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On Potential and Field Fluctuations in Classical Charged Systems

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Using electrostatic identities the potential and microfield in a plasma, important for determining line shapes, are expressed as limits of local quantities. These are shown to be well defined for typical configurations of macroscopic, i.e., infinite systems (under some mild clustering assumptions). Their covariance contains a slowly decaying part ($|x|^{-1}$, for the potential) whose coefficient is universal whenever the Stillinger–Lovett second moment condition holds. We show further that the contributions from distant regions (which are equal to suitable averages over local regions) have a Gaussian distribution.

KEY WORDS: Coulomb systems; potential fluctuations; microfield distribution; particle correlations; sum rules; clustering.

1. INTRODUCTION

We investigate the fluctuations of the potential and electric field in a classical system of charged particles in three dimensions. Knowledge of the distribution of the electric field, usually referred to as the microfield, is important for understanding the structure of charged systems and for determining the shape of spectral lines emitted by a neutral or partially ionized atom (radiator) in a plasma.(1)

The line shape problem was first considered by Holtsmark(2) and Margenau,(3) who developed the statistical theory of line broadening. Their computation of the microfield distribution neglected all correlations between the charges and much effort has since been devoted to improving the

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resulting Holtsmark distribution.[1,3–9] An important input into the approximation scheme used in Ref. 9 which appears to give the best agreement with computer simulations, is the exact value of the second moment of the electric field distribution at a charged ion in a one-component plasma (jellium). This shows the usefulness of exact relations for the microfield distribution and is one of the motivations of the present work.

In carrying out this analysis, it is necessary, owing to the long-range nature of the Coulomb potential, that careful attention be paid to the (infinite volume) limits required for defining the microfield in a macroscopic (formally infinite) charged system. It is the purpose of this note to prove, under some reasonable assumptions, the existence of these limits and to derive expressions (involving only low-order particle correlations) for the covariance of the field at different points in space. We hope that this will be useful both for the development of a general theory of Gibbs states of charged systems, as well as for developing microfield distributions in a manner similar to that of Ref. 9 in a general plasma.

We note here that in some cases, e.g., for high temperature and low-density plasmas, for charges on a lattice, for fully symmetric systems, our results follow, more or less explicitly, from first principle computations without any additional assumptions.[10] Another special case is the one-component plasma, jellium, in two dimensions at one particular temperature $T = 2e^2/K_B$. At this value the correlations are known[11] and the whole analysis can be carried out explicitly. This as well as the general two-dimensional case will be discussed in a paper by Alastuey and Jancovici.[12]

Formulation of Problem

We consider a system of N charged classical particles at equilibrium in a finite volume $\Lambda \subset \mathbb{R}^3$. A particle of species α carries a charge e_α and we may have an additional uniform external charge density ρ_B (jellium model). The system is globally neutral

$$\sum_{i=1}^{N} e_{\alpha_i} + |\Lambda| \rho_B = 0 \tag{1.1}$$

where $|\Lambda|$ is the volume of Λ.

The particles interact by a two-body potential

$$\phi(q_1, q_2) = \frac{e_{\alpha_1} e_{\alpha_2}}{|x_1 - x_2|} + \phi^s(q_1, q_2) \tag{1.2}$$

where we use the abbreviated notation $q = (\alpha, x)$, x denoting the position of the particle.

$\phi^s(q_1, q_2)$ is a short-range potential, invariant under translations and rotations, which includes the local repulsion effects needed for thermodynamic stability.

The equilibrium state of the system at inverse temperature β is described by the set of its correlation functions $\rho_\Lambda(q_1, \ldots, q_n)$ defined in the canonical ensemble, and we write $\langle F \rangle_\Lambda$ for the thermal average of a function F on configuration space.

Of particular importance is the (truncated) charge–charge correlation function

$$S_\Lambda(x_1, x_2) = \langle [Q(x)]_\Lambda [Q(y)]_\Lambda \rangle_\Lambda$$
$$= \sum_{\alpha_1 \alpha_2} e_{\alpha_1} e_{\alpha_2} [\rho_\Lambda(\alpha_1 x_1, \alpha_2 x_2) - \rho_\Lambda(\alpha_1 x_1)\rho_\Lambda(\alpha_2 x_2)$$
$$+ \delta_{\alpha_1 \alpha_2} \delta(x_1 - x_2) \rho_\Lambda(\alpha_1 x_1)] \tag{1.3}$$

where

$$Q(x) = \sum_{i=1}^{N} e_{\alpha_i} \delta(x - x_i) + \rho_B \tag{1.4}$$

is the charge density, and for any F we have set

$$[F]_\Lambda = F - \langle F \rangle_\Lambda \tag{1.5}$$

The charge neutrality condition (1.1) implies that

$$\int_\Lambda dx_2 \, S_\Lambda(x_1, x_2) = 0 \qquad \text{for all } x_1 \tag{1.6}$$

The electrostatic potential at some point of space x, due to a given particle configuration $(q_1, \ldots, q_n)$ in Λ, is

$$V(x) = \int_\Lambda dy \frac{1}{|x - y|} Q(y) \tag{1.7}$$

$E(x) = -\nabla V(x)$ is the corresponding electric field. We are interested in the fluctuations of the potential

$$W_\Lambda(x, y) = \langle [V(x)]_\Lambda [V(y)]_\Lambda \rangle_\Lambda$$
$$= \int_\Lambda dx_1 \int_\Lambda dy_1 \frac{1}{|x - x_1|} \frac{1}{|y - y_1|} S_\Lambda(x_1, y_1) \tag{1.8}$$

and more generally in the characteristic function

$$\left\langle \exp\left(i \sum_{k=1}^{m} \gamma_k [V(x_k)]_\Lambda \right) \right\rangle_\Lambda, \qquad \gamma_k \in \mathbb{R} \tag{1.9}$$

of the distribution of the potential as $\Lambda \to \mathbb{R}^3$. Even more important in many cases are the corresponding fluctuations in the electric field $E(x)$.

We note that for particles with short-range interactions (for instance with finite range d), the total potential and field are strictly local quantities, i.e., $V(x)$ depends only on the part of the particle configuration which is in a sphere of radius d around x. In this case, the infinite volume limits of (1.8) and (1.9) exist as soon as the state [i.e., the correlations functions $\rho_\Lambda(q_1, \ldots, q_n)$] has a thermodynamic limit, and thus potential and force fluctuations are well defined. This is not the case for the Coulomb potential: here $V(x)$ is genuinely nonlocal and particles far away will contribute to the fluctuations at x.

In this paper, we do not prove the existence of the limit (1.8) and (1.9) as $\Lambda \to \mathbb{R}^3$. Rather, by assuming some reasonable properties of the thermodynamic limit and of the bulk correlation functions, we derive various results about the behavior of the potential and electric field correlations which should generally hold in a large class of Coulomb states. Under these conditions, we mainly establish the following points.

Owing to some electrostatic identities which we derive in Section 2, it is still possible to compute the potential and field fluctuations as the limit of averages of strictly local functions.

We then give formulas for the correlations of the potential and field at both neutral and charged points. We find that even in states where the truncated particle correlations cluster exponentially fast (Debye screening), the potential and electric field correlations have a very slow decay (Sections 3–5). In Section 6, we discuss properties of the statistical distribution of the potential and field. There is a natural distinction between the contribution to the fluctuations of the nearby and the far away particles: we show that the latter contribution is asymptotically gaussian. Moreover, there exists a well-defined potential function for typical equilibrium configurations.

These results hold in three-dimensional homogeneous phases having sufficiently good cluster properties. With some appropriate modifications, very similar results are valid in two-dimensional homogeneous phases: this is discussed in Ref. 12. The statistics of the electric field in one dimension is not studied here since it can be explicitly computed by the method of functional integration.[13,14]

Crystalline phases (or phases with directional order) exhibit long-range order (i.e., weak clustering) in dimension $\nu \geqslant 2$[15] and we cannot draw any conclusion on the behavior of their potential and field fluctuations from the present analysis.

