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Large Charge Fluctuations in Classical Coulomb Systems

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The typical fluctuation of the net electric charge Q contained in a subregion Λ of an infinitely extended equilibrium Coulomb system is expected to grow only as $\sqrt{S}$, where S is the surface area of Λ. For some cases it has been previously shown that $Q/\sqrt{S}$ has a Gaussian distribution as $|\Lambda| \to \infty$. Here we study the probability law for larger charge fluctuations (large-deviation problem). We discuss the case when both $|\Lambda|$ and Q are large, but now with Q of an order larger than $\sqrt{S}$. For a given value of Q, the dominant microscopic configurations are assumed to be those associated with the formation of a double electrical layer along the surface of Λ. The probability law for Q is then determined by the free energy of the double electrical layer. In the case of a one-component plasma, this free energy can be computed, for large enough Q, by macroscopic electrostatics. There are solvable two-dimensional models for which exact microscopic calculations can be done, providing more complete results in these cases. A variety of behaviors of the probability law are exhibited.

KEY WORDS: Coulomb systems; charge fluctuations; large deviations; exact results.

1. INTRODUCTION

Charge fluctuations in equilibrium Coulomb systems (plasma, electrolyte,...) are known to be "abnormal".[1,2] Some time ago, Martin and Yalcin[3] considered the fluctuations of the net electric charge Q_Λ contained in some smooth domain Λ of an infinitely extended equilibrium classical Coulomb system. They showed that the mean square charge $\langle Q_\Lambda^2 \rangle$ grows

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only as the surface area S_Λ (not the volume) of Λ and, under some further assumptions, that $Q_\Lambda/\sqrt{S_\Lambda}$ has a Gaussian distribution as $|\Lambda| \to \infty$. The variance was expressed in terms of the first moment of the charge–charge correlation function $s(r)$; for a three-dimensional system,

$$\gamma_3 = \lim_{|\Lambda| \to \infty} \frac{\langle Q_\Lambda^2 \rangle}{S_\Lambda} = -\frac{1}{4} \int d^3\mathbf{r}\, rs(r) \tag{1.1}$$

The corresponding formula for two dimensions is

$$\gamma_2 = -\frac{1}{\pi} \int d^2\mathbf{r}\, rs(r) \tag{1.2}$$

Incidentally, (1.1) can be rewritten as

$$\gamma_3 = \frac{1}{4\pi^2} \int d^3\mathbf{k}\, \frac{s(k)}{k^4}$$

in terms of the experimentally accessible[4] charge structure factor

$$s(k) = (2\pi)^{-3} \int d^3\mathbf{k}\, \exp(i\mathbf{k} \cdot \mathbf{r})\, s(r)$$

Later Lebowitz[5] showed, under the same assumptions as in ref. 3, that, if we consider a cubical lattice LZ^d, i.e., we divide space into cubes (squares) of size L^d with centers on the lattice, then the normalized charge fluctuations in each cell, $\{q_j\}$, $q_j = Q_j/L^{(d-1)/2}$, become, in the limit $L \to \infty$, jointly Gaussian with covariance matrix $\mathbf{b}$, $b_{ij} = \gamma_d[\delta_{ij} - (1/2d)\,\delta_{i,j\pm 1}]$. This shows that any deviation from neutrality in cell i is compensated for in the $2d$ neighboring cells.

The aim of the present paper is to study the probability law for fluctuations of Q_Λ larger than those of order $\sqrt{S_\Lambda}$. We want to investigate the asymptotic behavior of the probability of Q_Λ when both Λ and $|Q_\Lambda|$ become large, but now in such a way that $Q_\Lambda/\sqrt{S_\Lambda}$ goes to infinity. The results provide an example of large-deviation behavior which is different (more suppressed) than for systems with short-range interactions. In fact, as we shall see, the surface area S plays here a role similar to the volume in "normal" system fluctuations.

