (Jancovici, Macris, and Martin, 1987). The only modification to the equations of motion (4.10) and (4.14) is that the electric force $e\mathbf{E}(\mathbf{r})$ has to be replaced by the full Lorentz force $e[\mathbf{E}(\mathbf{r})+\mathbf{v}\wedge\mathbf{B}]$.

1. Bulk properties

Assuming that general correlations of the positions and velocities still have the asymptotic form (4.22), an investigation of the cluster properties allowed by the structure of the dynamical equations shows that the correlations of the charge with a set of particles U behaves as

$$\rho_T(r,t\mid U)=\frac{w_4(\hat{r},t\mid U)}{|\mathbf{r}|^4}+o\left[\frac{1}{|\mathbf{r}|^4}\right]. \tag{4.58}$$

The structure function is invariant under the rotations around the direction of the magnetic field, and behaves as

$$S(\mathbf{r},t)=\frac{s_5(\hat{r},t)}{|\mathbf{r}|^5}+o\left[\frac{1}{|\mathbf{r}|^5}\right]. \tag{4.59}$$

The weaker algebraic decay (4.58) and (4.59) [compare with the decays (4.23) and (4.27)] is caused by the presence of the magnetic field.

In view of the behaviors (4.58) and (4.59), the dipole of the excess charge density and the second moment of the structure function are not defined as absolutely convergent integrals, and it is more convenient to study the small-$\mathbf{k}$ behavior of the Fourier transforms $\tilde{c}(\mathbf{k},t\mid U)$ and $\tilde{S}(\mathbf{k},t)$.

Because of the charge sum rule

$$\int d\mathbf{r}\, c(\mathbf{r},t\mid U)=0\ , \tag{4.60}$$

both $\tilde{c}(\mathbf{k},t \mid U)$ and $\tilde{S}(\mathbf{k},t)$ vanish at $\mathbf{k}=\mathbf{0}$. Setting

$$\tilde{c}(\mathbf{k},t \mid U)=|\mathbf{k}|c_1(\hat{k},t \mid U)+o(|\mathbf{k}|)\ ,\qquad \hat{k}=\frac{\mathbf{k}}{|\mathbf{k}|}\ , \tag{4.61}$$

one easily finds from the equations of motion that the coefficient $c_1(\hat{k},t \mid U)$ obeys the closed fourth-order equation

$$\left[\frac{\partial^4}{\partial t^4}+(\omega_p^2+\omega_c^2)\frac{\partial^2}{\partial t^2}+\omega_p^2\omega_c^2(\cos\vartheta)^2\right]c_1(\hat{k},t \mid U)=0\ . \tag{4.62}$$

Here $\omega_p=(4\pi e^2\rho/m)^{1/2}$ is the plasmon frequency, $\omega_c=e/m\,|\mathbf{B}|$ is the cyclotronic frequency, and $\cos\vartheta=\hat{k}\cdot\hat{B}$, $\hat{B}=\mathbf{B}/|\mathbf{B}|$. The characteristic frequencies of Eq. (4.62) are given by

$$\omega_\pm^2=\tfrac{1}{2}\{\omega_p^2+\omega_c^2\pm[(\omega_p^2+\omega_c^2)^2-4(\omega_p\omega_c\cos\vartheta)^2]^{1/2}\}\ . \tag{4.63}$$

These oscillations have also been obtained by Suttorp and Schoolderman (1987) in a similar analysis of the collective modes of a dense magnetized plasma. They can also be derived in the framework of macroscopic electrodynamics.

Solving Eq. (4.62) with initial conditions $c_1(\hat{k},t=0 \mid U)=0$ [the static dipole sum rule (4.29)], and the computed values of the time-zero derivatives, leads to the result

$$\begin{aligned}\lim_{|\mathbf{k}|\to 0,\ \vartheta\ \text{fixed}}\frac{1}{|\mathbf{k}|}\tilde{c}(\mathbf{k},t \mid U)&=c_1(\hat{k},t \mid U)\\&=-i\left[e\sum_{j=1}^{n}\mathbf{v}_j\right]\rho(U)\left[\frac{1}{\omega_+^2-\omega_-^2}\right]\left[\hat{B}\wedge\hat{k}(\cos\omega_+t-\cos\omega_-t)-\hat{B}(\hat{k}\cdot\hat{B})\omega_c^2\left[\frac{\sin\omega_-t}{\omega_-}-\frac{\sin\omega_+t}{\omega_+}\right]\right.\\&\qquad\left.+\hat{k}(\omega_-\sin\omega_-t-\omega_+\sin\omega_+t)\right]\ ,\end{aligned} \tag{4.64}$$

and, when this is averaged over the initial velocities,

$$\lim_{|\mathbf{k}|\to 0,\ \vartheta\ \text{fixed}}\frac{1}{|\mathbf{k}|}c(\mathbf{k},t \mid \mathbf{r}_1,\ldots,\mathbf{r}_n)=0\ . \tag{4.65}$$

Equations (4.64) and (4.65) are the exact analogs (in Fourier space) of the dipole sum rules (4.31) and (4.36), and coincide with them when $\mathbf{B}=\mathbf{0}$.

The coefficient of the term of order $|\mathbf{k}|^2$ in the structure factor defined by

$$\tilde{S}(\mathbf{k},t)=|\mathbf{k}|^2 s_2(\hat{k},t)+o(|\mathbf{k}|^2) \tag{4.66}$$

also obeys the simple differential equation (4.62): in this case, again, the sum rules (4.60) and (4.65) provide an exact closure of the BBGKY hierarchy. When the appropriate initial conditions are inserted (the static second-moment value) one finds the result

$$\begin{aligned}&4\pi\beta\lim_{|\mathbf{k}|\to 0,\ \vartheta\ \text{fixed}}\frac{\tilde{S}(\mathbf{k},t)}{|\mathbf{k}|^2}=I(t,\vartheta)\ ,\\&I(t,\theta)=\frac{1}{\omega_+^2-\omega_-^2}[(\omega_+^2-\omega_c^2)\cos\omega_+t\\&\qquad\qquad-(\omega_-^2-\omega_c^2)\cos\omega_-t]\ .\end{aligned} \tag{4.67}$$

This is the generalization of Eq. (4.37) to the magnetic field case.

Notice that Eq. (4.67) is equivalent to sum rules in space. Consider, for instance, a cylinder $\Lambda_{RL}(\hat{B})$ of radius R and length $2L$, with its axis parallel to $\mathbf{B}$. Then one has

$$\lim_{L\to\infty}\lim_{R\to\infty}\beta\int_{\Lambda_{RL}(\hat{B})}d\mathbf{r}'\int d\mathbf{r}\frac{1}{|\mathbf{r}'-\mathbf{r}|}S(\mathbf{r},t)=I(t,\vartheta=0)=\cos\omega_pt\ , \tag{4.68}$$

$$\begin{aligned}\lim_{R\to\infty}\lim_{L\to\infty}\beta\int_{\Lambda_{RL}(\hat{B})}d\mathbf{r}'\int d\mathbf{r}\frac{1}{|\mathbf{r}'-\mathbf{r}|}S(\mathbf{r},t)&=I\left[t,\vartheta=\frac{\pi}{2}\right]\\&=\frac{1}{\omega_p^2+\omega_c^2}\{\omega_p^2\cos[(\omega_p^2+\omega_c^2)^{1/2}t]+\omega_c^2\}\ .\end{aligned} \tag{4.69}$$

Going to Fourier space, the limit (4.68) [respectively, (4.69)] amounts to taking $\mathbf{k}$ parallel to $\mathbf{B}$ in Eq. (4.67) (respectively, $\mathbf{k}$ normal to $\mathbf{B}$). One can recover the general situation (4.67) by replacing $\Lambda_{RL}(\hat{B})$ in Eq. (4.68) with a cylinder $\Lambda_{RL}(\hat{u})$ with axis $\hat{u}$, making an angle ϑ with $\mathbf{B}$.

The nonanalytic behaviors of $\tilde{\rho}_T(\mathbf{k},t \mid U)$ and $\tilde{S}(\mathbf{k},t)$ as $|\mathbf{k}|$ and $|\mathbf{k}|^2$, respectively, times a function of the polar angles, generate the inverse-power-law decays (4.58) and (4.59).