2. SOME ELECTROSTATIC IDENTITIES

Let $Q(x)$ be some three-dimensional charge distribution (with $\int dx\,|Q(x)| < \infty$) and $V(y) = \int dz\,(1/|y-z|)Q(z)$ the corresponding potential at y. For any point x, we split the potential at y into a local "inside" part due to the charges located inside a sphere $\sum_R(x)$ of radius R centered at x:

$$V_R^{\text{in}}(x; y) = \int_{\sum_R(x)} dz \frac{1}{|y - z|} Q(z) \tag{2.1}$$

and a global "outside" part due to charges in the exterior $\sum_R^c(x)$, of this sphere,

$$V_R^{\text{out}}(x; y) = \int_{\sum_R^c(x)} dz \frac{1}{|y - z|} Q(z) \tag{2.2}$$

We have clearly

$$V(y) = V_R^{\text{in}}(x; y) + V_R^{\text{out}}(x; y) \tag{2.3}$$

and in particular

$$V(x) = V_R^{\text{in}}(x) + V_R^{\text{out}}(x) \tag{2.4}$$

where $V_R^{\text{in}}(x) \equiv V_R^{\text{in}}(x; x)$, ($V_R^{\text{out}}(x) \equiv V_R^{\text{out}}(x; x)$) is the potential at x due to the charge inside (outside) $\sum_R(x)$. We define, moreover,

$$\overline{V}_R(x) = \frac{1}{|\sum_R|} \int_{\sum_R(x)} dy\, V(y) \tag{2.5}$$

$$\overline{V}_R^{\text{in(out)}}(x) = \frac{1}{|\sum_R|} \int_{\sum_R(x)} dy\, V_R^{\text{in(out)}}(x; y) \tag{2.6}$$

the spatial average of the total potential (resp. of $V_R^{\text{in}}(x; y)$, $V_R^{\text{out}}(x; y)$) in $\sum_R(x)$, $|\sum_R| = 4\pi R^3/3$. Using the formula

$$\int_{|y| \leqslant R} dy \frac{1}{|x - y|} = \begin{cases} \dfrac{4\pi R^3}{3} \dfrac{1}{|x|}, & |x| \geqslant R \\ -\dfrac{2\pi}{3}|x|^2 + 2\pi R^2, & |x| \leqslant R \end{cases} \tag{2.7}$$

This yields

$$\overline{V}_R^{\text{out}}(x) = V_R^{\text{out}}(x) \tag{2.8}$$

$$\overline{V}_R^{\text{in}}(x) = \int_{\sum_R(x)} dz\, Q(z)\left(-\frac{1}{2R^3}|z - x|^2 + \frac{3}{2R}\right) \tag{2.9}$$

and thus, with (2.4),

$$V(x) = V_R^{\text{in}}(x) - \overline{V}_R^{\text{in}}(x) + \overline{V}_R(x) \tag{2.10}$$

$$V_R^{\text{out}}(x) = -\overline{V}_R^{\text{in}}(x) + \overline{V}_R(x) \tag{2.11}$$

Introducing similar definitions for the electric field vector $E(x) = -\nabla V(x)$

one gets in the same way the vector equation

$$E(x) = E_R^{\text{in}}(x) - \bar{E}_R^{\text{in}}(x) + \bar{E}_R(x) \tag{2.12}$$

$$E_R^{\text{out}}(x) = -\bar{E}_R^{\text{in}}(x) + \bar{E}_R(x) \tag{2.13}$$

with

$$E_R^{\text{in}}(x) = -\int_{\Sigma_R(x)} dz\ Q(z)\frac{(x-z)}{R^3} \tag{2.14}$$

The interest of the identities (2.10)–(2.13) is that they express the potential (or field) due to charges far from x, as well as the total potential, as a sum of a strictly local quantity plus the spatial average $\bar{V}_R(x)$. This is important for the following reason: if the potential fluctuations (1.8) have a thermodynamic limit and decay at large space separation, then $\bar{V}_R(x)$ does not contribute to them in the limit $R \to \infty$; cf. next proposition. Hence, by (2.10) the fluctuations of the potential around its average value can be computed locally from $V_R^{\text{in}}(x)$ and $\bar{V}_R^{\text{in}}(x)$. One should, however, remark that in an homogeneous state, $\lim_{\Lambda \to \mathbb{R}^3} \langle V_R^{\text{in}}(x) \rangle_\Lambda$ and $\lim_{\Lambda \to \mathbb{R}^3} \langle \bar{V}_R^{\text{in}}(x) \rangle_\Lambda$ vanish because of local neutrality, but the average of the total potential given by

$$\lim_{\Lambda \to \mathbb{R}^3} \langle V(x) \rangle_\Lambda = \lim_{R \to \infty} \lim_{\Lambda \to \mathbb{R}^3} \langle \bar{V}_R(x) \rangle$$

can be different from zero when the finite system carries surface charges on its boundaries.

Proposition 1. Assume that (i) the average of local functions F have a thermodynamic limit

$$\lim_{\Lambda \to \mathbb{R}} \langle F \rangle_\Lambda = \langle F \rangle$$

(ii) the thermodynamic limit $W(x-y) = \lim_{\Lambda \to \mathbb{R}^3} W_\Lambda(x, y)$ of the potential fluctuations (1.8) exists, and (iii) $\lim_{|x| \to \infty} W(x) = 0$. Then

$$W(x-y) = \lim_{R \to \infty} \langle [\hat{V}_R^{\text{in}}(x)][\hat{V}_R^{\text{in}}(y)] \rangle \tag{2.15}$$

and

$$\lim_{\Lambda \to \mathbb{R}^3} \left\langle \exp\left(i \sum_k \gamma_k [V(x_k)]_\Lambda \right) \right\rangle_\Lambda = \lim_{R \to \infty} \left\langle \exp\left(i \sum_k \gamma_k [\hat{V}_R^{\text{in}}(x_k)] \right) \right\rangle \tag{2.16}$$

$$\lim_{R \to \infty} \lim_{\Lambda \to \mathbb{R}^3} \left\langle \exp\left(i \sum_k \gamma_k [V_R^{\text{out}}(x_k)]_\Lambda \right\rangle_\Lambda = \lim_{R \to \infty} \left\langle \exp\left(-i \sum_k \gamma_k [\bar{V}_R^{\text{in}}(x_k)] \right) \right\rangle \tag{2.17}$$

with

$$\hat{V}_R^{\text{in}}(x) = V_R^{\text{in}}(x) - \bar{V}_R^{\text{in}}(x) \tag{2.18}$$

The existence of the limits of the bulk averages involved on the right-hand sides of (2.15)–(2.17) will be established in the next section.

Proof. The assumption (ii) implies that for each fixed R

$$\lim_{\Lambda\to\mathbb{R}^3} \langle [\bar{V}_R(x)]_\Lambda^2 \rangle_\Lambda = \frac{1}{|\Sigma_R|^2} \int_{\Sigma_R(x)} dx_1 \int_{\Sigma_R(x)} dx_2\, W(x_1 - x_2)$$

$$= \left(\frac{3}{4\pi}\right)^3 \int_{|x_1|\leqslant 1} dx_1 \int_{|x_2|\leqslant 1} dx_2\, W(R(x_1 - x_2))$$

and thus, by (iii),

$$\lim_{R\to\infty} \lim_{\Lambda\to\mathbb{R}^3} \langle [\bar{V}_R(x)]_\Lambda^2 \rangle_\Lambda = 0 \tag{2.19}$$

Introducing the decomposition (2.10) into (2.18), we have

$$W_\Lambda(x, y) = \langle [\hat{V}_R^{\text{in}}(x)]_\Lambda [\hat{V}_R^{\text{in}}(y)]_\Lambda \rangle_\Lambda + \langle [\hat{V}_R^{\text{in}}(x)]_\Lambda [\bar{V}_R(y)]_\Lambda \rangle_\Lambda$$
$$+ \langle [\bar{V}_R(x)]_\Lambda [\hat{V}_R^{\text{in}}(y)]_\Lambda \rangle_\Lambda + \langle [\bar{V}_R(x)]_\Lambda [\bar{V}_R(y)]_\Lambda \rangle_\Lambda \tag{2.20}$$

By the Schwartz inequality, the second term of the right-hand side of (2.20) is less than $\langle [\hat{V}_R^{\text{in}}(x)]_\Lambda^2 \rangle_\Lambda^{1/2} \langle [\bar{V}_R(y)]_\Lambda^2 \rangle_\Lambda^{1/2}$. Hence, using (2.19) and that $\langle [\hat{V}_R^{\text{in}}(x)]_\Lambda^2 \rangle_\Lambda$ remains finite (see Lemma 1, Section 3), this term tends to zero as $\Lambda \to \mathbb{R}^3$, $R \to \infty$. In the same way the two last terms of the right-hand side of (2.20) vanish in this limit, and we get (2.15).

