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On the properties of inhomogeneous charged systems

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We give a proof and an extension of equations previously derived by Wertheim and Lovett, Mou and Buff, relating the gradient of the density to an integral of the external force over the pair correlation function; when the system has boundaries it also involves a surface contribution. These equations are derived and used for systems which may contain free charges, dipoles, and a rigid background (jellium). In particular, we derive an equation for the density profile near a plane electrode and we show that the correlation function has to decay no faster than $|x|^{-N}$ ($N =$ space dimension) parallel to the electode.

I. INTRODUCTION

The structure of electrolyte solutions in the vicinity of an electrode is an important unsolved problem which continues to receive much attention.[1,2] Sum rules, giving exact relations among correlation functions of such systems near a wall, provide information which can and should be used both for a qualitative understanding, and as a guide in formulating and evaluating quantitative approximations for the electrolyte–electrode interface. This has in fact been done recently by various authors,[3] including ourselves,[4,5] using a variety of such sum rules. The present work is related to the analysis in Ref. 5: we argued there, on the basis of sum rules, that the correlation functions of an electrolyte near a flat hard wall (with the same dielectric constant everywhere) cannot decay uniformly in all directions faster than r^{-4}. In this note that argument is further strengthened by using a generalization of the Wertheim[6] and Lovett, Mou, and Buff[7] (WLMB) equation to systems containing charges and dipoles. The WLMB equation relates the gradient of the density to an integral of the external forces over the pair correlation function; when the system has boundaries it also involves a surface term which is important for the applications to the interface problem.

Our proof of the WLMB equation is based on the first two equations of the BGY hierarchy which are assumed always to be satisfied in equilibrium. It is in fact simpler than the original formal proofs which were based on the Mayer cluster expansion[6] or on functional derivation techniques.[7] Our derivation does require some clustering of the pair correlation functions; the equation is in fact unlikely to be true otherwise.

Let us note that for a finite system described by the canonical ensemble, the BGY equations are identities and the derivation of the WLMB equation is trivial. It is however irrelevant for real macroscopic systems since the appropriate mathematical representation of the latter is that of an infinite system obtained as the thermodynamic limit of finite systems[8] and relations based on integrating over the whole volume may not survive the interchange of limits, e.g., the integral of the Ursell function for a one component system with short range interactions is zero in a finite system represented by the canonical ensemble but is equal to the compressibility in the thermodynamic limit.[9] For systems with Coulomb forces, the taking of this thermodynamic limit involves many subtle mathematical points which are far from being all settled. Here we do not enter into these problems but we simply assume that the equilibrium states of the infinite system are described by a set of correlation functions satisfying the BGY hierarchy in which the integrals are well defined. This last condition will always be satisfied when either the forces or the truncated correlation functions are absolutely integrable. For charged systems, of course, only the latter can possibly be true.

The derivation of the WLMB equation is carried out in Sec. II; this derivation is rigorous except for a formal permutation of limit and integral. Section III is devoted to a discussion of some consequence of this

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equation, particularly when it is combined with the general screening sum rules for charged systems[10]; we consider in this section the problem of local inhomogeneities and the semi-infinite systems, first in the absence of a rigid background then for jellium. A proof of the sum rules for systems containing dipoles is given in Appendix A. In Appendix B we give a modified proof of the zeroth order screening sum rule for semi-infinite systems which requires weaker clustering along the wall. For the systems considered in Sec. III, the formal permutation is rigorously established in Appendix C.

II. DERIVATION OF THE WLMB EQUATION

We consider a mixture of m species of particles moving in a region $\mathfrak{D}$ of the N dimensional space $\mathbb{R}^N$. The particles of species α carry a charge e_α and a dipole moment of strength d_α (for some species α, e_α, or/and d_α can be zero, i.e., pure charge, pure dipole, or no electric properties). We introduce the abbreviated notation $q=(\alpha, x, \omega)$, where x and ω denote, respectively, the position of the particle and the orientation of its dipole moment $\mu_\alpha = d_\alpha \omega$. We normalize the angular integration over dipole angles to 1, $\int d\omega = 1$ and set

$$\int_{\mathfrak{D}} dq = \int_{\mathfrak{D}} dx \int d\omega \sum_{\alpha=1}^{m} .$$

The correlation functions of the system at temperature T are assumed to satisfy the usual BGY equations[10,11] which we write in the following form

$$kT\,\nabla_1 \rho(q_1) = F(q_1)\rho(q_1) + \int dq\, F(q_1, q)\,[\rho(q_1 q) - \rho(q)\,\rho(q_1)] , \tag{2.1}$$

$$kT\,\nabla_1 \rho(q_1 q_2) = [F(q_1) + F(q_1, q_2)]\,\rho(q_1 q_2) + \int dq\, F(q_1, q)\,[\rho(q_1 q_2 q) - \rho(q)\,\rho(q_1 q_2)] . \tag{2.2}$$

The two-body force has a short and long range part

$$F(q_1, q_2) = F^S(q_1, q_2) + F^L(q_1, q_2) = F_{\alpha_1 \alpha_2}(x_1 - x_2, \omega_1, \omega_2) \tag{2.3}$$

where F^S includes the local repulsion effects; we assume that F^S is antisymmetric under the exchange of the particles and integrable over $\mathfrak{D}$. The results of the paper will however remain valid in the presence of more singular repulsions or hard cores.

The Coulomb and dipole part F^L is given by

$$F^L(q_1, q_2) = [e_{\alpha_1} + (\mu_{\alpha_1} \cdot \nabla_1)]\,[e_{\alpha_2} + (\mu_{\alpha_2} \cdot \nabla_2)]\,F^C(x_1 - x_2) , \tag{2.3a}$$

where $F^C(x)$ is a twice differentiable function everywhere which is the Coulomb force at large distances

$$F^C(x) = \frac{x}{|x|^N} \quad |x| > R . \tag{2.3b}$$

We have introduced a cutoff in the definition of the Coulomb force for the technical reasons only. Indeed in the presence of dipoles the force Eq. (2.3) is not integrable at the origin and the proofs are simplified if we introduce the singular part of the Coulomb force as a contribution to F^S. For pure charge systems (no dipoles) the introduction of the cutoff is not necessary and in any case the final WLMB equation will be independent of the cutoff.

We assume here that the dielectric constant ϵ is the same inside and outside $\mathfrak{D}$ and we set $\epsilon = 1$. The case of different dielectric media will be treated elsewhere.