2. Inhomogeneous OCP

In the presence of a magnetic field, there is a simple generalization of the sum rule (4.69) for a restricted class of inhomogeneous OCP's. Using cylindrical coordinates

$\mathbf{r}=(R,\varphi,z)$, with the z axis parallel to the uniform magnetic field $\mathbf{B}$, one chooses the background density as a function $c_b(R,\varphi)$ independent of z, and assumes that it has a limit for almost all radial directions φ:

$$\lim_{R\to\infty} c_b(R,\varphi)=c_b(\varphi) \ . \tag{4.70}$$

Then one has the same sum rule (4.69), with ω_p^2 replaced by the averaged plasmon frequency

$$\lim_{R\to\infty}\lim_{L\to\infty}\beta\int_{\Lambda_{RL}(\hat{B})}d\mathbf{r}'\int d\mathbf{r}\frac{1}{|\mathbf{r}|}S(\mathbf{r},t\mid\mathbf{r}')$$
$$=\frac{1}{\varpi_p^2+\omega_c^2}\{\varpi_p^2\cos[(\varpi_p^2+\omega_c^2)^{1/2}t]+\omega_c^2\} \ ,$$
$$\varpi_p^2=\frac{2e^2}{m}\int_0^{2\pi}d\varphi\rho(\varphi),\quad \rho(\varphi)=\lim_{R\to\infty}\rho(R,\varphi) \ . \tag{4.71}$$

This can be established by linear response and macroscopic electrodynamics [generalizing the arguments (4.43)–(4.47) to the case of a magnetic field], or from the BBGKY hierarchy.

Special cases include a semi-infinite OCP bounded by a plane wall ($\varpi_p=\omega_p/\sqrt{2}$) with the magnetic field parallel to the wall, or the two-densities OCP ($\varpi_p=[(\omega^{+2}+\omega^{-2})/2]^{1/2}$) with the magnetic field in the plane of the interface. These two systems also verify dipole sum rules that are the generalizations of Eqs. (4.48) and (4.53) when there is a magnetic field. Let ϑ be the angle between the magnetic field and the normal to the wall. Then Eq. (4.48) becomes

$$4\pi\beta\int_0^\infty dx'\int_0^\infty dx\int d\mathbf{y}\,xS(x,\mathbf{y},t\mid x')=-I(t,\vartheta) \ , \tag{4.72}$$

with $I(t,\vartheta)$ given in Eq. (4.67), and one has the analogous generalization of Eqs. (4.53), with ω_p replaced by ω_p^+ (ω_p^-) for the region $x>0$ ($x<0$).

In the geometries where the sum rules (4.71) and (4.72) apply, translation invariance is preserved in at least one direction. In less special geometries there are apparently no simple sum rules involving only a finite number of pure oscillations. Using linear response and macroscopic electrodynamics, one finds, rather, sum rules involving continuous superpositions over whole frequency ranges (see, for instance, the case of the OCP bounded by a plane wall with the magnetic field perpendicular to the wall, in Jancovici, Macris, and Martin, 1987). The resulting oscillations are damped; this damping is due to dispersion effects and should not be related to any dissipation in the system.

V. QUANTUM CHARGED FLUIDS

A. Introduction

We are mainly concerned with the screening properties in the equilibrium quantum-mechanical electron fluid (the quantum OCP at nonzero temperatures), with an emphasis on similarities and differences with the classical case. The ground state will not be discussed. We also comment on some aspects of multicomponent systems.

Relevant quantities, belonging to a single electron of charge e and mass m, are the number density

$$N(\mathbf{r})=\delta(\mathbf{r}-\mathbf{q}) \tag{5.1}$$

and the current density

$$\mathbf{J}(\mathbf{r})=\frac{e}{2m}[\mathbf{p}\delta(\mathbf{r}-\mathbf{q})+\delta(\mathbf{r}-\mathbf{q})\mathbf{p}] \ , \tag{5.2}$$

where $\mathbf{p},\mathbf{q}$ are the usual quantum-mechanical momentum and position of an electron. Since the spin of the electron plays no role in the following, it will not be taken into account. We keep the same notation, $N(\mathbf{r})$ and $\mathbf{J}(\mathbf{r})$, for the corresponding second-quantized densities in the many-electron system. In particular, the particle and charge densities are

$$N(\mathbf{r})=a^*(\mathbf{r})a(\mathbf{r}) \ , \tag{5.3}$$

$$C(\mathbf{r})=eN(\mathbf{r})+c_b(\mathbf{r}) \ , \tag{5.4}$$

where $a^*(\mathbf{r}),a(\mathbf{r})$ are the creation and annihilation operators of a Fermi particle $[\{a^*(\mathbf{r})a(\mathbf{r}')+a(\mathbf{r}')a^*(\mathbf{r})\}=\delta(\mathbf{r}-\mathbf{r}')]$. Then the potential and total energy of the electron gas in a volume V are

$$U=\tfrac{1}{2}\int_V d\mathbf{r}\int_V d\mathbf{r}'\phi^c(\mathbf{r}-\mathbf{r}'):C(\mathbf{r})C(\mathbf{r}'): \ , \tag{5.5}$$

$$H=K+U \ , \tag{5.6}$$

where K is the kinetic energy defined with appropriate boundary conditions, and $:\cdots:$ means Wick ordering.

In a quantum-mechanical situation it is important to distinguish two types of sum rules that are conceptually different. The first ones refer to the shielding of classical external charges, whereas the second are linked to the shielding of the system's own charges, which are of true quantum-mechanical nature.

The shielding of external charges is best analyzed by linear-response theory. If one considers again the perturbation (1.12) caused by an infinitesimal static point charge e_0, the quantum-mechanical linear-response formula gives

$$\langle A\rangle_{e_0}=\langle A\rangle-e_0\int d\mathbf{r}\frac{1}{|\mathbf{r}|}\int_0^\beta d\tau\langle C_\tau(\mathbf{r})A\rangle_T \ , \tag{5.7}$$

where $\langle A\rangle_{e_0}$ (respectively, $\langle A\rangle$) denotes the average (in the infinite-volume limit) of an observable A in the perturbed (respectively, unperturbed) thermal state. For a pair of local observables A and B, the quantity $\langle A_\tau B\rangle$ (an imaginary-time Green's function) is defined by

$$\langle A_\tau B\rangle=\lim_{V\to\mathbb{R}^\nu}\frac{1}{Z_V}\mathrm{Tr}_V(e^{\beta\mu N}e^{-(\beta-\tau)H}Ae^{-\tau H}B) \ ,$$
$$0\le\tau\le\beta \ , \tag{5.8}$$

with Z_V the partition function, μ the chemical potential, and N the total number of particles. By the same arguments that lead to Eqs. (1.24) and (1.27), it is clear that the screening of a classical charge in the electron fluid implies the same sum rules, with the classical structure function (with the factor β) replaced by the quantum-mechanical response function (also called two-point Duhamel function)

$$\chi(\mathbf{r}\mid\mathbf{r}')=\int_0^\beta d\tau\langle C_\tau(\mathbf{r})C(\mathbf{r}')\rangle_T \ . \tag{5.9}$$

One may also investigate if the more general response functions

$$\chi(\mathbf{r}\mid A)=\int_0^\beta d\tau\langle C_\tau(\mathbf{r})A\rangle_T \tag{5.10}$$

satisfy the higher-order multipole sum rules (1.18).