To show (2.16), we use $|e^{ix} - e^{iy}| \leqslant |x - y|$, (2.10) and the Schwartz inequality to obtain

$$\left| \left\langle \exp\left(i \sum_k \gamma_k [V(x_k)]_\Lambda\right) \right\rangle_\Lambda - \left\langle \exp\left(i \sum_k \gamma_k [\hat{V}_R^{\text{in}}(x_k)]\right) \right\rangle_\Lambda \right|$$
$$\leqslant \left\langle \left| \sum_k \gamma_k [\bar{V}_R(x_k)]_\Lambda \right| \right\rangle_\Lambda \leqslant \sum_k |\gamma_k| \langle [\bar{V}_R(x_k)]_\Lambda^2 \rangle_\Lambda^{1/2}$$

(2.16) follows from (2.19) when we let $\Lambda \to \mathbb{R}^3$ and $R \to \infty$. (2.17) is proven in the same way. ■

Obviously, the same proposition holds for the electric field with the corresponding definitions of $\hat{E}_R^{\text{in}}(x), E_R^{\text{out}}(x)$, and the assumptions (ii) and (iii) being replaced by (iv) $e_\Lambda^{rs}(x, y) = \langle [E^r(x)]_\Lambda [E^s(y)]_\Lambda \rangle_\Lambda$ has a limit $e^{rs}(x - y)$ as $\Lambda \to \mathbb{R}^3$ and (v) $\lim_{|x|\to\infty} e^{rs}(x) = 0$.

3. POTENTIAL FLUCTUATIONS AT NEUTRAL POINTS

In this and the following sections, we deduce various properties of the potential fluctuations, assuming that the conditions of the Proposition 1 are true; i.e., we study the right-hand side of (2.15), (2.16), (2.17) for an infinitely extended state of the charged system. This state is described by the set of its correlation functions $\rho(q_1, \ldots, q_n)$ or equivalently by the corresponding truncated (Ursell) functions $\rho_T(q_1, \ldots, q_n)$ defined in the usual way:

$$\begin{aligned} \rho^T(q_1q_2) &= \rho(q_1q_2) - \rho(q_1)\rho(q_2) \\ \rho^T(q_1q_2q_3) &= \rho(q_1q_2q_3) - \rho(q_1)\rho^T(q_2q_3) \\ &\quad - \rho(q_2)\rho^T(q_1q_3) - \rho(q_3)\rho(q_1q_2) \end{aligned} \tag{3.1}$$

These truncated functions will have decay properties at large space separation characterized by an index η such that

$$|r^\eta \rho^T(q_1, \ldots, q_k)| \leqslant C_k, \qquad r = \sup_{ij} |x_i - x_j| \tag{3.2}$$

The screening properties in the bulk of Coulomb states are conveniently expressed in terms of the excess particle density at q when n particles are kept fixed at $q_1, \ldots, q_n$:

$$\rho(q \mid q_1, \ldots, q_n) = \frac{\rho(qq_1, \ldots, q_n)}{\rho(q_1, \ldots, q_n)} + \sum_{j=1}^{n} \delta_{qq_j} - \rho(q) \tag{3.3}$$

with

$$\delta_{qq_j} = \delta_{\alpha\alpha_j}\delta(x - x_j)$$

We start with the basic fact[16,17] that when (3.2) holds for $k \leqslant n + 2$, then $\rho(q \mid q_1, \ldots, q_n)$ has no multipole moments of order $l < \eta - 3$.

In particular, $l = 0$ gives the electroneutrality sum rules

$$\int dq\, e_\alpha \rho(q \mid q_1, \ldots, q_n) = 0 \tag{3.4}$$

In the case $n = 1$, this implies $\int dx\, S(x, y) = 0$, where $S(x, y)$ is the bulk charge–charge correlation defined in terms of the infinite volume correlations as in (1.3).

For translation invariant neutral states, i.e., $S(x, y) = S(x - y)$ and $\sum_\alpha e_\alpha \rho_\alpha + \rho_B = 0$, local neutrality implies $\langle \hat{V}_R^{\text{in}}(x) \rangle = 0$ and thus $[\hat{V}_R^{\text{in}}(x)] = \hat{V}_R^{\text{in}}(x)$. Then, we have

Proposition 2. If

$$\int dx\, S(x) = 0 \tag{3.5}$$

$$\int dx\, |x|\, |S(x)| < \infty \tag{3.6}$$

then $\lim_{R\to\infty}\langle \hat{V}_R^{\text{in}}(x)\hat{V}_R^{\text{in}}(y)\rangle = W(x-y)$ exists with

$$W(x) = -2\pi\int dy\,|x+y|S(y) = \int dy\,\frac{1}{|x-y|}\left[\int dz\,\frac{S(z)}{|y-z|}\right] \tag{3.7}$$

and $\lim_{|x|\to\infty} W(x) = 0$.

Moreover, if

$$\int dx\,|x|^2|S(x)| < \infty \tag{3.8}$$

then

$$W(x) = \frac{1}{|x|}\left[-\frac{2\pi}{3}\int dy\,|y|^2 S(y)\right] + o\left(\frac{1}{|x|}\right) = \frac{K_B T}{|x|} + o\left(\frac{1}{|x|}\right) \tag{3.9}$$

where the second equality follows from the Stillinger–Lovett second moment conditions when it holds.[18,19]

Before proving Proposition 2, let us make the following comments. We see from (3.7) that the square potential fluctuations are well defined under rather weak clustering conditions (3.6). However, (3.9) shows that they always decay as $K_B T/|x|$ even if the clustering is exponentially fast (as in the Debye–Hückel regime). The asymptotic behavior of $W(x)$ is thus universal, independent of the short-range part of the interaction. This can also be obtained from the Sine-Gordon transformation when the latter is applicable.[10]

Finally, (3.5) and (3.8) together with the space reflection invariance of $S(x)$ imply that its Fourier transform $\tilde{S}(k) = (2\pi)^{-3}\int e^{ikx}S(x)$ is $O(|k|^2)$ as $k\to 0$, and hence $\int dk\,(\hat{S}(k)/|k|^4) < \infty$. Under these conditions, by applying twice the convolution theorem of Fourier transforms to the last expression in the right-hand side of (3.7), we also have

$$W(x) = (4\pi)^2\int dk\,e^{ikx}\,\frac{\tilde{S}(k)}{|k|^4} \tag{3.10}$$

Proof of Proposition 2. We have that

$$\langle \hat{V}_R^{\text{in}}(x)\hat{V}_R^{\text{in}}(0)\rangle = \langle\left(V_R^{\text{in}}(x) - \bar{V}_R^{\text{in}}(x)\right)\left(V_R^{\text{in}}(0) - \bar{V}_R^{\text{in}}(0)\right)\rangle$$

is the sum of four terms which are calculated in the Appendix. The result is as follows.

Lemma 1. Under the conditions (3.5), (3.6) the following limits exist and are given by

$$\lim_{R\to\infty} \langle V_R^{\text{in}}(x) V_R^{\text{in}}(0)\rangle = -3\pi \int dy\, |y+x| S(y) \tag{3.11}$$

$$\begin{aligned}\lim_{R\to\infty} \langle V_R^{\text{in}}(x) \bar{V}_R^{\text{in}}(0)\rangle &= \lim_{R\to\infty} \langle \bar{V}_R^{\text{in}}(x) \bar{V}_R^{\text{in}}(0)\rangle \\ &= -\pi \int dy\, |y+x| S(y) \end{aligned}\tag{3.12}$$

$$\begin{aligned}\lim_{R_2\to\infty} \lim_{R_1\to\infty} \langle V_{R_2}^{\text{in}}(x) \bar{V}_{R_1}^{\text{in}}(0)\rangle &= \lim_{R_2\to\infty} \lim_{R_1\to\infty} \langle \hat{V}_{R_2}^{\text{in}}(x) \hat{V}_{R_1}^{\text{in}}(0)\rangle \\ &= -2\pi \int dy\, |y+x| S(y) \end{aligned}\tag{3.13}$$

The first expression of $W(x)$ in (3.7) results immediately from (3.11)–(3.12); the second expression can be obtained either from (3.13) or shown directly by using charge neutrality.

Because of electroneutrality and space reflection invariance, we can write

$$W(x) = -2\pi \int dy\, (|x+y| - |x| - y\cdot\hat{x}) S(y), \qquad \hat{x} = \frac{x}{|x|} \tag{3.14}$$

$\lim_{|x|\to\infty} W(x) = 0$ follows by dominated convergence from the fact that the integrand of (3.14) is bounded by $2|y|\,|S(y)|$ and converges pointwise to zero as $|x|\to\infty$.