The one-body force $F(q_1)$ represents the total average force on the particle q_1; it can be written as

$$F(q_1) = F^e(q_1) + \int dq\,[F(q_1, q) - e_{\alpha_1} e_\alpha F^C(-x)]\,\rho(q) . \tag{2.4}$$

The external force $F^e(q_1)$ includes the effect of some fixed distribution of external charges $C^e(x)$ or dipoles $\mu^e(x)$ in $\mathfrak{D}$. In particular for jellium systems $C^e(x) = \rho_B$ for $x \in \mathfrak{D}$ with ρ_B the uniform background density, and $F^e(q_1)$ also includes the effect of some fixed distribution of charges outside or on the boundaries of $\mathfrak{D}$, together with the system's charges located at infinity (polarization effect). In Eq. (2.4) we have subtracted from the two-body force its dominant asymptotic part $e_{\alpha_1} e_\alpha F^C(-x)$ in order that the integral be well defined (see Appendix C); therefore $F^e(q_1)$ is the external force up to a constant. The explicit expression for $F^e(q_1)$ is given below in Eq. (2.15).

We introduce the truncated (Ursell) functions defined in the usual way

$$\begin{aligned} \rho^T(q_1 q_2) &= \rho(q_1 q_2) - \rho(q_1)\,\rho(q_2) , \\ \rho^T(q_1 q_2 q_3) &= \rho(q_1 q_2 q_3) - \rho(q_1)\,\rho^T(q_2 q_3) - \rho(q_2)\,\rho^T(q_1 q_3) - \rho(q_3)\,\rho(q_1 q_2) . \end{aligned} \tag{2.5}$$

The rate of decay of the truncated correlations can be characterized by means of a parameter $\eta > N-1$ such that

$$|r^\eta \rho^T(q_1, \ldots, q_n)| \le M_n < \infty , \tag{2.6}$$

with

$$r = \sup_{i,j} |x_i - x_j| \quad i, j = 1, 2, \ldots, n , \quad x_i \in \mathfrak{D}$$

and we assume the additional integrability conditions

$$\begin{aligned} &\int |\rho^T(q_1, q_2)|\, dq_1 < \infty , \\ &\int |\rho^T(q_1, q_2, q_3)|\, dq_1 dq_2 < \infty . \end{aligned} \tag{2.7}$$

Under the conditions in Eq. (2.7) all terms of the BGY equations are well defined. Furthermore, we also assume that the following electroneutrality sum rule is satisfied for charged systems

$$e_{\alpha_1} \rho(q_1) + \int dq\, e_\alpha\, \rho^T(q_1, q) = 0 , \tag{2.8}$$

i.e.,

$$\int dq\, e_\alpha\, \rho(q|q_1) = 0 ,$$

where

$$\rho(q|q_1) = \frac{\rho(q q_1)}{\rho(q_1)} + \delta_{q q_1} - \rho(q) = \frac{\rho^T(q q_1)}{\rho(q_1)} + \delta_{q q_1} \tag{2.9}$$

represents the excess density of particle α at x when a particle of type α_1 is fixed at x_1. The electroneutrality sum rule is always satisfied if $\eta > N$ in Eq. (2.6)[9,10] and in special cases less stringent clustering conditions will be sufficient. (See Appendixes A and B.)

Combining Eqs. (2.1) and (2.2) and using the definition of the truncated three point correlation function gives

$$\beta^{-1}\nabla_1\rho^T(q_1q_2)=[F(q_1)+F(q_1q_2)]\rho^T(q_1q_2)\ , \tag{2.10a}$$

$$-F(q_2q_1)\rho(q_1)\rho(q_2)\ , \tag{2.10b}$$

$$-\int_{\mathfrak{D}} dq\, F(qq_1)\rho(q_1)\rho^T(qq_2)\ , \tag{2.10c}$$

$$+\int_{\mathfrak{D}} dq\, F(q_1q)\rho^T(q_1q_2q)\ . \tag{2.10d}$$

We integrate q_1 in Eq. (2.10) on a sequence of finite volumes V such that $V\to\mathfrak{D}$. Because of the antisymmetry of $F(q_1q)$ and Eq. (2.7) we have

$$\lim_{V\to\mathfrak{D}}\int_V dq_1\int_{\mathfrak{D}} dq\, F(q_1q)\rho^T(q_1q_2q)=0\ . \tag{2.11}$$

Therefore Eq. (2.10) gives

$$\beta^{-1}\int_{\mathfrak{D}} dq_1\nabla_1\rho^T(q_1q_2)=\int_{\mathfrak{D}} dq_1[F(q_1)+F(q_1q_2)]\rho^T(q_1q_2) \tag{2.12a}$$

$$-\lim_{V\to\mathfrak{D}}\left\{\int_V dq_1F(q_2q_1)\rho(q_1)\rho(q_2)+\int_{\mathfrak{D}} dq\left[\int_V dq_1F(qq_1)\rho(q_1)\right]\rho^T(qq_2)\right\}\ . \tag{2.12b}$$

Since the left-hand side and the term in Eq. (2.12a) are well defined under the integrability conditions in Eqs. (2.7) and (2.6), it is clear that the limit in Eq. (2.12b) exists. Using the electroneutrality sum rule we subtract from $F(q_2q_1)$ its dominant asymptotic part $e_{\alpha_2}e_{\alpha_1}F^C(-x_1)$; using Eq. (2.4) we can rewrite Eq. (2.12b) as

$$\lim_{V\to\mathfrak{D}}\int_V dq_1[F(q_2q_1)-e_{\alpha_2}e_{\alpha_1}F^C(-x_1)]\rho(q_1)\rho(q_2)+\int_{\mathfrak{D}} dq\,\rho^T(qq_2)\int_V dq_1[F(qq_1)-e_{\alpha}e_{\alpha_1}F^C(-x_1)]\rho(q_1)$$
$$=\rho(q_2)[F(q_2)-F^e(q_2)]+\int_{\mathfrak{D}} dq\,\rho^T(qq_2)[F(q)-F^e(q)] \tag{2.12c}$$

and we obtain from Eqs. (2.12a) and (2.12c)

$$\beta^{-1}\int_{\partial\mathfrak{D}} dS_1\rho^T(q_1q_2)=F^e(q_2)\rho(q_2)+\int dq_1F^e(q_1)\rho^T(q_1q_2)-F(q_2)\rho(q_2)-\int dq_1F(q_2q_1)\rho^T(q_1q_2)\ . \tag{2.13}$$