To study the internal screening properties of the quantum electrons themselves, one must rather consider the static charge-charge correlations (the quantum-mechanical structure function)

$$S(\mathbf{r}\mid\mathbf{r}')=\langle C(\mathbf{r})C(\mathbf{r}')\rangle_T \ . \tag{5.11}$$

More generally, one introduces the (symmetrized) correlation

$$c(\mathbf{r}\mid A)=\tfrac{1}{2}\langle C(\mathbf{r})A+AC(\mathbf{r})\rangle_T \ , \tag{5.12}$$

which can be interpreted as an excess charge density in a state conditioned by the specification of a local observable A. If $A=N(\mathbf{r}_1)\cdots N(\mathbf{r}_n)$ is a product of densities, $\mathbf{r}_1\neq\mathbf{r}_2\neq\cdots\neq\mathbf{r}_n$, the quantity $c[\mathbf{r}\mid N(\mathbf{r}_1)\cdots N(\mathbf{r}_n)]=c(\mathbf{r}\mid\mathbf{r}_1,\ldots,\mathbf{r}_n)$ has the same expression as the classical excess charge density (1.20) and (1.21), in terms of configurational correlations. The latter are the diagonal parts of the reduced density matrices defined by

$$\rho(\mathbf{r}_1,\ldots,\mathbf{r}_n\mid\mathbf{r}_1',\ldots,\mathbf{r}_n') =\langle a^*(\mathbf{r}_1)\cdots a^*(\mathbf{r}_n)a(\mathbf{r}_n')\cdots a(\mathbf{r}_1')\rangle \ . \tag{5.13}$$

If A is not a purely configurational observable, Eq. (5.12) involves the off-diagonal parts of the reduced density matrices. It is also of interest to know what kind of sum rules are verified by the correlations (5.11) or (5.12).

In quantum mechanics there is no direct link between functions (5.9) and (5.11), which coincide in the classical case.[25] It is therefore not possible to get any immediate information on the static structure function (5.11) of the electron gas from linear-response theory.

The conditional propositions 2.2 and 3.1 can be extended to the quantum fluid. By an analysis of the hierarchy equations for the imaginary-time Green's functions, or for the reduced density matrices, one can show that the excess charge densities (5.10) or (5.12) should satisfy multipole sum rules, if there is a sufficiently fast decay of the correlations (Martin and Gruber, 1984; Martin and Oguey, 1986). The point here is that the static correlations of the quantum Coulomb gas (in dimension $\nu=2,3$) do not have exponential clustering even when the thermodynamic parameters correspond to the classical Debye regime. Only a small number of sum rules remain true.

The features of the static quantum-mechanical screening are to some extent comparable to those occurring in classical dynamics. In both cases the nontrivial interplay of velocity and configuration distributions (because of the noncommutativity in the quantum case) induces an algebraic decay of the correlations.

B. Static properties

The existence of the infinite-volume limit of the reduced density matrices, and of the imaginary-time Green's functions, has been established for a charge-symmetric Coulomb gas without statistics (Fröhlich and Park, 1978) and with Bose statistics at sufficiently low activity (Fröhlich and Park, 1980). The results hold for all values of the thermodynamic parameters, and for a regularized Coulomb potential.

There are, unfortunately, no explicitly solvable quantum models even in one dimension. However, by a clever use of the properties of the logarithm-concave functions, Brascamp and Lieb (1975) were able to show that the electronic density of the quantum one-dimensional OCP with uniform background is nontrivially periodic, when the dimensionless coupling parameter $(m/\rho^3)^{1/2}e/\hbar$ is large enough. This provides an elementary model of a Wigner lattice.

In Secs. V.B.1–V.B.3 we will be concerned with the bulk properties of homogeneous phases in two and three dimensions.

1. Equilibrium equations for the quantum OCP

Since there is, at the moment, no rigorous proof of the thermodynamic limit of the correlations of the quantum OCP with Fermi statistics, we shall assume that the limits (5.8) exist for local observables, and inherit the natural relations that hold at finite volume. One has, in particular, the Kubo-Martin-Schwinger (KMS) equilibrium condition

$$\langle A_\tau B\rangle=\langle B_{\beta-\tau}A\rangle, \quad 0\le\tau\le\beta \ , \tag{5.14}$$

and the imaginary-time "equations of motion"

$$\frac{d}{d\tau}\langle A_\tau B\rangle=\langle[H,A]_\tau B\rangle=\langle B_{\beta-\tau}[H,A]\rangle \ . \tag{5.15}$$

Specifying $A=C(\mathbf{r})$ to be the charge-density operator one gets first from Eq. (5.15) the "continuity equation"

$$\frac{d}{d\tau}\langle C_\tau(\mathbf{r})A\rangle_T-i\hbar\nabla\cdot\langle \mathbf{J}_\tau(\mathbf{r})A\rangle_T=0 \ . \tag{5.16}$$

Working out the commutator of the current density with the Hamiltonian (5.6) gives

[25]However, function (5.9) is related to a frequency integral over the dynamical structure factor [see Eq. (5.56) below].

$$\frac{d}{d\tau}\langle J^j_\tau(\mathbf{r})A\rangle_T=i\hbar\nabla\cdot\langle \mathbf{K}^j_\tau(\mathbf{r})A\rangle_T-i\frac{\hbar\rho e^2}{m}\int d\mathbf{r}'F^j(\mathbf{r}-\mathbf{r}')\langle C_\tau(\mathbf{r}')A\rangle_T$$
$$-i\frac{\hbar e^3}{m}\int d\mathbf{r}'F^j(\mathbf{r}-\mathbf{r}')\langle :N_\tau(\mathbf{r})N_\tau(\mathbf{r}'):A\rangle_T,\quad j=1,\ldots,\nu\ . \tag{5.17}$$

In Eq. (5.17), $K^{jl}(\mathbf{r})$ is a kinetic energy tensor

$$K^{jl}(\mathbf{r})=\frac{1}{2m}[p^jJ^l(\mathbf{r})+J^l(\mathbf{r})p^j]\ , \tag{5.18}$$

and the truncated expectations are defined by

$$\langle AB\rangle_T=\langle (A-\langle A\rangle)(B-\langle B\rangle)\rangle,\quad \langle ABC\rangle_T=\langle (A-\langle A\rangle)(B-\langle B\rangle)(C-\langle C\rangle)\rangle\ . \tag{5.19}$$

Equation (5.17) is the analog of the classical-dynamical equation (4.15). Finally, the combination of Eqs. (5.16) and (5.17) leads to the second-order equation [cf. Eq. (4.20)]

$$\frac{d^2}{d\tau^2}\langle C_\tau(\mathbf{r})A\rangle_T-\hbar^2\omega_p^2\langle C_\tau(\mathbf{r})A\rangle_T=-\hbar^2\sum_{j,l=1}^{\nu}\frac{\partial^2}{\partial r^j\partial r^l}\langle K^{jl}(\mathbf{r})A\rangle_T \tag{5.20a}$$
$$+\frac{\hbar^2e^3}{m}\nabla_{\mathbf{r}}\int d\mathbf{r}'\mathbf{F}(\mathbf{r}-\mathbf{r}')\langle :N_\tau(\mathbf{r})N_\tau(\mathbf{r}'):A\rangle_T\ . \tag{5.20b}$$

In the two next subsections we discuss some exact consequences of these equations.

2. Spatial clustering compatible with the equilibrium equations

The discussion is similar to that presented in Sec. IV.B.1 (Alastuey and Martin, 1988). It turns out that the charge density $\langle C_\tau(\mathbf{r})A\rangle_T$ for a general local A has a nonzero dipole [see Eq. (5.36) below]. This implies that the second term on the RHS of Eq. (5.17) decays as $|\mathbf{r}|^{-3}$, and so must other terms of this equation.[26] We assume, therefore, that all correlations have an inverse-power asymptotic expansion as a point $\mathbf{r}$ tends to infinity, starting with a $|\mathbf{r}|^{-3}$ term. In particular we set

$$\langle C_\tau(\mathbf{r})A\rangle_T=\frac{w_3(\tau,A)}{|\mathbf{r}|^3}+\frac{w_4(\tau,A)}{|\mathbf{r}|^4}+\frac{w_5(\tau,A)}{|\mathbf{r}|^5}+\cdots\ . \tag{5.21}$$

By the same arguments used in the classical-dynamical case [see the discussion following Eq. (4.22)], one concludes that the terms (5.20a) and (5.20b) are $O(|\mathbf{r}|^{-5})$. Hence the coefficients $w_3(\tau,A)$ and $w_4(\tau,A)$ must satisfy the equation

$$\frac{d^2}{d\tau^2}w_k(\tau,A)-\hbar^2\omega_p^2w_k(\tau,A)=0\ ,\quad k=3,4,\quad 0\le\tau\le\beta\ . \tag{5.22}$$