To prove (3.9) we again use electroneutrality and spherical symmetry to write

$$\begin{aligned} &|x|\, W(x) + \frac{2\pi}{3} \int_{|y|\leqslant |x|/2} dy\, |y|^2 S(y) \\ &\quad= -2\pi \int_{|y|\leqslant |x|/2} dy\, S(y) \Bigg[|x| \Bigg(|x+y| - |x| - y\cdot\hat{x} \\ &\qquad\qquad - \frac{1}{2} \sum_{r,s}^{3} \left(\frac{\delta_{rs} - \hat{x}^r \hat{x}^s}{|x|} \right) y^r y^s \Bigg) \Bigg] \\ &\quad - 2\pi \int_{|y|\geqslant |x|/2} dy\, S(y) \big[|x| (|x+y| - |x|) \big] \end{aligned}\tag{3.15}$$

By the limited Taylor expansion, $|x+y| - |x| - y\cdot\hat{x} = O(|y|^2/|x|)$ for $|y| \leqslant |x|/2$ and the integrand of the first term on the right-hand side of (3.15) tends pointwise to zero. Dominated convergence implies again that this term vanishes as $|x|\to\infty$. Since the integrand of the second term is majorized by $(1/2)|y|^2|S(y)|$ for $|y| \geqslant |x|/2$, this contribution also vanishes as $|x|\to\infty$ by (3.8), and this proves (3.9). ■

4. ELECTRIC FIELD FLUCTUATIONS AT NEUTRAL POINTS

The properties of the fluctuations in the electric field can be derived in an analogous way as those of the potential. There is however one difference. Since the field $E^r(x)$ of a point particle at the origin behaves as $\hat{x}^r/|x|^2$, $|x|\to 0$, its square has a nonintegrable singularity at the origin in three dimensions. We suppress this local singularity by considering extended spherical charges with form factor $h_\alpha(x)$ such that $\int dx\, h_\alpha(x) = 1$.

This amounts to replacing everywhere the point charge density (1.4) by the smeared density $Q(x) = \sum_i e_{\alpha_i} h_{\alpha_i}(x - x_i) + \rho_B$.

Keeping the same notation as before for the charge–charge correlation, we have the following.

Proposition 3. Under the conditions (3.5) and (3.6),

$$\lim_{R\to\infty} \langle \hat{E}_R^{r(\text{in})}(x)\hat{E}_R^{s(\text{in})}(0)\rangle = e^{rs}(x)$$

exists with

$$e^{rs}(x) = 2\pi \int dy \frac{1}{|x+y|}\left(\delta_{rs} - \frac{(x+y)^r}{|x+y|}\frac{(x+y)^s}{|x+y|}\right)S(y) \tag{4.1}$$

$$= \int dy \frac{(x-y)^r}{|x-y|^3}\left[\int dz \frac{(z-y)^s}{|z-y|^3} S(y)\right] \tag{4.2}$$

and

$$\lim_{|x|\to\infty} e^{rs}(x) = 0 \tag{4.3}$$

Moreover, if

$$S(x) = O\left(\frac{1}{|x|^{3+l+\epsilon}}\right) \qquad \text{for} \quad l = 2, \ldots, n, \quad \epsilon > 0,$$

$$e^{rs}(x) = \left(\frac{\delta_{rs} - 3\hat{x}^r\hat{x}^s}{|x|^3}\right)\left[-\frac{2\pi}{3}\int dy\, |y|^2 S(y)\right] + o\left(\frac{1}{|x|^3}\right)$$

$$= \frac{K_B T}{|x|^3}(\delta_{rs} - 3\hat{x}^r\hat{x}^s) + o\left(\frac{1}{|x|^3}\right) \tag{4.4}$$

and

$$\sum_{r=1}^{3} e^{rr}(x) = 4\pi \int dy \frac{1}{|x+y|} S(y) = o\left(\frac{1}{|x|^{n+1}}\right) \tag{4.5}$$

where the second equality in (4.4) follows from the Stillinger–Lovett second moment condition. We see from (3.7) and (4.2) that the field correlations are related to those of the potential by $e^{rs}(x) = -(\partial^2/\partial x^r \partial x^s)W(x)$.

They have also a slow decay which takes the universal simple form $(kT/|x|^3)(\delta_{rs} - 3\hat{x}^r\hat{x}^s)$. However, the spherically invariant part of the tensor $e^{rs}(x)$ (i.e., its trace) has a faster decay when the state has strong clustering properties. In fact, if the clustering is exponentially fast, (4.5) shows that this quantity decays faster than any inverse power. Notice also that applying the convolution theorem to (4.2), one can as well write in Fourier representation

$$e^{rs}(x) = (4\pi)^2 \int dk\, e^{ikx} \tilde{S}(k) \frac{\hat{k}^r \hat{k}^s}{|k|^2} \tag{4.6}$$

Proof of Proposition 3. One uses Lemma 2 proven in the Appendix.

Lemma 2. Under the condition (3.5) and (3.6), the following limits exist and are given by

$$\begin{aligned}
&\lim_{R\to\infty} \langle E_R^{r(\text{in})}(x) E_R^{s(\text{in})}(0)\rangle \\
&\quad = \lim_{R_2\to\infty} \lim_{R_1\to\infty} \langle E_{R_2}^{r(\text{in})}(x) E_{R_1}^{s(\text{in})}(0)\rangle \\
&\quad = 2\pi \int dy \frac{1}{|x+y|} \left(\delta_{rs} - \frac{(x+y)^r}{|x+y|} \frac{(x+y)^s}{|x+y|} \right) S(y)
\end{aligned} \tag{4.7}$$

$$\begin{aligned}
&\lim_{R\to\infty} R^2 \langle \bar{E}_R^{r(\text{in})}(x) \bar{E}_R^{s(\text{in})}(0)\rangle \\
&\quad = -\frac{\pi}{4} \int dy\, |x+y| \left(\delta_{rs} + \frac{(x+y)^r}{|x+y|} \frac{(x+y)^s}{|x+y|} \right) S(y)
\end{aligned} \tag{4.8}$$

Equations (4.1) and (4.2) result immediately from (4.7) and from the fact that $\langle |\bar{E}_R^{r(\text{in})}(x)|^2\rangle^{1/2}$ being now $O(1/R)$ by (4.8) does not contribute to the limit. Moreover,

$$|e^{rs}(x)| \leqslant 8\pi \int dy \frac{1}{|x+y|} |S(y)|$$

tends to zero as $|x| \to \infty$. (4.5) follows from the fact that all multipole moments of $S(x)$ up to order n exist and vanish because of electroneutrality and spherical symmetry. Hence, only the second term in the integral (4.7) contributes to the asymptotic form of $e^{rs}(x)$. Using again electroneutrality and spherical symmetry we find (see Lemma 1 of Ref. 16)

$$\begin{aligned}
\lim_{|x|\to\infty} |x|^3 e^{rs}(x) &= -\pi \lim_{|x|\to\infty} |x|^3 \sum_{ij}^{3} \partial_{ij}^2 \left(\frac{x^r x^s}{|x|^3} \right) \int dy\, y^i y^j S(y) \\
&= (\delta_{rs} - 3\hat{x}^r\hat{x}^s) \left[-\frac{2\pi}{3} \int dy\, |y|^2 S(y) \right] \quad \blacksquare
\end{aligned}$$

To conclude this section, we show that we can recover the result of

Ref. 20 that the charge fluctuations $\langle Q_R^2 \rangle$ in a sphere of radius R behaves as the surface of this sphere. This is an immediate consequence of Gauss' theorem and of the properties of the field fluctuations. By Gauss' theorem and (4.6), we find

$$\frac{\langle Q_R^2 \rangle}{4\pi R^2} = \frac{1}{(4\pi)^3 R^2} \sum_{r,s}^{3} \int_{|x|=R} d\sigma_x^r \int_{|y|=R} d\sigma_y^s \langle E^r(x) E^s(y) \rangle$$

$$= \frac{1}{4\pi R^2} \int dk \frac{\tilde{S}(k)}{|k|^2} \left| \int_{|x|=R} e^{ik\cdot x} \hat{k} \cdot d\sigma \right|$$

$$= 4\pi \int dk \frac{\tilde{S}(k)}{|k|^4} \left[(\cos|k|R)^2 - \frac{\sin 2|k|R}{|k|R} + \left(\frac{\sin|k|R}{|k|R} \right)^2 \right] \tag{4.9}$$

The first term on the right-hand side of (4.9) converges to

$$2\pi \int dk \frac{\tilde{S}(k)}{|k|^4}$$

by the Riemann Lebesgue lemma [provided that $\tilde{S}(k)/|k|^4$ is integrable].

The other terms tend to zero because of the estimate

$$\left| \int dk \frac{\tilde{S}(k)}{|k|^4} \frac{\sin|k|R}{|k|R} \right| \leqslant \int_{|k|\leqslant \epsilon} dk \frac{|\tilde{S}(k)|}{|k|^4} + \frac{1}{\epsilon R} \int dk \frac{|\tilde{S}(k)|}{|k|^4}$$

Thus

$$\lim_{R\to\infty} \frac{\langle Q_R^2 \rangle}{4\pi R^2} = 2\pi \int dk \frac{\tilde{S}(k)}{|k|^4} = -\frac{1}{4} \int dx\, |x| S(x)$$

which is the result of Ref. 20.