By Eq. (2.1) the last term in Eq. (2.13) is $-\beta^{-1}\nabla_2\rho(q_2)$ and hence we obtain the WLMB *equation* relating the density gradient to the integral of ρ^T on the boundary surface $\partial\mathfrak{D}$ of the region $\mathfrak{D}$

$$\nabla_1\rho(q_1)=\beta F^e(q_1)\rho(q_1)+\beta\int_{\mathfrak{D}} dq\,F^e(q)\rho^T(qq_1)-\int_{\partial\mathfrak{D}} dS\,\rho^T(qq_1), \tag{2.14}$$

where

$$\int_{\partial\mathfrak{D}} dS=\int_{\partial\mathfrak{D}} ds(x)\int d\omega\sum_\alpha\ .$$

A. Remarks

(1) The electroneutrality sum rule implies that $F^e(q_1)$ in Eq. (2.14) can be defined up to a constant; therefore $F^e(q_1)$ in the WLMB equation can be taken as the actual external force given explicitly by

$$F^e(q_1)=F^s(q_1)+(e_{\alpha_1}+\mu_{\alpha_1}\cdot\nabla_1)E^e(x_1) \tag{2.15}$$

with

$$E^e(x_1)=E^{\rm out}(x_1)+\int dx\,C^e(x)[F^C(x_1-x)-F^C(-x)]-\nabla_1\int dx\{\mu^e(x)\cdot[F^C(x_1-x)-F^C(-x)]\}\ ,$$

where $F^s(q_1)$ denotes external forces which are not of electrostatic nature and $E^{\rm out}$, solution of $\nabla\cdot E^{\rm out}(x)=0$ for x in $\mathfrak{D}$, represents the field due to charges outside of $\mathfrak{D}$ (together with the polarization effect).

(2) Let us note that the one-body force in Eq. (2.4) in the BGY equation can be written equivalently as

$$F(q_1)=F^s(q_1)+\int dq\,F^S(q_1,q)\rho(q)+[e_{\alpha_1}+(\mu_{\alpha_1}\cdot\nabla_1)]E(x_1)\ ,$$

where $E(x_1)$ is the total electric field solution of

$$\nabla\cdot E(x)=\kappa_N[C(x)-\nabla\cdot\mu(x)]\ , \tag{2.16}$$

$$C(x)=\int d\omega\sum_\alpha e_\alpha\rho_\alpha(x,\omega)+C^e(x)\ , \tag{2.17}$$

$$\mu(x)=\int d\omega\sum_\alpha \mu_\alpha\rho_\alpha(x,\omega)+\mu^e(x)\ , \tag{2.18}$$

$$\kappa_N \text{ is a constant } (\kappa_1=2,\quad \kappa_2=2\pi,\quad \kappa_3=4\pi)\ . \tag{2.19}$$

(3) At this stage our derivation of Eq. (2.14) is purely formal. In the next section we shall give sufficient conditions under which the limit $V\to\mathfrak{D}$ in Eq. (2.12c) can be permuted with the integral over $\mathfrak{D}$ for several cases of interest. It is precisely to justify this permutation that it is necessary to substract in Eq. (2.12c) the dominant asymptotic part of the force.

(4) In the WLMB equation only the external force in Eq. (2.15) appears; since it is independent of the cutoff introduced in Eq. (2.3b) we can take F^C to be the true Coulomb force.

(5) It is of interest to note that the WLMB equation can also be written as

$$\nabla_1\rho(q_1)=\rho(q_1)\left[\beta\int_{\mathfrak{D}} dq\,F^e(q)\rho(q\,|\,q_1)-\int_{\partial\mathfrak{D}} dS\,\rho(q\,|\,q_1)\right]\ , \tag{2.20}$$

whenever x_1 is in $\mathfrak{D}$ with $\rho(q\,|\,q_1)$ the excess density of particle in Eq. (2.9).

(6) The integral on the boundary $\partial\mathfrak{D}$ of $\mathfrak{D}$ does not appear in the original papers (Refs. 6 and 7) because the authors have considered only the case where $\mathfrak{D}=\mathbb{R}^N$ is the whole space. As we shall see in the next section, when $\mathfrak{D}\neq\mathbb{R}^N$ this boundary contribution is important for applications.

(7) Introducing the direct correlation function $C(q_1,q_2)=C(1,2)$ defined as usual by the Ornstein–Zernicke equation

$$\rho^T(1,2) = \rho(1)\,C(1,2)\,\rho(2) + \int d3\,\rho^T(1,3)\,C(3,2)\,\rho(2)$$

$$= \int d3\,\hat{\rho}(1,3)\,C(3,2)\,\rho(2)\ , \qquad (2.21)$$

$$\hat{\rho}(1,2) = \rho^T(1,2) + \delta(1,2)\,\rho(2) = \rho(1|2)\,\rho(2)\ ,$$

and using the symmetry of ρ^T and C, we have in operator notation

$$1\rho = (1-\rho C)\,\hat{\rho} \quad \text{and} \quad \rho C \rho = (1-\rho C)\,\rho^T\ . \qquad (2.22)$$

Let us write the WLMB equation as

$$\nabla_2 \rho(2) = \beta \int_{\mathfrak{D}} d3\,\hat{\rho}(2,3)\,F^e(3) - \int_{\partial\mathfrak{D}} ds(3)\,\rho^T(2,3)\ . \qquad (2.23)$$

In the case of *short range forces* ($e_\alpha = d_\alpha = 0$) we expect that the operator $\hat{\rho}(1,2)$ does not have the eigenvalues zero; multiplying Eq. (2.23) by $(1-\rho C)(1,2)$ and integrating over 2 we obtain

$$\nabla_1 \rho(q_1) = \beta F^e(q_1)\,\rho(q_1) + \int_{\mathfrak{D}} dq\,\rho(q_1)\,C(q_1,q)\,\nabla_x \rho(q)$$

$$- \int_{\partial\mathfrak{D}} ds\,\rho(q_1)\,C(q_1,q)\,\rho(q)\ , \qquad (2.24)$$

i.e.,

$$\nabla_1 \rho(q_1) = \beta F^e(q_1)\,\rho(q_1) - \int_{\mathfrak{D}} dq\,\rho(q_1)\,\rho(q)\,\nabla_x C(q_1,q)\ . \qquad (2.25)$$

Equation (2.24) without the surface term was formally obtained for $\mathfrak{D} = \mathbb{R}^N$ already in Refs. 6 and 7.