While ordinary Coulomb systems are made up of at least two charged components, we shall mainly consider the mathematically simpler one-component plasma (OCP or Jellium). This frequently used model system consists of charged particles of one sign embedded in a uniform background of the opposite charge.

The Gibbs canonical distribution of such a d-dimensional system ($d=2, 3$) containing N particles of charge e in a ball (disk) Λ_R of radius R, $|\mathbf{r}_j| \leqslant R$, with uniform background density $-\rho e$, is

$$\operatorname{Prob}(\mathbf{r}_1,..., \mathbf{r}_N) = \exp[-\beta H_N(\mathbf{r}_1,..., \mathbf{r}_N; R)]/Z_N(\beta; R) \tag{1.3}$$

where β is the inverse temperature,

$$H_N = e^2 \sum_{i \neq j} |\mathbf{r}_i - \mathbf{r}_j|^{-1} + \tfrac{2}{3}\pi e^2 \rho \sum_{i=1}^{N} r_i^2, \qquad d=3 \tag{1.4}$$

$$H_N = -e^2 \sum_{i \neq j} \ln(|\mathbf{r}_i - \mathbf{r}_j|/L) + \tfrac{1}{2}\pi e^2 \rho \sum_{i=1}^{N} r_i^2, \qquad d=2 \tag{1.5}$$

and Z_N is a normalization factor.

The OCP has a well-defined thermodynamic limit,[6] $R \to \infty$, $N \to \infty$, for neutral systems, i.e., when the particle density $N_R/(4/3)\pi R^3$ ($N_R/\pi R^2$) approaches ρ. In this system charge fluctuations are the same as particle fluctuations and so the comparison with particle fluctuations in "normal" particle systems is direct. In fact the two-dimensional OCP at $\beta e^2 = 2$ provides an example of a solvable system with explicitly computable n-particle correlations which have strong clustering properties, in which our analysis can be carried out fully.

To find the probability distribution of charge fluctuations in a Coulomb system we shall, for simplicity, consider only spherical (circular) domains Λ_R. Let us begin with an overall neutral system confined to a region $\Lambda_{R'}$, $R' > R$. Let $F_{R,R'}(Q)$ be the free energy of the system constrained by the requirement that the charge in Λ_R be Q. Then, in the unconstrained system, the probability that the charge in Λ_R is Q is

$$P_{R,R'}(Q) = C_{R,R'} \exp\{-\beta[F_{R,R'}(Q) - F_{R,R'}(0)]\} \tag{1.6}$$

where $C_{R,R'}$ is a normalization constant. It is reasonable to assume that the limit

$$\delta F_R(Q) = \lim_{R' \to \infty} [F_{R,R'}(Q) - F_{R,R'}(0)]$$

exists, in which case we can define a probability

$$P_R(Q) = C_R e^{-\beta \delta F_R(Q)} \tag{1.7}$$

Thus, our problem is to evaluate $\delta F_R(Q)$ in the further limit $R \to \infty$, $|Q| \to \infty$. More precisely we set $Q = \xi_\alpha R^\alpha$, where α is constant and ξ_α is a random variable, and wish to study the probability $P(\xi_\alpha; R)$ as $R \to \infty$. The case $\alpha = 1$, $d=3$ ($\alpha = 1/2$, $d=2$) was studied by Martin and Yalcin.[3]

We are interested in larger deviations, therefore we consider the range $\alpha \geqslant 1$, $d=3$ ($\alpha \geqslant 1/2$, $d=2$).

Some information about $\delta F_R(Q)$ can be obtained from physical considerations, based in part on macroscopic electrostatics. Furthermore, for the two-dimensional OCP at $\beta e^2 = 2$, explicit microscopic calculations can be performed. This will let us check that the microscopic results confirm the macroscopic ones.

Section 2 is about the one-component plasma, in $d=2$ and 3. We also consider there, in some detail, the exactly solvable case $d=2$, $\beta e^2 = 2$. Section 3 is about the two-component plasma. The main results are summarized in Section 4.