5. POTENTIAL AND FIELD FLUCTUATIONS AT A CHARGED PARTICLE

In the preceding sections, we have investigated the properties of the fluctuations at a point x in space. It is also important in various physical situations (such as the spectral broadening problem[1]) to know the effects of the field fluctuations on a charged particle of type α_0 at x_0 in the system. Our previous results can easily be extended to this case by computing the potential and field fluctuations at x_0 in the state $\langle \cdots \rangle_0$ with correlations

$$\rho_0(q_1 \cdots q_n) = \frac{\rho(q_0 q_1 \cdots q_n)}{\rho(q_0)}, \qquad q_0 = (\alpha_0, x_0) \tag{5.1}$$

conditioned by the presence of a partical of type α_0 at x_0.

If $\rho_0(q \mid q_1 \cdots q_n)$ denotes, as in (3.3), the excess particle density at q in the state $\langle \cdots \rangle_0$, we obtain immediately that $\rho_0(q \mid q_1 \ldots q_k)$ satisfy the l-multipole sum rules for $k = 1, \ldots, n-1$ whenever the same is true for $\rho(q \mid q_1 \ldots q_k)$, $k = 1, \ldots, n$. This follows from the identity

$$\rho_0(q \mid q_1 \ldots q_n) = \rho(q \mid q_0 q_1 \ldots q_n) - \rho(q \mid q_0) \tag{5.2}$$

Moreover, the two-point truncated functions $\rho_0^T(q_1 q_2)$ in the conditioned state $\langle \cdots \rangle_0$ can be written as

$$\rho_0^T(q_1 q_2) = \rho^T(q_1 q_2) + \frac{\rho^T(q_0 q_1 q_2)}{\rho(q_0)} - \frac{\rho^T(q_0 q_1)}{\rho(q_0)} \frac{\rho^T(q_0 q_2)}{\rho(q_0)} \tag{5.3}$$

More generally, the higher-order truncated correlations of the state $\langle \cdots \rangle_0$ can be expressed as

$$\rho_0^T(q_1 \ldots q_n) = \rho^T(q_1 \ldots q_n) + S(q_0 q_1 \ldots q_n) \tag{5.4}$$

where $S(q_0 q_1 \ldots q_n)$ is a sum of products (up to density factors $\rho(q_0)$) of truncated functions $\rho^T(q_0 q_{i_1} \ldots q_{i_m})$ where the arguments $\{q_{i_1} \ldots q_{i_m}\} \subset \{q_1 \ldots q_n\}$ occur always in conjunction with q_0.

Under the assumption of $\mathscr{L}^1$-clustering (i.e., $\int dq_1 \ldots dq_n |\rho^T(q_0 q_1 \ldots q_n)| < \infty$) we see from (5.3) and (5.4) that the $\rho_0^T(q_1 \ldots q_n)$ differ from the $\rho^T(q_1 \ldots q_n)$ by a term which is jointly integrable in all variables $q_1 \ldots q_n$. As a consequence, the covergence problems occurring in the definition of the potential and field fluctuations at a charged point are reduced to those which have been treated in the previous sections. We shall therefore not reproduce the proofs for this case, but only give some relevant formulas, setting $\rho(q_0) = \rho_{\alpha_0}$ and $x_0 = 0$.

We first note that now $\langle \hat{V}_R^{\text{in}}(0) \rangle_0$ at $x_0 = 0$ is different from zero

$$\begin{aligned} \lim_{R\to\infty} \langle \hat{V}_R^{\text{in}}(0) \rangle_0 &= \lim_{R\to\infty} \int_{|x| \leqslant R} dq\, e_\alpha \left(\frac{1}{|x|} + \frac{|x|^2}{2R^3} - \frac{3}{2R} \right) \rho_0(q) \\ &= \frac{1}{\rho_{\alpha_0}} \int dq \frac{e_\alpha}{|x|} \rho^T(q, \alpha_0 0) \end{aligned} \tag{5.5}$$

Under the assumption of $\mathscr{L}^1$-clustering, (3.5) and (3.6), we prove as in Proposition 2 the existence of the potential fluctuations, using (5.3):

$$\begin{aligned} \lim_{R\to\infty} \langle (\hat{V}_R^{\text{in}}(0))^2 \rangle_0 &= W(0) + \frac{1}{\rho_{\alpha_0}} \int dq \left(\frac{e_\alpha}{|x|} \right)^2 \rho^T(q_1 \alpha_0 0) \\ &\quad + \frac{1}{\rho_{\alpha_0}} \int dq_1 \int dq_2 \frac{e_{\alpha_1}}{|x_1|} \frac{e_{\alpha_2}}{|x_2|} \rho^T(q_1 q_2, \alpha_0 0) \end{aligned} \tag{5.6}$$

with $W(0)$ given by (3.7).

To compute the electric field fluctuations at a charged particle, we consider first spherical extended charges with form factors $h_\alpha(x)$. The (smeared) field at the origin due to a particle of type α at x is

$$E^r(0,q) = \frac{1}{e_{\alpha_0}} F(q_0, q), \qquad \text{where} \quad q = (\alpha, x), \quad q_0 = (\alpha_0, 0)$$

$$F(q_1, q_2) = e_{\alpha_1} e_{\alpha_2} \int dz_1 \int dz_2 \, h_{\alpha_1}(z_1 - x_1) \frac{(z_1 - z_2)}{|z_1 - z_2|^3} h_{\alpha_2}(z_2 - x_2)$$

is the electric force between two charges at q_1 and q_2.

By spherical symmetry $\langle E^r(0) \rangle = 0$, and according to (5.3), we have

$$\begin{aligned} \langle E^r(0) E^s(0) \rangle_0 &= \int dq_2 \int dq_1 \, E^s(0, q_2) E^r(0, q_1) \\ &\quad \times \left\{ \rho^T(q_1 q_2) + \frac{1}{\rho_{\alpha_0}} \left[\rho^T(q_1 q_2 q_0) + \delta_{q_1 q_2} \rho(q_1 q_0) \right] \right\} \qquad (5.7) \\ &= \frac{1}{\rho_{\alpha_0} e_{\alpha_0}} \int dq_2 \, E^s(0, q_2) \int dq_1 \, F^r(q_0, q_1) \\ &\quad \times \left\{ \rho(q_1 q_2 q_0) - \rho(q_1) \rho(q_2 q_0) + \delta_{q_1 q_2} \rho(q_1 q_0) \right\} \qquad (5.8) \end{aligned}$$

To obtain (5.8), we used (3.1) and the first BGY equilibrium equation (for a homogeneous state)

$$\int dq_1 \, F(q_0, q_1) \rho^T(q_0 q_1) = K_B T \nabla_0 \rho(q_0) = 0$$

Equation (5.8) can be further simplified by using the second BGY equation

$$\begin{aligned} \int dq_1 \, F(q_0, q_1)(\rho(q_0 q_1 q_2) - \rho(q_1)\rho(q_0 q_2)) + F(q_0, q_2)\rho(q_0 q_2) \\ = k_B T \nabla_0 \rho(q_0 q_2) = -K_B T \nabla_2 \rho^T(q_0 q_2) \end{aligned}$$

to obtain an expression involving only two-point correlations

$$\langle E^r(0) E^S(0) \rangle_0 = -\frac{K_B T}{\rho_{\alpha_0} e_{\alpha_0}} \int dq \, E^s(0, q) \nabla^r \rho^T(q q_0) \qquad (5.9)$$

After an integration by part and using Poisson's equation (5.9) leads to

$$\sum_{r=1}^{3} \langle [E^r(0)]^2 \rangle_0 = -\frac{4\pi K_B T}{\rho_{\alpha_0} e_{\alpha_0}} \int dq \, e_\alpha \left[\int dz \, h_{\alpha_0}(z) h_\alpha(z - x) \right] \rho^T(q q_0) \qquad (5.10)$$

It is interesting to see that for a system of positive ions embedded in a uniform background of charge density ρ_B ($\rho_B < 0$) the right-hand side of (5.10) has a universal value. This is due to the fact that in this case, we can deal with point particles (no collapse) and that correlations vanish at coincident points because of the repulsive interactions between ions. Indeed, setting $h_{\alpha_0}(z) = h_\alpha(z) = \delta(z)$ in (5.10), we get

$$\sum_{r=1}^{3} \langle [E^r(0)]^2 \rangle_0 = -\frac{4\pi K_B T}{\rho_{\alpha_0} e_{\alpha_0}} \sum_\alpha e_\alpha \rho^T(\alpha 0, \alpha_0 0)$$

$$= \frac{4\pi K_B T}{e_{\alpha_0}} \sum_\alpha \rho_\alpha = 4\pi \frac{|\rho_B| K_B T}{e_{\alpha_0}} \qquad (5.11)$$

This exact value of the second moment of the field has been used in Ref. 9 to compute the microfield distribution approximately.