Moreover, the KMS condition (5.14) gives

$$\langle C_\beta(\mathbf{r})A\rangle_T-\langle C(\mathbf{r})A\rangle_T=\langle [A,C(\mathbf{r})]\rangle\ , \tag{5.23}$$

and from Eq. (5.16)

$$\left.\frac{d}{d\tau}\langle C_\tau(\mathbf{r})A\rangle_T\right|_{\tau=\beta}-\left.\frac{d}{d\tau}\langle C_\tau(\mathbf{r})A\rangle_T\right|_{\tau=0}=i\hbar\nabla\cdot\langle [A,\mathbf{J}(\mathbf{r})]\rangle\ . \tag{5.24}$$

Since A is local, the commutators $[A,C(\mathbf{r})]$ and $[A,\mathbf{J}(\mathbf{r})]$ vanish when $|\mathbf{r}|$ is large enough. This implies that the coefficients of the development (5.21) satisfy the boundary conditions

$$w_k(\beta,A)=w_k(0,A)\ ,\quad \left.\frac{d}{d\tau}w_k(\tau,A)\right|_{\tau=\beta}=\left.\frac{d}{d\tau}w_k(\tau,A)\right|_{\tau=0}\ . \tag{5.25}$$

The solution of Eq. (5.22) with the conditions (5.25) is

$$w_3(\tau,A)=w_4(\tau,A)=0,\quad 0\le\tau\le\beta\ . \tag{5.26}$$

Thus the correlations $\langle C_\tau(\mathbf{r})A\rangle_T$ of the charge with a general observable A decay at least as $|\mathbf{r}|^{-5}$.

We now form the charge-charge correlations $\langle C_\tau(\mathbf{r})C(0)\rangle_T$ in Eq. (5.20). Using the KMS condition and translation invariance, one can write

$$\langle K^{jl}_\tau(\mathbf{r})C(\mathbf{0})\rangle_T=\langle C_{\beta-\tau}(-\mathbf{r})K^{jl}(\mathbf{0})\rangle_T\ , \tag{5.27}$$

$$\langle :N_\tau(\mathbf{r})N_\tau(\mathbf{r}'):C(\mathbf{0})\rangle_T=\langle C_{\beta-\tau}(-\mathbf{r}):N(\mathbf{0})N(\mathbf{r}'-\mathbf{r}):\rangle_T\ . \tag{5.28}$$

[26]This is confirmed by the fact that the $\hbar^2$ term in the Wigner-Kirkwood expansion of the current-current correlations $\langle J^j(\mathbf{r})J^l(\mathbf{0})\rangle$ behaves as

$$-\hbar^2\beta\rho e^2\frac{1}{12m}\frac{\partial^2}{\partial r^j\partial r^l}\frac{1}{|\mathbf{r}|}$$

(Martin and Oguey, 1985).

By result (5.26), correlations (5.27) and (5.28) for fixed $\mathbf{r}'-\mathbf{r}$ decay as $|\mathbf{r}|^{-5}$. This allows us to conclude that terms (5.20a) and (5.20b) decay at least as $|\mathbf{r}|^{-6}$, as does $\langle C_\tau(\mathbf{r})C(\mathbf{0})\rangle_T$. We find, in particular, that the response function $\mathcal{X}(\mathbf{r})=\mathcal{X}(\mathbf{r}\,|\,\mathbf{0})$ (5.9) and the structure function $S(\mathbf{r})=S(\mathbf{r}\,|\,\mathbf{0})$ (5.11) are bounded by

$$|\mathcal{X}(\mathbf{r})|\le\frac{M}{|\mathbf{r}|^6},\quad |S(\mathbf{r})|\le\frac{M}{|\mathbf{r}|^6}\ . \tag{5.29}$$

The study of the $\hbar$ expansion of $S(\mathbf{r})$ indicates that the decay must be algebraic. The $\hbar^4$ term in the Wigner-Kirkwood expansion of $S(\mathbf{r})$ behaves as

$$\frac{7}{16\pi^2}\left[\frac{\hbar\beta e}{m}\right]^2\frac{1}{|\mathbf{r}|^{10}}\quad \text{as } |\mathbf{r}|\to\infty$$

(Alastuey and Martin, 1988). This result is true for Boltzmann statistics, but exchange terms coming from Fermi statistics are exponentially small in the classical limit $\hbar\to 0$, and cannot cancel this algebraic tail. The exact asymptotic form of $S(\mathbf{r})$ is not known, but one does not expect exponential clustering of the structure function of the quantum OCP, even when its classical counterpart is in the Debye regime. The absence of exponential screening in the quantum Coulomb system was conjectured by Brydges and Federbush (1981). Brydges and Seiler (1986) have rigorously shown that a certain type of imaginary-time correlation must have a long tail. An algebraic decay of correlations is a general feature of quantum jellia and multicomponent systems.[27]

3. Sum rules

a. Charge and dipole sum rules

Charge and dipole sum rules are easily derived from Eqs. (5.16) and (5.20) under the cluster properties discussed in the preceding subsection. Integrating Eq. (5.20) over $\mathbf{r}$ leads to

$$\frac{d^2}{d\tau^2}\int d\mathbf{r}\langle C_\tau(\mathbf{r})A\rangle_T=\hbar^2\omega_p^2\int d\mathbf{r}\langle C_\tau(\mathbf{r})A\rangle_T\ .$$

But this τ derivative must vanish because of the conservation implied by the "continuity" equation (5.16), hence

$$\int d\mathbf{r}\langle C_\tau(\mathbf{r})A\rangle_T=0\ . \tag{5.30}$$

This implies that the response functions (5.10) and the static correlations (5.12) obey the charge sum rule:

$$\int d\mathbf{r}\,\mathcal{X}(\mathbf{r}\,|\,A)=0,\quad \int d\mathbf{r}\,c(\mathbf{r}\,|\,A)=0\ . \tag{5.31}$$

One also finds from Eq. (5.20) that the dipole obeys the second-order differential equation [cf. Eq. (4.28) in the classical case]

$$\frac{d^2}{d\tau^2}\int d\mathbf{r}\,\mathbf{r}\langle C_\tau(\mathbf{r})A\rangle_T-\hbar^2\omega_p^2\int d\mathbf{r}\,\mathbf{r}\langle C_\tau(\mathbf{r})A\rangle_T=0\ . \tag{5.32}$$

Moreover, one deduces from the KMS condition (5.14)

$$\int d\mathbf{r}\,\mathbf{r}\langle C_\beta(\mathbf{r})A\rangle_T-\int d\mathbf{r}\,\mathbf{r}\langle C(\mathbf{r})A\rangle_T=\int d\mathbf{r}\,\mathbf{r}\langle[A,C(\mathbf{r})]\rangle_T\ , \tag{5.33}$$

and from Eq. (5.16), using the KMS condition again,

$$\frac{d}{d\tau}\int d\mathbf{r}\,\mathbf{r}\langle C_\tau(\mathbf{r})A\rangle_T\bigg|_{\tau=\beta}-\frac{d}{d\tau}\int d\mathbf{r}\,\mathbf{r}\langle C_\tau(\mathbf{r})A\rangle_T\bigg|_{\tau=0}=i\hbar\int d\mathbf{r}\,\mathbf{r}(\nabla\cdot\langle[A,\mathbf{J}(\mathbf{r})]\rangle_T)=0\ . \tag{5.34}$$

Indeed, the integral

$$\int d\mathbf{r}\,\mathbf{r}(\nabla\cdot\langle[A,\mathbf{J}(\mathbf{r})]\rangle_T)=-\int d\mathbf{r}\langle[A,\mathbf{J}(\mathbf{r})]\rangle_T \tag{5.35}$$

vanishes, since the state is translation invariant.[28] The solution of Eq. (5.32) with conditions (5.33) and (5.34) is

$$\int d\mathbf{r}\,\mathbf{r}\langle C_\tau(\mathbf{r})A\rangle_T=\frac{1}{2}\left[\frac{e^{\hbar\omega_p\tau}}{e^{\hbar\omega_p\beta}-1}-\frac{e^{-\hbar\omega_p\tau}}{1-e^{-\hbar\omega_p\beta}}\right]\int d\mathbf{r}\,\mathbf{r}\langle[A,C(\mathbf{r})]\rangle_T\ . \tag{5.36}$$