In the case of *charged systems* however the electroneutrality sum rules implies that $\hat{\rho}(1,2)$ has the eigenvalue zero

$$\int_{\mathfrak{D}} dq_2\, e_{\alpha_2}\,\hat{\rho}(q_1,q_2) = 0$$

and it is not clear whether Eqs. (2.24) and (2.25) are still correct. If this is the case, introducing the usual notation

$$C(q_1,q_2) = -\beta\,\frac{e_{\alpha_1} e_{\alpha_2}}{|x_1 - x_2|} + C^S(q_1,q_2)$$

we obtain for purely charged system ($N=3$)

$$\nabla_1 \rho(q_1) = \beta\,[F^s(q_1) + e_{\alpha_1} E(x_1)]\,\rho(q_1)$$

$$- \int_{\mathfrak{D}} dq\,\rho(q_1)\,\rho(q)\,\nabla_x C^S(q_1,q)$$

which differs by the surface contribution from the formula used by Totsuji in[12] but implies the Gouy–Chapman equation in the approximation $C^S = 0$.

(8) Finally let us note that the WLMB equation is the first member of the following hierarchy connecting the n and $(n+1)$ correlation functions:

$$\sum_{j=1}^{n} \nabla_j\,\rho(q_1\cdots q_n) = \beta \sum_{j=1}^{n} F^e(q_j)\,\rho(q_1\cdots q_n)$$

$$+ \beta \int_{\mathfrak{D}} dq\,F^e(q)\,[\rho(qq_1\cdots q_n) - \rho(q)\,\rho(q_1\cdots q_n)]$$

$$- \int_{\partial\mathfrak{D}} ds\,[\rho(qq_1\cdots q_n) - \rho(q)\,\rho(q_1\cdots q_n)]\ . \qquad (2.26)$$

These equations are obtained combining the nth and $(n+1)$th member of the BGY hierarchy as we have combined Eqs. (2.1) and (2.2) to obtain Eq. (2.14).

III. APPLICATIONS

A. Short range forces: $e_\alpha = d_\alpha = 0$ for all species

In this case, Eq. (2.7) implies that $F(q_1,q)\,\rho^T(qq_2) = F^S(q_1,q)\,\rho^T(qq_2)$ is jointly integrable in q, q_1 which justifies Eq. (2.12c), whereas $F^e(q)$ reduces trivially to $F^S(q)$.

It should be noted that if the force satisfies the slightly stronger condition

$$\int dx\,|x|^N\,|F^S_{\alpha_1\alpha}(x)| < \infty$$

then the WLMB can be rigorously established under the clustering condition $\eta > N-1$ in Eq. (2.6) without Eq. (2.7). This extension is obtained by the same argument as the one used in the Appendix of Ref. 13.

Let us remark that when $\mathfrak{D} = \mathbb{R}^N$ and $F^{(e)}(q) = 0$, Eq. (2.26) reduces to $\sum_j \nabla_j \rho(q_1\cdots q_n) = 0$; we thus recover a version of the Goldstone theorem discussed in Ref. 13, namely that such clustering states are necessarily invariant under translation.

B. Local imhomogeneities in Coulomb systems ($\rho_B = 0$)

We consider a charged system in the presence of a localized distribution of charges and dipoles $C^{(e)}(x)$, $\mu^{(e)}(x)$. The system may have additional inhomogeneities due to localized obstacles in $\mathbb{R}^N$, such as fixed extended hard ions, i.e., $\mathfrak{D}$ consists of the outside of some finite region.

Sufficient conditions for the validity of the WLMB equation are:

(i) Equation (2.7);

(ii) Equation (2.6) with

$$\eta > N+1\ ; \qquad (3.1)$$

(iii)

$$C(x) \le \frac{M}{|x|^\epsilon}\ , \quad \mu(x) \le \frac{M}{|x|^\epsilon} \text{ as } |x| \to \infty\ , \quad \epsilon > 0\ . \qquad (3.2)$$

(The proof is given in Appendix C.)

Condition (iii) is the assumption that the state has asymptotically homogeneous, isotropic, and neutral densities and condition (ii) implies that the trucated correlation functions have integrable first moments in all directions

$$\int dq_1\,|x_1|\,|\rho^T(qq_1)| < \infty \qquad (3.3)$$

and that the electroneutrality sum rule Eq. (2.8) holds (see Appendix A).

C. The semi-infinite system ($\rho_B = 0$)

$\mathfrak{D}$ is the half-plane $\{x = (u,z);\ u = x^1, \ldots, x^{N-1}),\ z = x^N \ge 0\}$. Planar electrodes located at $z=0$ (respectively, $z=+\infty$) carry uniform charge densities σ (respectively, $-\sigma$) producing a constant electric field

$\kappa_N \sigma$ along the z direction in $\mathfrak{D}(\kappa_1=2,\ \kappa_2=2\pi,\ \kappa_3=4\pi)$. There are no additional external forces in $\mathfrak{D}$:

$$C^{(e)}(x)=0 \quad \mu^{(e)}(x)=0 \quad F^{(S)}(x)=0 \ .$$

We investigate the properties of states which are translation invariant in the u direction and rotation invariant around the z axis, i.e.,

$$C(x)=C(z), \quad \mu(x)=[0,0,\ldots,\mu(z)\ , \quad E(x)=[0,0,\ldots,E(z)].$$

Using this symmetry, the following conditions [supplementing Eqs. (2.7) and (2.8)]

$$\lim_{z\to\infty} C(z)=0 \quad \lim_{z\to\infty}\mu(z)=\mu^b \ , \tag{3.4}$$

$$\int dq\ |z\rho^T(q,q_1)|<\infty \tag{3.5}$$

are sufficient for the derivation of the WLMB equation (see Appendix C).

Because of the uniform charge distribution on the electrodes $F^{(e)}$ is constant over $\mathfrak{D}$; taking into account the electrality sum rule Eq. (2.8) and the translation invariance in the u directions, the WLMB equation reduces to the simple form

$$\frac{\partial}{\partial z_1}\rho_{\alpha_1}[(0,z_1),\omega_1]=\int du\int d\omega\sum_\alpha \rho^T_{\alpha_1\alpha}[(u,z_1),\omega_1;0,\omega]\ . \tag{3.6}$$

Several interesting conclusions can be drawn from Eq. (3.6).

1. The compressibility of the film absorbed at the electrode

Evaluating the right-hand side of Eq. (3.6) at $z_1=0$, we obtain a formula for the compressibility $\mathcal{K}$ of the film absorbed at the electrode, $\mathcal{K}$ being defined as the derivative at contact of the singlet density.