6. DISTRIBUTION OF THE POTENTIAL AND FIELD

In the previous sections we gave explicit formulas for the second moment of the potential and field distribution. It is of interest in relation to the line shape problem to have informations on higher-order moments as well as on the full distribution of these quantities.

According to the splitting introduced in Section 2, the potential fluctuations are due to both $V_R^{\text{in}}(x)$ and $V_R^{\text{out}}(x)$. The statistical distribution of $V_R^{\text{in}}(x)$ has apparently no simple properties since it is affected by the local correlations of the particles around x.

The next proposition shows however that a central limit theorem holds for the distribution of $V_R^{\text{out}}(x)$: the fluctuations due to the particles far from x [i.e., outside of any finite sphere $\sum_R(x)$] are asymptotically Gaussian as $R \to \infty$. In view of Proposition 1 and (2.17), it is sufficient to determine the statistical properties of $\bar{V}_R^{\text{in}}(x)$, and we have the following.

Proposition 4. Assume that (3.2) holds with $\eta > 3$ for $k = 2, 3, 4$ and

$$\int dx_1 \, |x_1| \, |\rho^T(\alpha_1 x_1 ; \alpha_2 0)| < \infty$$

$$\int dq_1 \ldots dq_{n-1} \, |\rho^T(q_1 \ldots q_{n-1}, \alpha_n 0)| < \infty \qquad (\mathscr{L}^1 \text{clustering})$$

Then $\bar{V}_R^{\text{in}}(x_1), \bar{V}_R^{\text{in}}(x_2), \ldots,$ are jointly Gaussian as $R \to \infty$ with covariance

$$W^{\text{out}}(x) = -\pi \int dy \, |x + y| S(y) \qquad (6.1)$$

This is just half of the covariance (3.7) of the full potential fluctuation.

Proof. The proof is similar to that given in Proposition 4 of Ref. 20 for the charge fluctuations. We show that all the cumulants of the distribution of $\overline{V}_R^{\text{in}}(x)$,

$$M_R^{(n)}(x_1 \ldots x_n) = \int dy_1 \ldots dy_n \prod_{j=1}^{n} f_R(x_j - y_j) \times \sum_{\alpha_1 \ldots \alpha_n} e_{\alpha_1} \ldots e_{\alpha_n} \hat{\rho}^T(\alpha_1 y_1, \ldots, \alpha_n y_n)$$

with $f_R(x) = (x^2/2R^3 - 3/2R)X_R(x)$, vanish as $R \to \infty$ except for $n = 2$ [remember that $M_R^{(1)}(x) = \langle \overline{V}_R^{\text{in}}(x) \rangle = 0$ by neutrality]. For the definitions of the cumulants and of the $\hat{\rho}_T(q_1 \ldots q_n)$, see Ref. 20.

Since $|f_R(x)| \leqslant M/R$, we get

$$|M_R^{(n)}(x_1 \ldots x_n)| \leqslant \left(\frac{M}{R}\right)^n \frac{4\pi}{3} R^3 \left(\sup_\alpha |e_\alpha|\right)^n \int dq_1 \ldots dq_{n-1} |\rho^T(q_1 \ldots q_{n-1}, \alpha_n 0)|$$

which vanishes as $R \to \infty$ when $n > 3$. After the change of variables $y_1 - y_3 = u$, $y_2 - y_3 = v$ and $y_3 = Ry$, we get

$$M_R^{(3)}(x_1 x_2 x_3) = \int du \int dv \sum_{\alpha_1 \alpha_2 \alpha_3} e_{\alpha_1} e_{\alpha_2} e_{\alpha_3} \hat{\rho}^T(\alpha_1 u, \alpha_2 v, \alpha_3 0) \times \left[\int dy\, f_1\left(y + \frac{u - x_1}{R}\right) f_1\left(y + \frac{v - x_2}{R}\right) f_1\left(y - \frac{x_3}{R}\right)\right] \tag{6.2}$$

The term in the brackets, $[\cdots]$, in (6.2) is uniformly bounded in R, u and v and converges to $a = \int dy\, [f_1(y)]^3$ as $R \to \infty$. Thus we find

$$\lim_{R\to\infty} M_R^3(x_1 x_2 x_3) = a \sum_{\alpha_3} e_{\alpha_3} \int dq_1 \int dq_2\, e_{\alpha_1} e_{\alpha_2} \hat{\rho}^T(q_1, q_2, \alpha_3 0)$$

Under our clustering assumptions, the electroneutrality sum rule (3.4) holds for $n = 3$[16] implying $\int dq_1\, e_{\alpha_1} \hat{\rho}^T(q_1 q_2 q_3) = 0$ (see Lemma 2 in Ref. 20), and hence

$$\lim_{R\to\infty} M_R^{(3)}(x_1 x_2 x_3) = 0$$

Finally

$$W^{\text{out}}(x) = \lim_{R\to\infty} M_R^{(2)}(x, 0) = \lim_{R\to\infty} \langle \overline{V}_R^{\text{in}}(x) \overline{V}_R^{\text{in}}(0) \rangle$$

has been calculated in Lemma 1. ■

Let us remark that the distribution of $V^{\text{out}}(0)$ at a charged point is also Gaussian with the same covariance (6.1), i.e., Proposition 4 holds without modifications for the state $\langle \cdots \rangle_0$. This follows from the fact that using

(5.3) and (5.4)

$$\langle [\bar{V}_R^{\text{in}}(0)]^n\rangle_0 = \langle [\bar{V}_R^{\text{in}}(0)]^n\rangle + \int_{|x|\leqslant R} dq\, e_\alpha^n\left(-\frac{|x|^2}{2R^3}+\frac{3}{2R}\right)^n S(q_0q_1\dots q_n)$$
$$= \langle [\bar{V}_R^{\text{in}}(0)]^n\rangle + O\left(\frac{1}{R^n}\right)$$

We can, as for the potential, consider the distribution of the field $E_R^{\text{out}}(x)$ due to the far away particles. Here, because of the faster decay of the field, the local effects on the fluctuations of the particles outside of the sphere $\sum_R(x)$ vanish as $1/R$, $R\to\infty$ [see (4.8) in Lemma 3]. However, we have still a central limit theorem for the scaled field $RE_R^{\text{out}}(x)$.

Proposition 5. Under the same assumptions as in Proposition 4, $R\bar{E}_R^{r(\text{in})}(x)$ are jointly Gaussian as $R\to\infty$ with covariance given by (4.8).

In view of (2.14), the proof is the same as that of Proposition 3 with $f_R(x)$ equal to $(x^r/R^3)\chi_R(x)$.

A more detailed question that we can ask for the charged system is the following: what are the potential and field at x due to a typical configuration of the particles? In other words, are the total potential and field well defined random variables in an equilibrium state of the infinite system? The problem was considered and solved in Ref. 14 for the one-dimensional Coulomb system.

If $d\mu_\beta$ denotes the equilibrium measure corresponding to the correlation functions $\rho(q_1\dots q_n)$, the next lemma shows that we can define a potential function on the phase space of the infinitely extended system up to null sets with respect to $d\mu_\beta$.

Lemma 3. Assume that (3.5), (3.6), and (3.2) hold with $\eta > 2$. Then

$$\lim_{R\to\infty} \hat{V}_R^{\text{in}}(x) = V(x)$$

exists in $\mathscr{L}^1(d\mu_\beta)$.

Proof. Since $d\mu_\beta$ has a finite total mass (i.e., $\int d\mu_\beta = 1$) it is sufficient to prove the covergence of $\hat{V}_R^{\text{in}}(x)$ in $\mathscr{L}^2(d\mu_\beta)$. We first show that $\hat{V}_R^{\text{in}}(x)$ converges weakly in $\mathscr{L}^2(d\mu_\beta)$. For this we consider the dense set $\mathscr{D}$ of strictly local functions in $\mathscr{L}^2(d\mu_\beta)$ (a local function depends only on the coordinates of the particles located in some finite region of $\mathbb{R}^3$). From the definition of $\hat{V}_r^{\text{in}}(x)$ and $F\in\mathscr{D}$ we have

$$\langle \hat{V}_R^{\text{in}}(x)F\rangle = \int dy\, \chi_R(y-x)\left(\frac{1}{|y-x|}+\frac{|x-y|^2}{2R^3}-\frac{3}{2R}\right)$$
$$\times[\langle Q(y)F\rangle - \langle Q(y)\rangle\langle F\rangle] \tag{6.3}$$

In (6.3) the neutrality condition $\langle Q(y)\rangle = 0$ has been used.