2. ONE-COMPONENT PLASMA

2.1. Two-Dimensional Case. General Picture

Since the *two-dimensional* one-component plasma happens to be exactly solvable[7–9] at the temperature such that $\beta e^2 = 2$, we first study the two-dimensional case. We consider a circular subregion of radius R within an infinite system. For the charge Q in that disk we set $Q = \xi_\alpha R^\alpha$, and we want to study the probability distribution of ξ_α in the limit $R \to \infty$. Macroscopic electrostatics of conductors implies that, for a given value of Q, the dominant configurations are such that Q is concentrated in a layer on the inner side of the boundary of the disk, while a charge $-Q$ accumulates in a layer on the outer side. Thus, using the language of electrochemists, we can regard the free energy difference $\delta F_R(Q)$ as the free energy of a double electrical layer formed at the interface between the inside and the outside of the disk, as if the surface was impermeable to the particles.

In a one-component plasma the net charge density is bounded on one side: the bound is reached when the particle density is zero, in which case the net charge density has its minimum value, i.e., the background charge density $-e\rho$. Thus, for the large values of both R and $|Q|$ that we are interested in, two regimes have to be distinguished.

Microscopic Regime. $1/2 \leqslant \alpha \leqslant 1$, i.e., $|Q|$ does not grow faster than the perimeter of the disk. The thickness of the double electrical layer (Fig. 1) does not increase as $R \to \infty$, and curvature effects can be neglected. In terms of $f(e\sigma)$, the free energy per unit length of a *rectilinear* double electrical layer with a line charge density $e\sigma = Q/2\pi R = \xi_\alpha R^{\alpha-1}/2\pi$ on one side (and $-e\sigma$ on the other side), the relevant free energy becomes

$$\delta F_R(Q) \sim 2\pi R f(Q/2\pi R) = 2\pi R f(\xi_\alpha R^{\alpha-1}/2\pi) \tag{2.1}$$

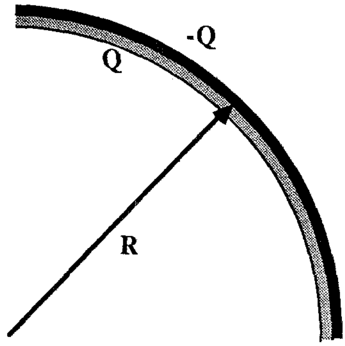

Fig. 1. The double electrical layer in the microscopic regime (one-component or two-component plasma).

For $\alpha=1$, the layer free energy density f is some more or less complicated function of $\xi_1/2\pi$, and so is the probability $P(\xi_1; R)$. But, for $\alpha<1$, as $R\to\infty$, $\sigma\to 0$ and f can be replaced by the first nonzero term of its power expansion, i.e.,

$$f \sim B(e\sigma)^2 \tag{2.2}$$

where B is a constant (f must vanish and be minimum at $\sigma=0$). In this limit, one recovers for (1.7) a Gaussian probability law,

$$P(\xi_\alpha; R) \sim \exp[-\beta B(2\pi)^{-1} R^{2\alpha-1}\xi_\alpha^2] \tag{2.3}$$

and by identification with the variance (1.2) calculated by Martin and Yalcin[3] one infers that

$$(2\beta B)^{-1} = \lim_{R\to\infty} \frac{\langle Q^2\rangle}{2\pi R} = -\frac{1}{\pi}\int d^2\mathbf{r}\, rs(r) \tag{2.4}$$

where $s(r)$ is the charge–charge correlation function in the infinite Coulomb system. It is also possible to rederive (2.4) directly by adapting the approach of ref. 3 to the present plane interface geometry.