Introducing definition (5.10) and (5.12) one concludes from Eq. (5.36) that the response function and the symmetrized correlations obey the dipole sum rules for any local A:

$$\int d\mathbf{r}\,\mathbf{r}\,\mathcal{X}(\mathbf{r}\,|\,A)=0,\quad \int d\mathbf{r}\,\mathbf{r}\,c(\mathbf{r}\,|\,A)=0\ . \tag{5.37}$$

[27]However, generalizing the work of Kennedy (1983), Fontaine (1986) has shown that there exists a scaling limit, in which the correlations of a charge-symmetric quantum gas approach those predicted by the classical Debye-Hückel approximation. In this scaling, one simultaneously takes a weak coupling limit $\Gamma\to 0$ (Γ is the plasma parameter) and a classical limit $\lambda_0/\lambda_D\to 0$ [$\lambda_0=(\beta\hbar^2/m)^{1/2}$ is the de Broglie length]. Of course, the limit is not uniform with respect to the spatial separation, and the decay remains algebraic for all nonzero values of λ_0/λ_D.

[28]From definition (5.2), $\int d\mathbf{r}\,\mathbf{J}(\mathbf{r})=(e/m)\mathbf{p}$ is proportional to the generator of space translations. If $A_{\mathbf{a}}$ is a space translate of A, $\int d\mathbf{r}\langle[A,\mathbf{J}(\mathbf{r})]\rangle_T$ is proportional to the derivative at $\mathbf{a}=\mathbf{0}$ of $\langle A_{\mathbf{a}}\rangle=\langle A\rangle$, and thus vanishes in homogeneous state.

When A is a purely configurational observable, which commutes with the charge density $C(\mathbf{r})$, Eq. (5.36) implies the stronger dipole sum rule

$$\int d\mathbf{r}\,\mathbf{r}\langle C_\tau(\mathbf{r})A\rangle_T=0 \quad ([A,C(\mathbf{r})]=0)\ , \tag{5.38}$$

valid for all τ, $0\le\tau\le\beta$. It can be checked in the $\hbar$ expansion that the function $\langle C(\mathbf{r})A\rangle_T$ does not obey quadrupole or higher-order multipole sum rules.

b. Second moments

The perfect screening relation for the response function

$$\begin{aligned}\int d\mathbf{r}\,|r^j|^2\chi(\mathbf{r})&=\tfrac{1}{3}\int d\mathbf{r}\,|\mathbf{r}|^2\chi(\mathbf{r})\\&=\tfrac{1}{3}\int_0^\beta d\tau\int d\mathbf{r}\,|\mathbf{r}|^2\langle C_\tau(\mathbf{r})C(\mathbf{0})\rangle_T\\&=-\frac{1}{2\pi}\end{aligned} \tag{5.39}$$

can also be deduced from the equilibrium equations. It follows from Eq. (5.20) that the second moment of $\langle C_\tau(\mathbf{r})C(\mathbf{0})\rangle_T$ obeys the simple differential equation

$$\frac{d^2}{d\tau^2}\int d\mathbf{r}\,|\mathbf{r}|^2\langle C_\tau(\mathbf{r})C(\mathbf{0})\rangle_T -\hbar^2\omega_p^2\int d\mathbf{r}\,|\mathbf{r}|^2\langle C_\tau(\mathbf{r})C(\mathbf{0})\rangle_T=0\ . \tag{5.40}$$

As in the derivation leading to Eq. (4.39), the kinetic energy term (5.20a) and the three-point function (5.20b) do not contribute, because of the sum rules (5.30) and (5.38). Integrating Eq. (5.40) over τ, $0\le\tau\le\beta$, one finds, with the "continuity equation" (5.16) and the KMS condition, that

$$\begin{aligned}\hbar^2\omega_p^2\int d\mathbf{r}\,|\mathbf{r}|^2\chi(\mathbf{r})&=\frac{d}{d\tau}\int d\mathbf{r}\,|\mathbf{r}|^2\langle C_\tau(\mathbf{r})C(\mathbf{0})\rangle_T\Bigg|_{\tau=0}^{\tau=\beta}\\&=2i\hbar\int d\mathbf{r}\,\mathbf{r}\cdot\langle[C(\mathbf{r}),\mathbf{J}(\mathbf{0})]\rangle\ .\end{aligned} \tag{5.41}$$

Since $\int d\mathbf{r}\,\mathbf{r}C(\mathbf{r})$ is the dipole $e\mathbf{q}$, its commutator with the current (5.2) is readily calculated from the canonical commutation relations

$$\int d\mathbf{r}\,\mathbf{r}\cdot\langle[C(\mathbf{r}),\mathbf{J}(\mathbf{0})]\rangle=3i\hbar\frac{e^2\rho}{m}=\frac{3i\hbar}{4\pi}\omega_p^2\ , \tag{5.42}$$

and this leads to the result (5.39).

Moreover, the KMS condition, together with translation and rotation invariances, implies

$$\int d\mathbf{r}\,|\mathbf{r}|^2\langle C_\beta(\mathbf{r})C(\mathbf{0})\rangle_T=\int d\mathbf{r}\,|\mathbf{r}|^2\langle C(\mathbf{r})C(\mathbf{0})\rangle_T\ . \tag{5.43}$$

The solution of Eq. (5.40) with conditions (5.39) and (5.43) is

$$\int d\mathbf{r}\,|\mathbf{r}|^2\langle C_\tau(\mathbf{r})C(\mathbf{0})\rangle_T=-\frac{3}{2\pi\beta}f(\omega_p,\tau)\ , \tag{5.44}$$

$$f(\omega,\tau)=\frac{\hbar\omega\beta}{2}\left[\frac{e^{\hbar\omega\tau}}{e^{\hbar\omega\beta}-1}+\frac{e^{-\hbar\omega\tau}}{1-e^{-\hbar\omega\tau}}\right]\ . \tag{5.45}$$

When $\tau=0$ one recovers a well-known sum rule for the structure function of the OCP (Pines and Nozières, 1966):

$$\begin{aligned}\frac{\beta}{3}\int d\mathbf{r}\,|\mathbf{r}|^2S(\mathbf{r})&=-\frac{1}{2\pi}f(\omega_p,0)\\&=-\frac{1}{2\pi}\left[\frac{\hbar\omega_p\beta}{2}\coth\left[\frac{\hbar\omega_p\beta}{2}\right]\right]\ .\end{aligned} \tag{5.46}$$

The sum rule (5.39) is the quantum analog of the classical Stillinger-Lovett second-moment condition: it characterizes a plasma phase. This sum rule, as well as the charge and dipole sum rules (5.30) and (5.38) when A is a configurational observable, will also hold in a plasma phase of a general quantum multicomponent system (Martin and Oguey, 1986). However, Eq. (5.46) holds only in the OCP; it can also be derived from energy-entropy balance correlation inequalities, which characterize the equilibrium state (Martin and Oguey, 1985). Because of inertia effects due to the different masses, there is apparently no simple sum rule for the second moment of the structure function in a several-component quantum charged fluid.

The implications of the charge sum rule on the charge, potential, and field fluctuations are the same as in the classical case. These quantities have the same behavior (2.59), (2.89), and (2.93), where the second moment of course has to be evaluated quantum mechanically.

4. Inhomogeneous fluids

In this subsection we describe some properties of a quantum semi-infinite OCP with asymptotic uniform densities (4.40).