2. A sum rule for the two point function

Integrating Eq. (3.6) on z_1 from z to ∞ and summing over charges or dipoles yields the densities

$$C(z)=-\int_z^\infty dz_1\int du_1\int d\omega\int d\omega_1\sum_{\alpha_1\alpha} e_{\alpha_1}\rho^T_{\alpha_1\alpha}(u_1z_1\omega_1;0\omega)\ , \tag{3.7}$$

$$\mu(z)-\mu^b=-\int_z^\infty dz_1\int du_1\int d\omega\int d\omega_1 \times\sum_{\alpha_1\alpha} d_{\alpha_1}\omega_1\rho^T_{\alpha_1\alpha}(u_1z_1\omega_1;0\omega)\ , \tag{3.8}$$

we get from Eq. (3.7) the integrated density profile

$$\int_0^\infty dz\,C(z)=-\int d\omega\sum_\alpha\int_{\mathfrak{D}} dq_1 e_{\alpha_1}z_1\rho^T(q_1;\alpha,0,\omega)\ . \tag{3.9}$$

The total electric field determined by these densities and subject to the boundary condition $E(0)=\kappa_N[\sigma-\mu(0)]$ is

$$E(z_1)=E(0)+\kappa_N\left[\int_0^{z_1}dz\,C(z)-\mu(z_1)+\mu(0)\right]\ . \tag{3.10}$$

Combining Eqs. (3.8), (3.9), and (3.10), we have:

$$E(0)-E^b=\kappa_N\int d\omega\sum_\alpha\int_{\mathfrak{D}} dq_1(e_{\alpha_1}z_1+d_{\alpha_1}\omega_1^z)\rho^T(q_1;\alpha,0,\omega) \tag{3.11}$$

with $E^b=\lim_{z\to\infty}E(z)$ the bulk electric field.

When perfect screening of the electrode occurs, i.e., $E^b=0$, Eq. (3.11) together with Eq. (2.18) and the boundary condition for $E(0)$ give the following sum rule for the two point function:

$$\sigma=\int d\omega\sum_\alpha\left[d_\alpha\omega^z\rho_\alpha(0,\omega) +\int dq_1(e_{\alpha_1}z_1+d_{\alpha_1}\omega_1^z)\rho^T(q_1;\alpha,0,\omega)\right]\ . \tag{3.12}$$

Introducing the excess particle density $\rho(q_1|q)$ when a particle is at the wall, this sum rule takes the form

$$\sigma=\int d\omega\sum_\alpha\int dq_1(e_{\alpha_1}z_1+d_{\alpha_1}\omega_1^z)\rho(q_1|\alpha 0\omega)\rho_\alpha(0,\omega)\ . \tag{3.13}$$

The physical interpretation of Eq. (3.13) is that the total dipole moment of the excess density due to particles at the wall equals the surface charge of the plate. An alternative derivation of Eq. (3.13) in the case where there are no dipoles has been presented in Ref. 5.

3. Weak clustering along the wall

The WLMB equation and the sum rule Eq. (3.13) were derived under the assumption of the electroneutrality Eq. (2.8). Equation (2.8) was proven in Ref. 10 for charged systems and arbitrary domains $\mathfrak{D}$ under the condition in Eq. (2.6) with $\eta>N$; this condition requires an isotropic decay of the correlations in $\mathfrak{D}$. However, for the particular geometry of the half-space, one can introduce a weaker condition allowing a slower decay along the wall: $\rho^T(q_1,\ldots,q_n)$ satisfies the condition of Eq. (2.6) in any cone

$$\mathfrak{D}^\delta=\{x|\,x\cdot\hat{z}\geq\delta>0\}\ . \tag{3.14}$$

The proof of Eq. (2.8) under the condition of Eq. (3.14) with $\eta>N$ [in addition to the integrability of correlation in Eq. (2.7) in $\mathfrak{D}$] can be found in the Appendix B.

Moreover, when the first moments of the correlations are integrable in all directions in $\mathfrak{D}$, i.e.,

$$\int_{\mathfrak{D}}dq_1|x_1|\ |\rho^T(q_1q_2)|<\infty\ , \qquad \int_{\mathfrak{D}}dq_1|x_1|\ |\rho^T(q_1q_2q_3)|<\infty\ , \tag{3.15}$$

and the condition in Eq. (3.14) holds with $\eta>N+1$, the excess particle density carries no dipole moment [see Eq. (A5) and Appendix B], i.e.,

$$\int dq_1(e_{\alpha_1}z_1+d_{\alpha_1}\omega_1)\rho(q_1|q)=0\ . \tag{3.16}$$

If one assumes that there is a decay perpendicular to the electrode of the type $z^{-(N+1+\epsilon)}$, one sees that Eq. (3.14) holds with $\eta>N+1$, and thus Eqs. (2.8) and (3.13) are true. Then Eq. (3.13) with $\sigma\neq0$ implies that the dipole sum rule Eq. (3.16) is not verified, and therefore, the correlations cannot have finite first moment in all directions. Since there are good decay properties in the bulk, this implies weak clustering along the electrode, namely, if $\sigma\neq0$, $\rho^T(q_1,q_2)$ has to decay as or slower as $|u_1|^{-N}$, $|u_1|\to\infty$ for fixed z_1 and q_2.

In fact a $|u|^{-N}$ behavior has been found in the 2-dim jellium for a special value of the temperature by explicit calculations, and in the three dimensional one and two component plasmas in a weak coupling approximation.[14,15] Although we cannot draw such conclusions here when $\sigma=0$, these model calculations show that the weak decay occurs also when $\sigma=0$.

Notice that with this $|u|^{-N}$ and $z^{-(N+1+\epsilon)}$ decay the truncated functions are integrable on $\mathfrak{D}$ and satisfy Eq. (3.14) with $\eta>N+1$ which implies the validity of the electroneutrality rule of Eq. (2.8).

D. Jellium systems ($\rho_B \neq 0$, $d_\alpha = 0$)

We now treat the case where there is a fixed background of uniform charge density ρ_B in $\mathfrak{D}$. For simplicity we set $d_\alpha=0$ for all α and $\mu^{(e)}(x)=0$ (no dipoles). In this case, one does not need to cut-off the Coulomb force at the origin, i.e., $F^C(x)=x/|x|^N$ everywhere.