Macroscopic Regime. $\alpha>1$, i.e., $|Q|$ grows faster than the perimeter of the disk. Since the charge density has the lower bound $-e\rho$, on the negative side of the interface the thickness of the electrical layer becomes macroscopic (Fig. 2). Then, it is reasonable to assume that $\delta F_R(Q)$ should have as its leading term the macroscopic electrostatic energy of one of the circular arrangements shown in Fig. 2 (this statement

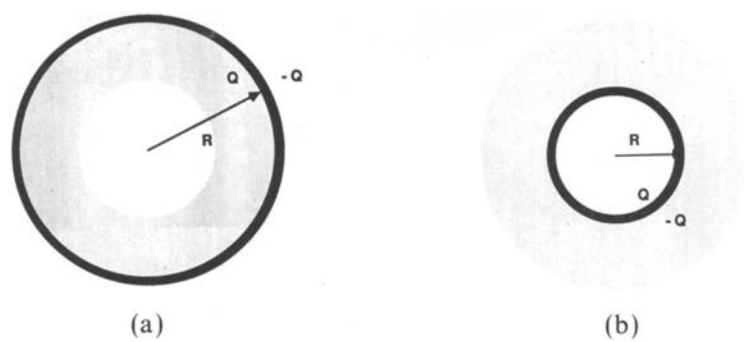

Fig. 2. The double electrical layer in the macroscopic regime (one-component plasma). Case (a) is when there is an excess of negative background inside the sphere or disk ($Q<0$). Case (b) is when there is an excess of positive particles inside the sphere or disk ($Q>0$).

is a generalization of what has been proved in the simpler case of one body carrying a surface charge density[6,10]).

The calculation of the electrostatic energy is straightforward. The electrical field $\mathbf{E}$ does not vanish only in the shaded area shown in Fig. 2; in this area, $\mathbf{E}$ is determined by div $\mathbf{E} = -2\pi e\rho$ with the boundary condition $\mathbf{E}(R) = (Q/R)\,\mathbf{u}_r$, where $\mathbf{u}_r$ is the radial unit vector. Therefore

$$\mathbf{E}(r) = \left[\frac{Q}{r} + \pi e\rho\left(\frac{R^2}{r} - r\right)\right]\mathbf{u}_r$$

and the relevant free energy is

$$\begin{aligned}\delta F_R(Q) &= \frac{1}{4\pi}\int E^2(r)\, d^2\mathbf{r} \\ &\sim Q_0^2 \frac{Q}{|Q|}\left[-\frac{1}{4}\frac{Q}{Q_0} - \frac{3}{8}\left(\frac{Q}{Q_0}\right)^2 \right. \\ &\quad \left. + \frac{1}{4}\left(1+\frac{Q}{Q_0}\right)^2 \ln\left(1+\frac{Q}{Q_0}\right)\right] \end{aligned} \tag{2.5}$$

where $Q_0 = \pi R^2 e\rho$.

The macroscopic regime $\alpha > 1$ can be further subdivided.

1. If $1<\alpha<2$, $Q/Q_0 = \xi_\alpha(\pi e\rho)^{-1} R^{\alpha-2} \to 0$ as $R\to\infty$, (2.5) behaves like $|Q|^3/12Q_0$, and (1.7) becomes

$$P(\xi_\alpha; R) \sim \exp\left(-\frac{\beta\,|Q|^3}{12Q_0}\right) = \exp[-\beta(12\pi e\rho)^{-1} R^{3\alpha-2}\,|\xi_\alpha|^3] \tag{2.6}$$

In this regime, the thickness of the double electrical layer is of order $|Q|/R = \xi_\alpha R^{\alpha-1} = o(R)$, and curvature effects can still be neglected. Indeed, (2.6) can also be obtained from $f(e\sigma)$, the free energy per unit length of a rectilinear double electrical layer, in the limit $e\sigma \to \infty$, because in that limit the rectilinear double electrical layer becomes a charged line with a line charge density $e|\sigma| = |Q|/2\pi R$ adjacent to a strip of bare background of width $|\sigma|/\rho$. One easily computes the corresponding electrostatic energy per unit length $(\pi/3)\, e^2 |\sigma|^3/\rho$, in agreement with the result obtained from (2.5) for $|Q|/Q_0 \to 0$.