The second-moment relation (5.44) has the generalization

$$\beta\int_D d\mathbf{r}'\int_D d\mathbf{r}\frac{1}{|\mathbf{r}|}\langle C_\tau(\mathbf{r})C(\mathbf{r}')\rangle_T=f(\overline{\omega}_p,\tau)\ , \tag{5.47}$$

where $\overline{\omega}_p$ is the averaged plasmon frequency (4.42). If one sets $\tau=0$ in Eq. (5.47) one acquires the corresponding sum rule for the static structure function $S(\mathbf{r}\,|\,\mathbf{r}')$:

$$\beta\int_D d\mathbf{r}'\int_D d\mathbf{r}\frac{1}{|\mathbf{r}|}S(\mathbf{r}\,|\,\mathbf{r}')=\frac{\hbar\overline{\omega}_p\beta}{2}\coth\left[\frac{\hbar\overline{\omega}_p\beta}{2}\right]\ . \tag{5.48}$$

When Eq. (5.47) is integrated over τ $(0\le\tau\le\beta)$, one deduces the quantum-mechanical equivalent of the Carnie-Chan sum rule for the response function:

$$\int_D d\mathbf{r}' \int_D d\mathbf{r} \frac{1}{|\mathbf{r}|} \chi(\mathbf{r} \mid \mathbf{r}') = 1 \ . \tag{5.49}$$

The sum rule (5.49) is also valid in inhomogeneous plasma phases of general quantum multicomponent systems.

It is clear that the results of Secs. III.C and III.D immediately extend to the quantum-mechanical case. The applications of the Carnie-Chan formula to varied geometries are similar, with the only modification due to the quantum-mechanical form of the RHS of Eqs. (5.47), (5.48), and (5.49), depending on the type of correlations under consideration. We give a few examples (Jancovici, 1985).

Both the response and the structure functions have a $|\mathbf{r}|^{-\nu}$ decay along a plane insulating wall. In the OCP the dipole sum rule at the wall (3.9) holds with -1 replaced by $-f(\omega_p,0)$, and the quantum-mechanical generalization of Eq. (3.27) is (with $\varepsilon_w=1$, $\nu=3$)

$$\int_0^\infty dx' \int_0^\infty dx f(x,x') = -\frac{1}{8\pi^2\beta}[2f(\overline{\omega}_p,0)-f(\omega_p,0)] \ , \tag{5.50}$$

where $\overline{\omega}_p=\omega_p/\sqrt{2}$ is the surface-plasmon frequency.

In the slab, the quantum-mechanical sum rule is identical to the classical one (3.39), because here the corresponding plasmon frequency vanishes in the long-wavelength limit.

In the quantum two-densities OCP one finds an algebraic decay parallel to the interface. With the same notation as in Sec. IV.C one gets the asymptotic behavior as $|\mathbf{y}| \to \infty$:

$$\int_{-\infty}^\infty dx' \int_{-\infty}^\infty dx [S(x,\mathbf{y} \mid x') - S^b(x,\mathbf{y} \mid x')] \simeq -\frac{1}{|\mathbf{y}|^3} \frac{1}{8\pi^2\beta}[2f(\overline{\omega}_p,0)-f(\omega_p^+,0)-f(\omega_p^-,0)] \ . \tag{5.51}$$

As in the dynamics (4.57), the fast decay and the strong screening properties of the classical conducting interface are spoilt in quantum mechanics.

C. Time-displaced correlations

The time-displaced correlations of two observables A and B are defined as the equilibrium average $\langle A(t)B \rangle$ (in the thermodynamic limit), where

$$A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar} \tag{5.52}$$

is the observable A at time t, evolving with the complete Hamiltonian. In particular, the time-dependent structure function of the OCP is

$$S(\mathbf{r},t \mid \mathbf{r}') = \langle C(\mathbf{r},t) C(\mathbf{r}',0) \rangle_T \ , \tag{5.53}$$

with $C(\mathbf{r},0)$ the charge density (5.4). One considers also the excess charge density at time t when an observable A is fixed at time zero [cf. Eq. (5.12)],

$$c(\mathbf{r},t \mid A) = \tfrac{1}{2} \langle C(\mathbf{r},t) A + A C(\mathbf{r},t) \rangle_T \ . \tag{5.54}$$

1. Homogeneous OCP

A time-displaced correlation $\langle A(t)B \rangle$ can be formally considered as the analytic continuation to $\tau=it/\hbar$ of the corresponding static function $\langle A_\tau B \rangle$ (5.8). The time-dependent charge and current correlations of a homogeneous OCP are linked by the dynamical equations (5.16), (5.17), and (5.20), with τ changed into $it/\hbar$.

As in the classical case it is possible to evaluate the derivatives at time zero of $S(\mathbf{r},t)$. This leads to frequency sum rules for the structure factor

$$\tilde{S}(\mathbf{k},\omega) = \int d\mathbf{r} \int dt \exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)] S(\mathbf{r},t) \ .$$

A well-known example is the f-sum rule:

$$\frac{\partial}{\partial t} \tilde{S}(\mathbf{k},t) \bigg|_{t=0} = -i \int d\omega\, \omega \tilde{S}(\mathbf{k},\omega) = -i \frac{\hbar e^2 \rho}{2m} |\mathbf{k}|^2 \ . \tag{5.55}$$

Moreover, the Fourier transform $\tilde{\chi}(\mathbf{k})$ of the static response function (5.9) has a frequency-integral representation, which leads to the following form of the perfect screening condition (5.39):

$$\tilde{\chi}(\mathbf{k}) = \frac{1}{2\pi} \int d\omega \left[\frac{1-e^{-\hbar\omega\beta}}{\hbar\omega} \right] \tilde{S}(\mathbf{k},\omega) = \frac{1}{4\pi} |\mathbf{k}|^2 + o(|\mathbf{k}|^2) \ . \tag{5.56}$$

We refer to Pines and Nozières (1966) for a discussion of this kind of sum rule, and their implications for the dielectric function.

Because of the simple relation between the imaginary- and real-time correlation functions, one immediately obtains that the dipole $\int d\mathbf{r}\, \mathbf{r} \langle C(\mathbf{r},t) A \rangle_T$ and the second moment $\int d\mathbf{r} |\mathbf{r}|^2 S(\mathbf{r},t)$ at time t are given, respectively, by the right-hand sides of Eqs. (5.36) and (5.44) with $\tau=it/\hbar$. One finds, in particular, that the dipole of the symmetrized distribution (5.54) for a general A is given by

$$\int d\mathbf{r}\, \mathbf{r} c(\mathbf{r},t \mid A) = \sin\omega_p t \coth\left[\frac{\hbar\omega_p\beta}{2}\right] \frac{i}{2} \times \int d\mathbf{r}\, \mathbf{r} \langle [A, C(\mathbf{r})] \rangle_T \ . \tag{5.57}$$

This is the quantum analog of the classical dipole oscillation (4.31), and is equivalent to it in the classical limit. Moreover, the dipole sum rule

$$\int d\mathbf{r}\, \mathbf{r} \langle C(\mathbf{r},t) A \rangle_T = 0 \quad ([A, C(\mathbf{r})]=0) \tag{5.58}$$

is true for all times, when A is a configurational observable [cf. Eq. (5.38)].

In fact, one can obtain these results from the quantum-dynamical equations exactly as in the classical case (Sec. IV.B.2). The dipole and the second moment obey the second-order equations (4.28) and (4.39), which must be solved with the initial conditions corresponding to the quantum statics. For instance, the sum rule

$$\int d\mathbf{r}\,|\mathbf{r}|^2 S(\mathbf{r},t) = -\frac{3}{2\pi} f(\omega_p, it/\hbar)\,, \qquad (5.59)$$

$$f(\omega, it/\hbar) = \frac{\hbar\omega\beta}{2}\left[\frac{e^{i\omega t}}{e^{\hbar\omega\beta}-1} + \frac{e^{-i\omega t}}{1-e^{-\hbar\omega\beta}}\right]\,, \qquad (5.60)$$

is the solution of the second-order differential equation (4.39) with initial conditions given by Eq. (5.44) at $\tau=0$ and the f-sum rule (5.55).