Since $||y|^2/2R^3 - 3/2R| = O(1/|y|)$, $|y| \geqslant R$, and $\langle Q(y)F\rangle - \langle Q(y)\rangle\langle F\rangle = O(1/|y|^\eta)$, $\eta > 2$, by the clustering assumption, we obtain by dominated convergence that

$$\lim_{R\to\infty} \langle \hat{V}_R^{\text{in}}(x)F\rangle = \int dy \frac{1}{|x-y|} \langle Q(y)F\rangle \tag{6.4}$$

for all local functions F in $\mathscr{D}$.

Since the norm $\langle(\hat{V}_R^{\text{in}}(x))^2\rangle$ remains uniformly bounded as $R \to \infty$ (see Proposition 2), the weak convergence (6.4) can be extended from $\mathscr{D}$ to the whole of $\mathscr{L}^2(d\mu_\beta)$.

Hence there exists a function $V(x)$ in $\mathscr{L}^2(d\mu_\beta)$ such that $V(x) = w - \lim V_R^{\text{in}}(x)$; $V(x)$ is defined by the right-hand side of (6.4). Lemma 1 shows that

$$\begin{aligned}\lim_{R\to\infty} \langle \hat{V}_R^{\text{in}}(x)V(x)\rangle &= \lim_{R_2\to\infty}\lim_{R_1\to\infty} \langle \hat{V}_{R_2}^{\text{in}}(x)\hat{V}_{R_1}(x)\rangle \\ &= \lim_{R\to\infty} \langle(\hat{V}_R^{\text{in}}(x))^2\rangle\end{aligned}$$

implying $\lim_{R\to\infty}\langle[\hat{V}_R^{\text{in}}(x) - V(x)]^2\rangle = 0$, i.e., $\hat{V}_R^{\text{in}}(x)$ converges strongly to $V(x)$ in $\mathscr{L}^2(d\mu_\beta)$, and hence in $\mathscr{L}^1(d\mu_\beta)$. ■

We remark that the limiting function $V(x)$ defined by (6.4) is the usual Coulomb potential when interpreted in the sense of weak convergence.

However, the $\mathscr{L}^1$ convergence of $\hat{V}_R^{\text{in}}(x)$ gives us information on the typical configurations in the equilibrium state represented by the Gibbs measure $d\mu_\beta$. The $\mathscr{L}^1$ convergence of $\hat{V}_R^{\text{in}}(x)$ implies that there exists a subsequence $\{R_n\}$ such that

$$\lim_{n\to\infty} \sum_{|x_i|\leqslant R_n} e_{\alpha_i}\left(\frac{1}{|x-x_i|} + \frac{|x-x_i|^2}{2R^3} - \frac{3}{2R}\right) = V(x) \tag{6.5}$$

for almost all configurations $\{e_{\alpha_i}, x_i\}_i$.

In this way, we can in principle calculate the potential at x due to a typical infinite configuration of charged particles, up to a constant (see the remarks in Section 2 before the Proposition 1). As a consequence of Lemma 3, we obtain immediately the existence of a limiting generating function (2.16)

$$\lim_{R\to\infty}\left\langle \exp\left[i\sum_k \gamma_k \hat{V}_R^{\text{in}}(x_k)\right]\right\rangle = \left\langle \exp\left[i\sum_k \gamma_k V(x_k)\right]\right\rangle$$

[This, however, does not prove the existence of a unique probability distribution for $V(x)$ or that of higher-order moments $\langle V(x_1)\ldots V(x_k)\rangle$, $k > 2$.]

We have the analog of the Lemma 3 for the field: there exists an electric vector field $E^r(x)$ on the phase space of the infinite system. $E^r(x)$ is defined up to null sets with respect to the Gibbs measure $d\mu_\beta$ and corresponds in the weak sense to the usual electric field function.

Lemma 4. Assume that (3.5), (3.6), and (3.2) with $\eta > 1$ hold true. Then $\lim_{R\to\infty} \hat{E}_R^{r(\text{in})}(x) = E^r(x)$ exists in $\mathscr{L}^1(d\mu_\beta)$.

The proof is analogous to that of Lemma 3.

7. CONCLUDING REMARKS

Our whole analysis was based on the assumption of the existence of the thermodynamic limit for the potential and field fluctuations [assumptions (i), (ii), and (iii) of Proposition 1].

As concluding remarks, we present an argument suggested by Alastuey and Jancovici for the existence of these limits. We take for Λ a sphere of radius R_0 and assume that the finite volume charge–charge correlation $S_{R_0}(x, y)$ and its bulk limit $S(x-y) = \lim_{R_0\to\infty} S_{R_0}(x, y)$ obey an estimate of the following structure:

$$|S_{R_0}(x, y) - S(x-y)| \leqslant f(x-y)\, g(R_0 - |x|) \tag{7.1}$$

with

$$\int dx\, |x|\, |f(x)| < \infty, \qquad \int_0^\infty dr\, r |g(r)| < \infty \tag{7.2}$$

In (7.1) $f(x-y)$ takes into account that both $S_{R_0}(x, y)$ and $S(x-y)$ are small as $|x-y|$ is large (clustering), $g(R_0 - |x|)$ insures that $S_{R_0}(x, y)$ is close to $S(x-y)$ when x or y (since f is short ranged) are far from the boundary.

Using the neutrality (1.6), the potential fluctuations at the origin $x = y = 0$ can be written as

$$W_{R_0}(0,0) = \int_{|x|\leqslant R_0} dx \int_{|y|\leqslant R_0} dy \frac{1}{|x|}\left(\frac{1}{|y|} - \frac{1}{|x|}\right) S_{R_0}(x, y)$$

and thus, with (7.1), (7.2),

$$\left| W_{R_0}(0,0) - \int_{|x|\leqslant R_0} dx \int_{|y|\leqslant R_0} dy \frac{1}{|x|}\left(\frac{1}{|y|} - \frac{1}{|x|}\right) S(x-y) \right|$$

$$\leqslant \int_{|x|\leqslant R_0} dx \frac{|g(R_0 - |x|)|}{|x|} \left[\int_{|y|\leqslant R_0} \left| \frac{1}{|y-x|} - \frac{1}{|x|} \right| |f(y)| \right] \tag{7.3}$$

$$\leqslant 4\pi M \int_0^{R_0} dr \frac{|g(R_0 - r)|}{r+1} = 4\pi M \int_0^{R_0} dr \frac{|q(r)|}{(R_0 - r) + 1} = O\left(\frac{1}{R_0}\right) \tag{7.4}$$

In obtaining (7.4) we have used the fact that the bracket in (7.3) is $O(1/|x|)$ as $|x|\to 0$ and $O(1/|x|^2)$ as $|x|\to\infty$; it is therefore bounded by $M/|x|(|x|+1)$, M being a constant.

Thus we find from (7.2) and the result of the Appendix [see (A13)]

$$\begin{aligned} W(0) &= \lim_{R_0\to\infty} W_{R_0}(0,0) \\ &= \lim_{R_0\to\infty} \int_{|x|\leq R_0} d^3x \int_{y\leq R_0} dy \frac{1}{|x|}\left(\frac{1}{|y|}-\frac{1}{|x|}\right)S(x-y) \\ &= -2\pi\int dx\,|x|S(x) \end{aligned} \tag{7.5}$$

recovering thus the expression (3.7). This shows that an estimate of type (7.1), (7.2), together with neutrality insure the finiteness of the potential fluctuations in three dimensions.

One should note that the situation is different in two dimensions. If one replaces $1/|x|$ by $-\ln|x|$ in (7.3), (7.4), one sees easily that one obtains only a bound $O(\ln R_0)$ in (7.4). This indicates that two-dimensional potential fluctuations diverge, a fact which can be established in the two-dimensional OCP at $\Gamma = 2$.(12)

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APPENDIX

Proof of Lemma 1. According to (2.18), (2.1), and (2.9), the quantities to be evaluated in (3.11), (3.12) are, for $x = 0$,

$$A^{\alpha\beta} = \lim_{R\to\infty}\int dx_1\int dy_1\, S(x_1-y_1)\chi_R(x_1)f_R^{\alpha}(x_1)\chi_R(y_1)f_R^{\beta}(y_1) \qquad \alpha,\beta = 1,2 \tag{A1}$$

with

$$f_R^1(x) = \frac{1}{|x|}, \qquad f_R^2(x) = -\frac{|x|^2}{2R^3} + \frac{3}{2R} \tag{A2}$$

The general case will be obtained by substituting the translated function $S(x_1 - y_1 + x)$ in the final result.