2. If $\alpha = 2$, the full expression (2.5), with $Q/Q_0 = (\pi e \rho)^{-1} \xi_2$, must be used in (1.7).

The special case $Q = -Q_0$, i.e., $\xi_2 = -\pi e \rho$, corresponds to an empty hole (only the background and no particle within the disk). Then, from (2.5) and (1.7) one obtains

$$P(\xi_2 = -\pi e \rho;\, R) \sim \exp(-\beta Q_0^2/8) = \exp(-\beta e^2 \pi^2 \rho^2 R^4/8) \tag{2.7}$$

3. If $\alpha > 2$ (this is possible only for $Q > 0$, since Q has the lower bound $-Q_0$), (2.5) behaves like $(1/4)\, Q^2 \ln(Q/Q_0)$ (the dominant contribution is the self-energy of the bare background), and

$$P(\xi_\alpha;\, R) \sim \exp\left(-\frac{\beta}{4} Q^2 \ln \frac{Q}{Q_0}\right) \sim \exp\left[-\frac{\beta}{4} R^{2\alpha} \xi_\alpha^2 \ln(R^{\alpha-2} \xi_\alpha)\right] \tag{2.8}$$

2.2. Two-Dimensional Case. Exact Results

The above considerations are supported by the exact microscopic results which can be obtained at the temperature such that $\beta e^2 = 2$. Then, an exact expression for $f(e\sigma)$, the free energy per unit length of a rectilinear double electrical layer, has been obtained by Rosinberg and Blum.[11] They started with a circular interface and considered the large-radius limit. Therefore, their approach is a check that the large-R limit of $\delta F_R(Q)$ is indeed of the form used in (2.1): $\delta F_R(Q) \sim 2\pi R f(Q/2\pi R)$.

Ref. 11 deals with the more general case of an interface between two one-component plasmas of different background densities. Here, there is only one background density ρ, i.e., the parameter m of ref. 11 must be taken as $m = 1$. Then, a slight rearrangement of the results in ref. 11 gives for the free energy density $f(e\sigma)$ the following integral representation in terms of an auxiliary parameter z: the function $f(e\sigma)$ is implicitly determined by the relations

$$\sigma = -\left(\frac{\rho}{8\pi}\right)^{1/2} (z-1) \int_{-\infty}^{\infty} \left[\frac{z}{1-\Phi(t)} + \frac{1}{1+\Phi(t)}\right]^{-1} dt \tag{2.9a}$$

and

$$f = -e^2 \left(\frac{\rho}{8\pi}\right)^{1/2} \left\{ \int_{-\infty}^{0} \ln \frac{z[1+\Phi(t)]+[1-\Phi(t)]}{2} dt \right.$$
$$\left. + \int_0^{\infty} \ln \frac{z[1+\Phi(t)]+1-\Phi(t)}{2z} \right\} - \frac{e^2}{2} \sigma \ln z \qquad (2.9b)$$

where $\Phi(t)$ is the error function

$$\Phi(t) = \frac{2}{\sqrt{\pi}} \int_0^t e^{-u^2} du$$

Therefore, (2.9), (2.1), and (1.7) give the probability law in the microscopic regime $1/2 \leqslant \alpha \leqslant 1$.

For $\alpha = 1$, $e\sigma = Q/2\pi R = \xi_1/2\pi$, and the full function $f(\xi_1/2\pi)$ must be used in (2.1).