1. Local inhomogeneities

We consider first local inhomogeneities as described in Application B. Now $C^{(e)}(x)$ is of the form

$$C^{(e)}(x)=\rho_B\,\chi_D(x)+\tilde{C}^{(e)}(x)\ , \tag{3.17}$$

where $\chi_D(x)=1$, $x\in\mathfrak{D}$, $\chi_D(x)=0$ otherwise and $\tilde{C}^{(e)}(x)$ is some local additional charge distribution in $\mathfrak{D}$.

The conditions of application 2 are again sufficient for the derivation of the WLMB equation (see Appendix C). In this case, we write $F^e(q)$ of Eq. (2.15) in the form

$$F^e(q)=\tilde{F}^e(q)+e_\alpha\rho_B\lim_{R\to\infty}\int_{\substack{|x_1|<R\\ x_1\in\mathfrak{D}}} dx_1[F^C(x-x_1)-F^C(-x_1)]\ , \tag{3.18}$$

where $\tilde{F}^e(q)$ represents the sum of all external forces (including the system's charges at infinity) with the exception of the background contribution which has been singled out explicitly in Eq. (3.18)

This later contribution can then be written as

$$e_\alpha\rho_B\left\{\lim_{R\to\infty}\int_{|x_1|<R} dx_1[F^c(x-x_1)-F^c(-x_1)] - \int_{\mathbb{R}^N|\mathfrak{D}} dx_1[F^c(x-x_1)-F^c(-x_1)]\right\}=e_\alpha\left[\rho_B\frac{\kappa_N}{N}x-J(x)\right], \tag{3.19}$$

where $J(x)$ is simply the electric field produced by a uniform charge density ρ_B in the complementary region $\mathbb{R}^N|\mathfrak{D}$ (which is assumed to be finite here).

Inserting now Eqs. (3.18) and (3.19) into Eq. (2.14), we obtain the WLMB equation appropriate to this case

$$\nabla_1\rho(q_1)=\beta[\tilde{F}^e(q_1)-e_{\alpha_1}J(x_1)]\,\rho(q_1)+\beta\int_{\mathfrak{D}} dq[\tilde{F}^e(q) - e_\alpha J(x)]\,\rho^T(qq_1)-\int_{\partial\mathfrak{D}} ds\,\rho^T(qq_1)\ . \tag{3.20}$$

In Eq. (3.20) we have used the dipole sum rule of Eq. (A5) which is true under our clustering condition Eq. (2.6) with $\eta>N+1$ (see Appendix A).

We notice that when $\mathfrak{D}=\mathbb{R}^N$ and $\tilde{F}^e(q)=0$, Eq. (3.20) reduces to $\nabla_1\rho(q_1)=0$, establishing the translation invariance of jellium systems under the same clustering conditions as in Ref. 13.

2. The semi-infinite jellium

We take the same situation as in Application C with no dipoles, one type of ions of charge e, and $C^{(e)}(z)=\rho_B$, $z\ge 0$, $F^{(s)}(q)=0$.

The conditions of Application 3 are again sufficient for the derivation of the WLMB equation (see Appendix C). In this case:

$$F^{(e)}(x_1)=F^{(e)}(z_1)=eE^{(e)}+e\rho_B\lim_{L\to\infty}\int_0^L dz\int d^{N-1}u \times[F^c(u,z_1-z)-F^c(u,-z)] = eE^{(e)}+e\kappa_N\rho_B z_1\ . \tag{3.21}$$

Introducing Eq. (3.21) in Eq. (2.14) and using the electroneutrality sum rule yields

$$\frac{d}{dz_1}\rho(z_1)=\int d^{N-1}u\,\rho^T(uz_1,0)+\kappa_N\beta\rho_B\,\rho(z_1)\int dq\,ez\,\rho(q|q_1). \tag{3.22}$$

Let us show that, as in the case of a several component system, Eq. (3.22) implies a weak decay parallel to the electrode.

If one assumes that $\rho^T(qq_1)$ decays as $z^{-(N+1+\epsilon)}$ in the bulk and has finite first moments in the u plane, the last term of Eq. (3.22) vanishes by the dipole sum rule. Repeating the arguments leading to Eq. (3.13) we will get assuming $E^b=0$

$$\sigma=\rho(0)\int_{\mathfrak{D}} dq\,ez\,\rho(q|0)=0$$

a contradiction when $\sigma\neq 0$! Therefore $\rho^T(qq_1)$ cannot have integrable moments in the u plane.

The dipole sum rule is however expected to hold asymptotically in the bulk, i.e.,

$$\lim_{z_1\to\infty}\int_{\mathfrak{D}} dq\,ez\,\rho(q|q_1)=0\ . \tag{3.23}$$

If the above quantity vanishes as $z_1^{-(2+\epsilon)}$ as $z_1\to\infty$, we can compute from Eq. (3.22) the charge density and the integrated profile, as in Eqs. (3.7) and (3.19). This leads to the sum rule

$$\sigma=\int dq\,ez\,\rho^T(q,0)+\kappa_N\beta\rho_B\int_0^\infty dz_1\,ez_1\left[\int dq\,ez\,\rho^T(q,z_1)\right]. \tag{3.24}$$

APPENDIX A

In this Appendix, we generalize the results of Ref. 10 to mixtures of ions and dipoles for general domains $\mathfrak{D}$.

1. Proposition

Let $\mathfrak{D}$ be some domain in $\mathbb{R}^N$ extending to infinity at least in one direction and assume that the charged particles have nonvanishing density in $\mathfrak{D}$. Then if Eq. (2.6) holds with $\eta>N$ for $n=2,3$, the charge sum rule Eq. (2.8) is true. If Eq. (2.6) holds with $\eta>N+1$ for $n=2$, 3, then the dipole sum rule Eq. (A5) is true.

2. Proof

We proceed exactly as in § *B*, *C*, *D* of Ref. 10, letting $|x_1|\to\infty$ in $\mathfrak{D}$ and examining the asymptotic behavior of the terms in Eq. (2.13).