2. Inhomogeneous OCP

In a semi-infinite quantum OCP satisfying condition (3.5) one has the following generalization of Eq. (5.59) (Jancovici, Lebowitz, and Martin, 1985):

$$\beta \int_D d\mathbf{r}' \int_D d\mathbf{r} \frac{1}{|\mathbf{r}|} S(\mathbf{r},t\,|\,\mathbf{r}') = f(\overline{\omega}_p, it/\hbar)\,, \qquad (5.61)$$

with $\overline{\omega}_p$ defined by Eq. (4.42). This can be obtained from a quantum-mechanical linear-response argument similar to that presented in Sec. IV.C.1. It is also a solution of the second-order equation (A14), with initial conditions (5.48) and

$$\frac{\partial}{\partial t} \int_D d\mathbf{r}' \int_D d\mathbf{r} \frac{1}{|\mathbf{r}|} S(\mathbf{r},t\,|\,\mathbf{r}')\bigg|_{t=0} = -i\hbar \frac{\overline{\omega}_p^2}{2}\,, \qquad (5.62)$$

which is the generalization of the f-sum rule (5.55) to this class of inhomogeneous OCP. When $\hbar=0$, Eq. (5.61) agrees with the classical time-dependent Carnie-Chan rule (4.41). The results are the same as in the classical case (Sec. IV.C.2), with the cosine replaced by its quantum-mechanical counterpart (5.60).

3. Constant magnetic field

The same remark applies to the quantum OCP subjected to a constant magnetic field. The small-wave-number behavior of the charge-charge correlations $\widetilde{S}_{\mathbf{B}}(\mathbf{k},t)$ is given by Eq. (4.67), with $\cos\omega_{\pm}t$ replaced by the quantum-mechanical equation (5.60). Contrary to the classical case, the static correlations are sensitive to the presence of the magnetic field:

$$4\pi\beta \lim_{|\mathbf{k}|\to 0,\ \vartheta\ \text{fixed}} \frac{\widetilde{S}_{\mathbf{B}}(\mathbf{k})}{|\mathbf{k}|^2} = \frac{1}{\omega_+^2-\omega_-^2}\left[(\omega_+^2-\omega_c^2) f(\omega_+,0) - (\omega_-^2-\omega_c^2) f(\omega_-,0)\right]\,. \qquad (5.63)$$

However, the response function $\widetilde{\chi}_{\mathbf{B}}(\mathbf{k})$ in the presence of the field $\mathbf{B}$ still satisfies the perfect screening relation in its usual form (5.56):

$$4\pi \lim_{|\mathbf{k}|\to 0} \frac{\widetilde{\chi}_{\mathbf{B}}(\mathbf{k})}{|\mathbf{k}|^2} = 1\,. \qquad (5.64)$$

These long-wavelength oscillations of a quantum plasma in a magnetic field have been obtained in the framework of the RPA approximation (Mermin and Canel, 1964).

ACKNOWLEDGMENTS

I am grateful for fruitful and enjoyable work with the co-authors of several papers reported in this review. In particular, I greatly benefited from the close collaboration of A. Alastuey, Ch. Gruber, B. Jancovici, and J. L. Lebowitz. I thank Ph. Choquard and E. Lieb for their stimulating interest in the statistical mechanics of Coulomb systems. This work was partially supported by the Swiss National Foundation for Science.

APPENDIX: A DERIVATION OF THE CARNIE-CHAN SUM RULE

1. Fluids with asymptotically constant densities

Using the first BGY equation

$$\beta^{-1}\nabla_1\rho(q_1) = e_{\alpha_1}\mathbf{E}(\mathbf{r}_1)\rho(q_1) + \int_D dq\,\mathbf{F}(q_1,q)\rho_T(q_1,q) \qquad (A1)$$

and proceedings as in Eqs. (2.37) and (2.38), we get from Eq. (3.2)

$$\beta^{-1}\nabla_1\left[\sum_{\alpha_2} e_{\alpha_2}\rho_T(q_1,q_2)\right] + \delta(\mathbf{r}_1-\mathbf{r}_2)e_{\alpha_1}\beta^{-1}\nabla_1\rho(q_1) \qquad (A2a)$$

$$= e_{\alpha_1}\rho(q_1)\int_D d\mathbf{r}\,\mathbf{F}(\mathbf{r}_1-\mathbf{r})S(\mathbf{r}_1\,|\,\mathbf{r}_2) \qquad (A2b)$$

$$+ e_{\alpha_1}\mathbf{E}(\mathbf{r}_1)c(\mathbf{r}_2\,|\,q_1) + \int_D dq\,\mathbf{F}(q_1,q)c_T(\mathbf{r}_2\,|\,q_1,q)\,. \qquad (A2c)$$

This equation obviously simplifies to the form (2.38) in the homogeneous situation.

We multiply Eq. (A2) by $\nabla_1(1/|\mathbf{r}_1|)$, and integrate it over $\mathbf{r}_1$ and $\mathbf{r}_2$ in D. Setting $\phi(\mathbf{r}_1,\mathbf{r}_2) = \int_D d\mathbf{r}\,\phi(\mathbf{r}_1-\mathbf{r})S(\mathbf{r}\,|\,\mathbf{r}_2)$, term (A2b) becomes, after an integration by parts,

$$(\text{A2b}) = -e_{\alpha_1}\int_D d\mathbf{r}_2\int_D d\mathbf{r}_1\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\cdot\rho(q_1)\nabla_1\phi(\mathbf{r}_1,\mathbf{r}_2)$$

$$= e_{\alpha_1}\int_D d\mathbf{r}_2\int_D d\mathbf{r}_1\nabla_1\cdot\left[\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\rho(q_1)\right]\phi(\mathbf{r}_1,\mathbf{r}_2) - e_{\alpha_1}\int_D d\mathbf{r}_2\int_{\partial D} d\mathbf{s}_1\cdot\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\rho(q_1)\phi(\mathbf{r}_1,\mathbf{r}_2)\,. \qquad (A3)$$

Exchanging now the $\mathbf{r}_1$ and $\mathbf{r}_2$ integrals, and using the fact that $\int_D d\mathbf{r}_2\phi(\mathbf{r}_1,\mathbf{r}_2)=\int_D d\mathbf{r}_2\phi(\mathbf{0},\mathbf{r}_2)$ is independent of $\mathbf{r}_1$ [Eq. (3.6)], we get

$$(\mathrm{A2b})=-e_{\alpha_1}\bar{\rho}_{\alpha_1}\int_D dr_2\phi(\mathbf{0},\mathbf{r}_2)\ . \tag{A4}$$

By property (3.5), we find that the density $\bar{\rho}_{\alpha_1}$ is the average of all asymptotic densities $\rho_{\alpha_1}(\Omega)$:[29]

$$\begin{aligned}\bar{\rho}_{\alpha_1}&=-\int_D d\mathbf{r}_1\nabla_1\cdot\left[\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\rho(q_1)\right]+\int_{\partial D}d\mathbf{s}_1\cdot\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\rho(q_1)\\&=-\lim_{R\to\infty}\int_{|\mathbf{r}_1|=R}d\mathbf{s}_1\cdot\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\rho(q_1)=\lim_{R\to\infty}\int d\Omega\,\rho(\alpha_1,R,\Omega)=\int d\Omega\,\rho_{\alpha_1}(\Omega)\ .\end{aligned}\tag{A5}$$

We perform the same operations on term (A2a):

$$\begin{aligned}(\mathrm{A2a})&=\beta^{-1}\int d\mathbf{r}_2\left[4\pi\sum_{\alpha_2}e_{\alpha_2}\rho_T(\alpha_1,\mathbf{0},q_2)+\int_{\partial D}d\mathbf{s}_1\cdot\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\sum_{\alpha_2}e_{\alpha_2}\rho_T(q_1,q_2)\right]+\beta^{-1}e_{\alpha_1}\int d\mathbf{r}_1\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\cdot\nabla_1\rho(q_1)\\&=-\beta^{-1}e_{\alpha_1}\left[4\pi\rho(q_1)+\int_{\partial D}d\mathbf{s}_1\cdot\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\rho(q_1)\right]+\beta^{-1}e_{\alpha_1}\int_D d\mathbf{r}_1\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\cdot\nabla_1\rho(q_1)\\&=\beta^{-1}e_{\alpha_1}\left\{\int_D d\mathbf{r}_1\nabla_1\cdot\left[\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\rho(q_1)\right]-\int_{\partial D}d\mathbf{s}_1\cdot\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\rho(q_1)\right\}=-\beta^{-1}e_{\alpha_1}\bar{\rho}_{\alpha_1}\ .\end{aligned}\tag{A6}$$

We have used the charge sum rule to obtain the second equality, and the result follows as in Eq. (A5).