The simpler case $\alpha < 1$, which corresponds to the limit $e\sigma = Q/2\pi R = \xi_\alpha R^{\alpha-1}/2\pi \to 0$, is obtained when $z \to 1$. Then, by expansions in powers of $z-1$,

$$\sigma \sim -\left(\frac{\rho}{8\pi}\right)^{1/2} (z-1) \frac{1}{4} \int_0^{\infty} \{1 - [\Phi(t)]^2\} dt = -\frac{\rho^{1/2}}{2\pi} (z-1)$$

and

$$f \sim -e^2 \left(\frac{\rho}{8\pi}\right)^{1/2} (z-1)^2 \frac{1}{4} \int_0^{\infty} \{1 - [\Phi(t)]^2\} dt - \frac{e^2}{2} \sigma(z-1)$$
$$= -\frac{\rho^{1/2}}{4\pi} (z-1)^2 - \frac{e^2}{2} \sigma(z-1)$$

Thus,

$$f \sim \frac{\pi e^2 \sigma^2}{2\rho^{1/2}} = \frac{\pi}{2\rho^{1/2}} \left(\frac{Q}{2\pi R}\right)^2$$

and (1.7) becomes

$$P(\xi_\alpha; R) \sim \exp\left(-\frac{\beta\pi}{2\rho^{1/2}} \frac{Q^2}{2\pi R}\right) = \exp\left(-\frac{\beta}{4\rho^{1/2}} R^{2\alpha-1} \xi_\alpha^2\right) \qquad (2.10)$$

This is the Gaussian law (2.3). Here, the charge–charge correlation function is known,[8]

$$rs(r) = -e^2 \rho^2 r \exp(-\pi\rho r^2)$$

and it can be explicitly checked that the variance in (2.10), $\langle Q^2 \rangle / 2\pi R = \rho^{1/2}/\beta\pi = e^2 \rho^{1/2}/2\pi$, is indeed in agreement with the general expression (1.2).

The macroscopic result (2.6), valid for $1 < \alpha < 2$, can also be obtained, when $\beta e^2 = 2$, by a microscopic calculation using (2.9), in the limits $e\sigma \to \pm\infty$. The limit $e\sigma \to +\infty$ is obtained when $z \to 0$ (for a plane interface, f is an even function of σ, and therefore our results apply also to the case $e\sigma \to -\infty$). The behavior of (2.9) as $z \to 0$ can be obtained by setting $z = \exp(-\tau^2)$ and changing the integration variable t to $u = t/\tau$. Then, as $\tau \to \infty$, the integrand in (2.9a) goes to 2 for $u \in [0, 1]$ and to 0 for $u \notin [0, 1]$, and

$$\sigma \sim \left(\frac{\rho}{8\pi}\right)^{1/2} \int_0^1 2\tau \, du = \left(\frac{\rho}{2\pi}\right)^{1/2} \tau$$

After the same change of variable in (2.9b), as $\tau \to \infty$, the integrand of the first integral goes to zero while the integrand of the second integral goes to $\tau^2(1-u^2)$ for $0 < u < 1$ and to 0 for $u > 1$. One obtains

$$\begin{aligned}\beta f &\sim -e^2 \left(\frac{\rho}{8\pi}\right)^{1/2} \int_0^1 \tau^2(1-u^2)\,\tau \, du + \frac{e^2}{2}\sigma\tau^2 \\ &= -e^2\left(\frac{\rho}{2\pi}\right)^{1/2} \frac{\tau^3}{3} + \frac{e^2}{2}\sigma\tau^2\end{aligned}$$

Thus, as $\sigma \to \pm\infty$,

$$f \sim \frac{e^2\pi}{3\rho} |\sigma|^3 \tag{2.11}$$

and one recovers (2.6). Therefore, in this case, we have checked that macroscopic electrostatics agrees with the here feasible microscopic calculation.

Finally, the macroscopic result (2.7), valid for $\alpha = 2$ in the special case $Q = -Q_0$, i.e., for $\xi_2 = -\pi e\rho$ (bare background within the disk), can be checked by a microscopic calculation when $\beta e^2 = 2$. Indeed, the probability $P_R(-Q_0)$ that the disk contains zero particles is related to the particle density $\rho(R)$ just outside the disk by

$$\frac{d \ln P_R}{dR} = -2\pi R\rho(R) \tag{2.12}$$

[since the probability P_{R+dR} is equal to the probability P_R times the probability $1 - \rho(R)\, 2\pi R\, dR$ that there is no particle between R and $R + dR$]. For large R, the microscopic calculation described in the Appendix gives

$$\rho(R) \sim \tfrac{1}{2}\pi\rho^2 R^2 \tag{2.13}$$

and from (2.12) one recovers (2.7).