Let q_1 be a charged particle with nonvanishing density $\rho(q_1)\neq 0$. The longest range part of the interaction is the Coulomb term

$$F(q_1,q_2)=e_{\alpha_1}e_{\alpha_2}\frac{x_1-x_2}{|x_1-x_2|^N}+o\left(\frac{1}{|x_1-x_2|^{N-1}}\right), \quad e_{\alpha_1}\neq 0. \tag{A1}$$

The only difference with a pure ionic gas is that the force and the correlations depend now on the additional dipole variables. But it follows from the hypothesis of Eq. (2.6) that they satisfy all the conditions of the Lemmas 1 and 2 of Ref. 10 with $\gamma=N-1$ *and* $l=0$ uniformly with respect to the dipole variables. Since these variables are integrated over a compact space, the result of these Lemmas remains true by dominated convergence. One finds as in § *B* of Ref. 10 that

$$\rho(q_1)\int dq\, F(q_1,q)\,\rho(q\,|q_2)=o\left(\frac{1}{|x_1|^{N-1}}\right). \tag{A2}$$

As in Ref. 10, one must average Eq. (2.10) on a local region around x_1 to take care of the gradient term in the left-hand side on Eq. (2.10) and assume the nonvanishing density (S_1) of Ref. 10. In view of Eq. (A1) and the fact that $\rho(q_1)\neq 0$, this implies the charge sum rule Eq. (2.8).

We now use the charge sum rule to substract the asymptotic behavior of the Coulomb force in Eqs. (2.10b) and (2.10c). We apply the Lemma 2 of Ref. 10 to find

$$\rho(q_1)\int dq\left[F(q_1,q)-e_\alpha e_{\alpha_1}\frac{x_1}{|x_1|^N}\right]\rho(q\,|q_2)=o\left(\frac{1}{|x_1|^N}\right). \tag{A3}$$

From Eq. (2.3), one gets the asymptotic behavior

$$F^j(q_1,q)-e_\alpha e_{\alpha_1}\frac{x_1^j}{|x_1|^N}=-d_i^j(\hat{x}_1)\frac{1}{|x_1|^N}(e_{\alpha_1}e_\alpha x^i+e_{\alpha_1}\mu_\alpha^i-e_\alpha\mu_{\alpha_1}^i)+o\left(\frac{1}{|x_1|^N}\right), \tag{A4}$$

with

$$d_i^j(\hat{x})=\delta_{ij}-Nx^ix^j\ .$$

The first contribution in Eq. (A4) is the first term in the Taylor expansion of the Coulomb force for large $|x_1|$; the second one comes from the charge-dipole interaction. The Lemma 1 of Ref. 10 with Eqs. (A3) and (A4) and the fact that the matrix $d_i^j(\hat{x})$ is invertible imply

$$\int dq(e_{\alpha_1}e_\alpha x+e_{\alpha_1}\mu_\alpha-e_\alpha\mu_{\alpha_1})\,\rho(q\,|q_2)=0$$

giving the dipole sum rule

$$\int dq(e_\alpha x+\mu_\alpha)\,\rho(q\,|q_2)=0\ . \tag{A5}$$

In the derivation of the dipole sum rule, one has to use The Lemmas 1, 2 of Ref. 10 with $\gamma=N-1$ *and* $l=1$ to control the Coulomb force, and with $\gamma=N$ *and* $l=0$ to control the charge-dipole force.

3. Remarks

One can prove in the same way

$$\int dq(e_\alpha x+\mu_\alpha)\,\rho(q\,|q_1,\,\ldots,\,q_k)=0\ ,$$

when Eq. (2.6) holds with $\eta>N+1$ for $n=2,3,\ldots,k+2$.

If the system consists in a mixture of pure charges and pure dipoles, the condition $\eta>N+1$ used for the derivation of the dipole sum rule is not needed for the dipole–dipole correlations.

APPENDIX B

In this Appendix, we show that the $l=0$ (respectively, $l=1$) sum rules are valid under conditions which are weaker than in Ref. 10 for semi-infinite systems. For this we prove that the Lemmas 1 and 2 of Ref. 10 with $l=0$ (respectively $l=1$) remain true when the truncated correlations are integrable in the half-space, i.e., Eq. (2.7) and the condition of Eq. (3.14) holds with $\eta>N$ [respectively , when the truncated functions have finite first moments, i.e., Eqs. (3.15), and (3.14) holds with $\eta>N+1$].

We set $\bar{\mathfrak{D}}^\delta=\mathfrak{D}|\mathfrak{D}^\delta$ and write all integrals on $\mathfrak{D}$ occurring in the statements of Lemmas 1 and 2 as sums of integrals on the disjoint domains $\mathfrak{D}^\delta$ and $\bar{\mathfrak{D}}^\delta$. We set $x_1=\lambda\hat{n}+y$ in Eq. (A2), where y is some fixed vector. Both Lemmas apply in $\mathfrak{D}^\delta$ with $\gamma=N-1$ and $l=0$ (respectively, $l=1$) for any δ by hypothesis.

Moreover if $x\in\bar{\mathfrak{D}}^\delta$, one has

$$|x_1-x|=|\lambda\hat{n}+y-x|\geq|\lambda\hat{n}-x|-|y|\geq\sqrt{1-\delta}\,\sqrt{\lambda^2+|x|^2}-|y|\,.$$

Hence $x\in\bar{\mathfrak{D}}^\delta$ implies $\lambda/|x_1-x|=O(1)$. One finds from Eq. (2.3)

$$\lambda^{N-1}F(q_1,q)=O(1)$$

and, using the limited Taylor expansion

$$\lambda^N\left[F(q_1,q)-e_{\alpha_1}e_\alpha\frac{x_1}{|x_1|^N}\right]=O(|x|)$$

uniformly with respect to $\lambda\geq 0$, and uniformly with respect to y in compact sets.

Since the truncated correlated functions are integrable on $\bar{\mathfrak{D}}^\delta$ (respectively, have finite first moment), one finds that

$$\lambda^{N-1}\int_{\bar{\mathfrak{D}}^\delta}dq\,|F(q_1,q)\,\rho(q\,|q_2)|\leq M_1\int_{\bar{\mathfrak{D}}^\delta}dq\,|\rho(q\,|q_2)|$$

$$\lambda^N\int_{\bar{\mathfrak{D}}^\delta}dq\left|\left[F(q_1,q)-e_{\alpha_1}e_\alpha\frac{x_1}{|x_1|^N}\right]\rho(q\,|q_2)\right|$$

$$\leq M_2\int_{\bar{\mathfrak{D}}^\delta}dq\,|x|\;|\rho(q\,|q_2)|$$

tend to zero as $\delta\to 0$ uniformly with respect to λ and y in compact sets.

The results of Lemmas 1 and 2 are obtained by first taking the limit $\lambda\to\infty$ and then $\delta\to 0$.