The terms (A2c) do not contribute. One can argue, as in Jancovici, Lebowitz, and Martin (1985, Sec. 3.3), that the q and q_1 integrals may be exchanged, and these terms vanish by the charge sum rule again. For instance, the electric field $\mathbf{E}(\mathbf{r}_1)$ is $O(1/|\mathbf{r}_1|^2)$, since the plasma is asymptotically uniform and neutral. Thus $\nabla_1(1/|r_1|)\cdot\mathbf{E}(r_1)=O(1/|\mathbf{r}_1|^4)$, and we are allowed to write

$$\int_D dr_2\int_D dr_1\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\cdot\mathbf{E}(\mathbf{r}_1)c(\mathbf{r}_2|q_1)=\int_D d\mathbf{r}_1\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\cdot\mathbf{E}(\mathbf{r}_1)\int_D d\mathbf{r}_2 c(\mathbf{r}_2|q_1)=0\ . \tag{A7}$$

A similar reasoning applies to the second term of Eq. (A2c). Therefore we conclude that the terms (A4) and (A6) are equal. This implies $\int_D d\mathbf{r}_2\phi(\mathbf{0},\mathbf{r}_2)=\beta^{-1}$, which is precisely the Carnie and Chan relation (3.4).

2. Periodic OCP

We assume that the conditions of Proposition 3.1 hold for $l=0,1$, so the charge and dipole sum rules are verified. We multiply Eq. (A2) by $\mathbf{r}_2$ and integrate over $\mathbf{r}_2$. The two last terms do not contribute because of the sum rules, and we find [cf. also Eq. (2.40)]

$$\beta^{-1}\left[\nabla_1\cdot e\int d\mathbf{r}_2\mathbf{r}_2\rho_T(\mathbf{r}_1,\mathbf{r}_2)+e\mathbf{r}_1\cdot\nabla_1\rho(\mathbf{r}_1)\right]=e_{\alpha_1}\rho(\mathbf{r}_1)\int d\mathbf{r}_2\mathbf{r}_2\cdot\int d\mathbf{r}\,\mathbf{F}(\mathbf{r}_1-\mathbf{r})S(\mathbf{r}|\mathbf{r}_2)\ . \tag{A8}$$

By the dipole sum rule $\int d\mathbf{r}_2\mathbf{r}_2\rho_T(\mathbf{r}_1,\mathbf{r}_2)=-\mathbf{r}_1\rho(\mathbf{r})$, this leads to the equality

$$\int d\mathbf{r}_2\mathbf{r}_2\cdot\int d\mathbf{r}\,\mathbf{F}(\mathbf{r}_1-\mathbf{r})S(\mathbf{r}|\mathbf{r}_2)=-\beta^{-1}\nu\ . \tag{A9}$$

Notice that the integration of (A2) over $\mathbf{r}_2$, with the charge sum rules, leads to

$$\int d\mathbf{r}_2\int d\mathbf{r}\,\mathbf{F}(\mathbf{r}_1-\mathbf{r})S(\mathbf{r}|\mathbf{r}_2)=0\ . \tag{A10}$$

Introducing the averaged structure function on a cell $\bar{S}(\mathbf{r}-\mathbf{r}')=(1/|\Delta|)\int_\Delta d\mathbf{a}\,S(\mathbf{r}+\mathbf{a}|\mathbf{r}'+\mathbf{a})$, the left-hand side of Eq. (A9) can be transformed to [using Eq. (A10) and setting $\mathbf{r}_1=\mathbf{a}$]

[29] We set $\rho(\alpha,|\mathbf{r}|,\Omega)$ and $\rho_\alpha(\Omega)$ equal to zero when the direction Ω does not belong to D.

$$\frac{1}{|\Delta|}\int_\Delta d\mathbf{a}\int d\mathbf{r}_2(\mathbf{r}_2-\mathbf{a})\cdot\int d\mathbf{r}\,\mathbf{F}(\mathbf{a}-\mathbf{r})S(\mathbf{r}\mid\mathbf{r}_2)=\frac{1}{|\Delta|}\int_\Delta d\mathbf{a}\int d\mathbf{r}_2\mathbf{r}_2\cdot\int d\mathbf{r}\,\nabla\phi(\mathbf{r})S(\mathbf{r}+\mathbf{a}\mid\mathbf{r}_2+\mathbf{a})$$
$$=\int d\mathbf{r}_2\mathbf{r}_2\cdot\nabla_2\int d\mathbf{r}\,\phi(\mathbf{r}_2-\mathbf{r})\bar{S}(\mathbf{r})$$
$$=-\nu\int d\mathbf{r}_2\int d\mathbf{r}\,\phi(\mathbf{r}_2-\mathbf{r})\bar{S}(\mathbf{r})=-\beta^{-1}\nu\;. \tag{A11}$$

This is equivalent to the second-moment condition (1.29) for the averaged function $\bar{S}(\mathbf{r})$.

3. The time-dependent Carnie-Chan sum rule

We consider a OCP with asymptotically constant densities (4.40). One finds from Eq. (4.14), and the definitions given in Sec. IV.A, that the dynamical structure function of the inhomogeneous fluid obeys the equation

$$\frac{\partial^2}{\partial t^2}S(\mathbf{r}_1,t\mid\mathbf{r}_2)+\frac{e^2}{m}\nabla_1\cdot\left[\rho(r_1)\int_D d\mathbf{r}\,\mathbf{F}(\mathbf{r}_1-\mathbf{r})S(\mathbf{r},t\mid\mathbf{r}_2)\right]$$
$$=-\frac{e}{m}\nabla_1\cdot[\mathbf{E}(\mathbf{r}_1)S(\mathbf{r}_1,t\mid\mathbf{r}_2)]+e^2\int d\mathbf{v}_1(\mathbf{v}_1\cdot\nabla_1)^2\rho_T(\mathbf{r}_1,\mathbf{v}_1,t\mid\mathbf{r}_2)-\frac{e^4}{m}\nabla_1\cdot\int_D d\mathbf{r}\,\mathbf{F}(\mathbf{r}_1-\mathbf{r})\rho_T(\mathbf{r}_1,\mathbf{r},t\mid\mathbf{r}_2)\;. \tag{A12}$$

This equation obviously simplifies to the form (4.24) for a uniform OCP. We multiply it by $1/|\mathbf{r}_1|$ and integrate over $\mathbf{r}_1$ and $\mathbf{r}_2$. Setting $\phi(\mathbf{r}_1,\mathbf{r}_2,t)=\int d\mathbf{r}\,\phi(\mathbf{r}_1-\mathbf{r})S(\mathbf{r},t\mid\mathbf{r}_2)$, the second term on the LHS of Eq. (A12) can be transformed to (Jancovici, Lebowitz, and Martin, 1985)

$$\frac{e^2}{m}\int_D d\mathbf{r}_2\int_D d\mathbf{r}_1\left[\nabla_1\frac{1}{|\mathbf{r}_1|}\right]\cdot[\rho(\mathbf{r}_1)\nabla_1\phi(\mathbf{r}_1,\mathbf{r}_2,t)]$$
$$=\frac{e^2}{m}\bar{\rho}\int_D d\mathbf{r}_2\phi(\mathbf{0},\mathbf{r}_2,t)=\varpi_p^2\int_D d\mathbf{r}_2\phi(\mathbf{0},\mathbf{r}_2,t) \tag{A13}$$

in the same manner as in Eqs. (A3), (A4), and (A5). Arguing as in the static case, the RHS of Eq. (A12) gives no contribution, and we obtain the simple differential equation

$$\left[\frac{\partial^2}{\partial t^2}+\varpi_p^2\right]\int_D d\mathbf{r}_2\int_D d\mathbf{r}_1\frac{1}{|\mathbf{r}_1|}S(\mathbf{r}_1,t\mid\mathbf{r}_2)=0\;. \tag{A14}$$

The sum rule (4.41) results when one solves Eq. (A14) with the appropriate initial conditions given by the statics.

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