Changing the variables $y_1 = x_1 - u$, $x_1 = Rv$ and using the scaling properties of the functions $f_R^{\alpha}(x)$, (A1) can be written in the form

$$A^{\alpha\beta} = \lim_{R\to\infty}\int du\, S(u)\left[C_R^{\alpha\beta}(u) - \bar{C}_R^{\alpha\beta}(u)\right]\chi_{2R}(u) \tag{A3}$$

with

$$C_R^{\alpha\beta}(u) = R\int dv\, \chi_1(v) f_1^\alpha(v) f_1^\beta\left(v - \frac{u}{R}\right) \tag{A4}$$

$$\overline{C}_R^{\alpha\beta}(u) = R\int dv\, \chi_1(v)\overline{\chi}_1\left(v - \frac{u}{R}\right) f_1^\alpha(v) f_1^\alpha\left(v - \frac{u}{R}\right) \tag{A5}$$

$$\overline{\chi}_R(x) = 1 - \chi_R(x)$$

Notice that the integrand in (A1) vanishes if $|x_1| > R$ or $|x_2| > R$, and hence if $|u| \geqslant |x_1 - x_2| \geqslant 2R$.

An explicit integration leads to

$$C_R^{11}(u) = \begin{cases} 4\pi R - 2\pi|u|, & |u| \leqslant R \\ \dfrac{2\pi R^2}{|u|}, & |u| \geqslant R \end{cases} \tag{A6}$$

$$C_R^{21}(u) = \begin{cases} \dfrac{5\pi}{2} R - \dfrac{\pi|u|^2}{R} + \dfrac{\pi}{10}\dfrac{|u|^4}{R^3}, & |u| \leqslant R \\ \dfrac{8\pi}{5}\dfrac{R^2}{|u|}, & |u| \geqslant R \end{cases}$$

$$C_R^{12}(u) = \frac{5\pi R}{2} - \frac{\pi|u|^2}{R} \tag{A7}$$

$$C_R^{22}(u) = \frac{68\pi R}{35} - \frac{4\pi}{5}\frac{|u|^2}{R}$$

The conditions (3.5), (3.6) imply

$$\lim_{R\to\infty}\left|R\int_{|u|\leqslant 2R} du\, S(u)\right| = \lim_{R\to\infty}\left|R\int_{|u|\geqslant 2R} du\, S(u)\right| \leqslant \lim_{R\to\infty}\int_{|u|\geqslant 2R} du\, |u|\,|S(u)| = 0 \tag{A8}$$

and by dominated convergence

$$\lim_{R\to\infty}\int_{|u|\leqslant 2R} du\, S(u)\frac{|u|^2}{R} = 0$$

Thus we find

$$\lim_{R\to\infty}\int du\, S(u) C_R^{\alpha\beta}(u) X_{2R}(u) = \begin{cases} -2\pi\int du\, |u| S(u), & \alpha = \beta = 1 \\ 0, & \text{otherwise} \end{cases} \tag{A9}$$

To evaluate the contribution of $\overline{C}^{\alpha\beta}(u)$ to (A3), we consider first the case where $|u| \geqslant R/4$. One finds from (A6) that

$$|\overline{C}^{11}(u)| \leqslant R\int dv\, \chi_1(v) f_1^1(v) f_1^1\left(v - \frac{u}{R}\right) = C^{11}(u) = O(|u|), \qquad |u| \geqslant \frac{R}{4},$$

and also that $C_R^{12}(u)$ and $C_R^{22}(u)$ are $O(|u|)$ for $|u| \geqslant R/4$. Thus

$$\lim_{R\to\infty} \left| \int_{R/4 \leqslant |u| \leqslant 2R} du\, \overline{C}^{\alpha\beta}(u) S(u) \right| \leqslant M \lim_{R\to\infty} \int_{R/4 \leqslant |u|} du\, |u|\, |S(u)| = 0 \tag{A10}$$

Consider now the case where $|u| \leqslant R/4$. In the integrand of (A5) we have always $|v| \leqslant 1$, $|v - u/R| \geqslant 1$, hence $|v - \hat{v}| \leqslant |u|/R \leqslant 1/4$ and $|v - \hat{v} - u/R| \leqslant 2|u|/R \leqslant 1/2$, $\hat{v} = v|v|$. For v, u lying in this domain, a limited Taylor expansion around $v = \hat{v}$ yields

$$f^{\alpha}(v) f^{\beta}(v - u/R) = 1 + O(|u|/R) \tag{A11}$$

For each fixed u we have that $\int dv\, \chi_1(v) \overline{\chi}_1(v - u/R)$ is $O(1)$ and tends to zero as $R \to \infty$. Moreover, $R \int dv\, \chi_1(v) \chi_1(v - u/R)$ is $O(|u|)$ and

$$\lim_{R\to\infty} R \int dv\, \chi_1(v) \chi_1\!\left(v - \frac{u}{R}\right) = \pi |u|$$

Therefore, with this and (A11), we find again by dominated converge that

$$\lim_{R\to\infty} \int_{|u| \leqslant R/4} du\, \overline{C}^{\alpha\beta}(u) S(u) = \pi \int du\, |u| S(u) \tag{A12}$$

Combining (A9), (A10), (A12), in (A3) leads to the result (3.11), (3.12) of the lemma.

Taking first the limit $R_1 \to \infty$ in $\langle V_{R_2}^{\text{in}}(0) V_{R_1}^{\text{in}}(0) \rangle, \langle V_{R_2}^{\text{in}}(0) \overline{V}_{R_1}^{\text{in}}(0) \rangle, \ldots,$ we see that the double limit is given by the first term of (A3). Therefore (3.13) follows immediately from (A9). This concludes the proof of the lemma. ∎

In view of (3.11), to establish (7.5) it is sufficient to show that

$$\begin{aligned}
&\lim_{R\to\infty} \left[-\int dx \int dy\, S(x-y) \frac{1}{|x|^2} \chi_R(x) \chi_R(y) \right] \\
&\quad = \lim_{R\to\infty} \left[-4\pi R \int_{|u| \leqslant 2R} du\, S(u) \right. \\
&\qquad \left. + \int_{|u| \leqslant 2R} du\, S(u) \int dz \frac{1}{|z|^2} \chi_1(z) \overline{\chi}_1\!\left(z - \frac{u}{R}\right) \right] \\
&\quad = \pi \int dx\, |x| S(x)
\end{aligned} \tag{A13}$$

Indeed the first term of (A13) tends to zero as in (A8) and the second term gives the same results as (A12) by the same arguments.

Proof of Lemma 2. Proceeding as in Lemma 1, we write

$$\langle E_{R_1}^{r(\text{in})}(0) E_{R_2}^{s(\text{in})}(0) \rangle = \int du\, S(u) \int dx \frac{x^r}{|x|^3} \frac{(x-u)^s}{|x-u|^3} \chi_{R_1}(x) \chi_{R_2}(x-u)$$

For fixed u, the x integral is absolutely convergent as $R_1 \to \infty$, $R_2 \to \infty$ (or $R_1 = R_2 = R \to \infty$) and tends to $(2\pi/|u|)(\delta_{rs} - \hat{u}^r\hat{u}^s)$. Moreover, it is majorized by

$$\int dx \frac{1}{|x|^2} \frac{1}{|x-u|^2} = \frac{\pi}{|u|} \int_0^\infty dr \ln\left(\frac{r+1}{r-1}\right)^2 = O\left(\frac{1}{|u|}\right)$$

Hence, (4.7) follows by dominated convergence. We get from (2.14)

$$\begin{aligned} R^2\langle E_R^{r(\text{in})}(0)E_R^{s(\text{in})}(0)\rangle &= \int dx_1 \int dy_1\, S(x_1 - y_1)\chi_R(x_1)\chi_R(y_1)\frac{x_1^r y_1^s}{R^4} \\ &= \int du\, S(u)\left[d_R^{rs}(u) - \bar{d}_R^{rs}(u)\right]\chi_{2R}(u) \qquad \text{(A14)} \end{aligned}$$

with

$$d_R^{rs}(u) = R\int dv\, \chi_1(v) v^r \left(v - \frac{u}{R}\right)^s = \frac{4\pi}{15} R\delta_{rs}$$

$$\bar{d}_R^{rs}(u) = R\int dv\, \chi_1(v)\bar{\chi}_1\left(v - \frac{u}{R}\right) v^r \left(v - \frac{u}{R}\right)^s$$

The first term in (A14) does not contribute because of electroneutrality. For the second term, we have

$$\bar{d}_R^{rs}(u) = O\left(\frac{|u|^2}{R}\right) = O(|u|) \qquad (\text{since } |u| \leqslant 2R)$$

and

$$\lim_{R\to\infty} \bar{d}_R^{rs}(u) = \frac{1}{2}\int_{\partial\Sigma(1)} |u \cdot d\sigma_v| v^r v^s = \frac{\pi}{4}(\delta_{rs} + \hat{u}^r\hat{u}^s)|u|$$

where $\partial\sum(1)$ is the surface of the unit sphere. This leads to (4.8). ∎

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