APPENDIX C

In order to demonstrate Eq. (2.12c), we show that

$$\begin{aligned}\int_V dq[F^L(q_1,q) - e_{\alpha_1}e_\alpha F^c(-x)]\rho(q) \\ = e_{\alpha_1}\int_V dx[F^c(x_1-x) - F^c(-x)]C^S(x) \\ - \int_V dx(\mu_{\alpha_1}\cdot\nabla_x)F^c(x_1-x)C^S(x) \\ + e_{\alpha_1}\int_V dx[\mu^S(x)\cdot\nabla_x]F^C(x_1-x) \\ + \int_V dx[\mu^S(x)\cdot\nabla_x](\mu_{\alpha_1}\cdot\nabla_{x_1})F^C(x_1-x)\end{aligned} \tag{C1}$$

converges as $V\to\mathfrak{D}$ for a suitable sequence of volumes V, and these terms are $O(|x_1|)$ (Application B) or $O(|z_1|)$ (Application C) uniformly with respect to V. Then with Eq. (3.3) or (3.5) the validity of Eq. (2.12c) follows by dominated convergence.

In Eq. (C1), $C^S(x) = \int d\omega \sum_\alpha e_\alpha \rho_\alpha(x,\omega)$ and $\mu^S(x) = \int d\omega \sum_\alpha \mu_\alpha \rho_\alpha(x,\omega)$ are the local system's charge and dipole density.

1. Application B

We show that $C^S(x)\,[F^c(x_1-x) - F^C(-x)]$ is absolutely integrable on $\mathfrak{D}$ and the integral is $O(|x_1|)$.

Choose $a \ge R$, R given in Eq. (2.3b) and for fixed x_1 divide $\mathfrak{D}$ into the sets $\mathfrak{D}' = \{x\in\mathfrak{D}';\ |x| > 2|x_1| + a\}$ and $\mathfrak{D}'' = \{x\in\mathfrak{D};\ |x|\le 2|x_1|+a\}$. When $x\in\mathfrak{D}'$, $|x-x_1| > (|x|+a)/2$ and $|x_1 - x| > a$, and one can estimate $F^C(x_1-x) - F^C(-x)$ by a limited Taylor expansion

$$\begin{aligned}|F^C(x_1-x) - F^C(-x)| &= \left|\frac{x_1-x}{|x_1-x|^N} - \frac{x}{|x|^N}\right| \\ &\le \sup_{0\le\theta\le 1}\frac{M|x_1|}{|x_1-\theta x|^N} \le \frac{2M|x_1|}{|x|^N}\ .\end{aligned}$$

This shows with Eq. (3.2) that $|F^C(x_1-x) - F^C(-x)|$ is integrable on $\mathfrak{D}'$ and

$$\int_{\mathfrak{D}'} dx|C^S(x)[F^C(x_1-x) - F^C(-x)| = O(|x_1|)\ .$$

The corresponding integral over $\mathfrak{D}''$ is also $O(|x_1|)$ by the Lemma 4 of Ref. 16, p. 70.

With the same decomposition $\mathfrak{D} = \mathfrak{D}'\cup\mathfrak{D}''$, we have

$$|\nabla_x F^C(x_1-x)| \le \frac{M}{|x_1-x|^N} \le \frac{2M}{|x|^N},\quad x\in\mathfrak{D}'.$$

Hence

$$\int_{\mathfrak{D}'} dx\,|\mu^S(x)\cdot\nabla_x F^C(x_1-x)| = O(1)$$

and an application of the Lemma 4,[15] gives

$$\int_{\mathfrak{D}''} dx\,|\mu^S(x)\cdot\nabla_x F^C(x_1-x)| = O(\ln(|x_1|))\ .$$

In the same way, all terms in Eq. (C1) are integrable on $\mathfrak{D}$ and at least $O(|x_1|)$. This gives the results (2.12c). Moreover, since terms in Eq. (C1) involving gradients are absolutely integrable, integrals and gradients can be exchanged implying that Eq. (2.15) holds true.

2. Application C

Let V_L be a sequence of slabs $\{x;\ u\in\mathbb{R}^{N-1},\ 0\le z\le L\}$; set $x_1 = (0,z_1)$ and consider the z component of the force. Notice that for $z > R$ [R given in Eq. (2.3b)], one finds

$$\int d^{N-1}u\,F^C(u,z) = \int d^{N-1}u\,\frac{z}{(u^2+z^2)^{N/2}} = \frac{\kappa_N}{2}\,\mathrm{sign}\,z = \frac{\kappa_N}{2}\ . \tag{C2}$$

Moreover $\int d^{N-1}u\,F^C(u,z)$ is a continuous function of z, and hence also bounded for $0\le z\le R$.

Since for $z > R + z_1$, $|z_1 - z| > R$, and $z > R$, the integrand in Eq. (C3) vanishes in virtue of Eq. (C2) for L large enough

$$\begin{aligned}\int_{V_L} dx[F^C(x_1-x) - F^C(-x)]C^S(x) \\ = \int_0^{R+z_1} dz\,C^S(z)\int d^{N-1}u[F^C(u,z_1-z) - F^C(u_1-z)]\ .\end{aligned} \tag{C3}$$

The integrand of Eq. (C3) being uniformly bounded in z and z_1, it is clear that Eq. (C3) is $O(z_1)$ uniformly in L.

The terms in Eq. (C1) involving derivatives are treated in the same way, and it can be checked that the limit $L\to\infty$ and derivatives can be exchanged everywhere.

3. Application D

(i) Local inhomogeneities. Let $V_R = \{x;\ |x|\le R\}$ be a sequence of spheres, and write the first term of the right-hand side of Eq. (C1) as [since $C(x) = C^S(x) + \rho_B$]

$$\begin{aligned}e_{\alpha_1}\int_{V_R} dx[F^C(x_1-x) - F^C(-x)]\,C(x) \\ - e_{\alpha_1}\rho_B\int_{V_R} dx[F^C(x_1-x) - F^C(-x)]\end{aligned} \tag{C4}$$

with Eq. (3.2), the first integral is absolutely convergent and the integral in $O(|x_1|)$ as in the Application 2.

The second term can be calculated explicitly with the result

$$\int_{V_R} dx\left(\frac{x_1-x}{|x_1-x|^N} + \frac{x}{|x|^N}\right) = \begin{cases}\dfrac{\kappa_N}{N}x_1 & |x_1| < R \\ \dfrac{\kappa_N}{N}R^N\dfrac{x_1}{|x_1|^N} & |x_1| > R\end{cases} \tag{C5}$$

showing that this integral is $O(|x_1|)$ uniformly with respect to V_R. Thus Eq. (2.12c) holds true.

(ii) The arguments needed to control Eq. (2.12c) in the case of the semi-infinite jellium are the same as in Application C.

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