2.3. Three-Dimensional Case

Many results for the two-dimensional one-component plasma could be obtained in Section 2.1 by arguments based on macroscopic electrostatics. These arguments can be easily adapted to the three-dimensional case. What will be missing in the three-dimensional case is an explicit expression for the free energy of the microscopic double electrical layer pictured on Fig. 1.

We now consider a spherical subregion of radius R within an infinite three-dimensional one-component plasma. For the charge Q in that sphere we set again $Q = \xi_\alpha R^\alpha$ and we study the probability distribution of ξ_α in the limit $R \to \infty$. Again we expect the dominant configurations to be described by a double electrical layer. The different regimes are now as follows.

Microscopic Regime. $1 \leqslant \alpha \leqslant 2$, i.e., $|Q|$ does not grow faster than the surface of the sphere (Fig. 1). The analog of (2.1), in terms now of the surface charge density $e\sigma = Q/4\pi R^2$, is

$$\delta F_R(Q) \sim 4\pi R^2 f(Q/4\pi R^2) = 4\pi R^2 f(\xi_\alpha R^{\alpha-2}/4\pi) \tag{2.14}$$

For $\alpha = 2$, the probability law $P(\xi_2; R)$ is governed by the function $f(\xi_2/4\pi)$, for which no exact expression is known. However, for $\alpha < 2$, the limiting form (2.2) of f is valid, and we obtain the Gaussian probability law analog of (2.3):

$$P(\xi_\alpha; R) \sim \exp[-\beta B (4\pi)^{-1} R^{2\alpha-2} \xi_\alpha^2] \tag{2.15}$$

with the variance (1.1).

Macroscopic Regime. $\alpha > 2$, i.e., $|Q|$ grows faster than the surface of the sphere. The analog of (2.5), obtained by similar methods, is

$$\delta F_R(Q) = \frac{1}{8\pi} \int E^2(r)\, d^3\mathbf{r}$$

$$\sim \frac{Q_0^2}{R} \frac{Q}{|Q|} \left[\frac{9}{10} + \frac{3}{2}\frac{Q}{Q_0} + \frac{1}{2}\left(\frac{Q}{Q_0}\right)^2 - \frac{9}{10}\left(1 + \frac{Q}{Q_0}\right)^{5/3} \right] \tag{2.16}$$

where $Q_0 = (4\pi R^3/3)\, e\rho$. The subdivisions of the macroscopic regime now are as follows:

1. If $2 < \alpha < 3$, $Q/Q_0 = 3(4\pi e\rho)^{-1} R^{\alpha-3} \xi_\alpha \to 0$ as $R \to \infty$, (2.16) behaves like $|Q|^3/18RQ_0$, and (1.7) becomes

$$P(\xi_\alpha; R) \sim \exp\left(-\frac{\beta |Q|^3}{18RQ_0}\right) = \exp[-\beta(24\pi e\rho)^{-1} R^{3\alpha-4} |\xi_\alpha|^3] \tag{2.17}$$

In this regime, the curvature effects can be neglected [the thickness of the double electrical layer is of order $|Q|/R^2 = \xi_\alpha R^{\alpha-2} = o(R)$] and (2.17) can also be obtained in a plane geometry: a charged plane adjacent to a slab of bare background.

2. If $\alpha = 3$, the full expression (2.16), with $Q/Q_0 = 3(4\pi e\rho)^{-1}\,\xi_3$, must be used in (1.7).

In the special case $Q = -Q_0$, i.e., $\xi_3 = -4\pi e\rho/3$, corresponding to an empty hole, one now obtains

$$P(\xi_3 = -4\pi e\rho/3;\, R) \sim \exp[-\beta(8\pi^2/45)\, e^2\rho^2 R^5] \tag{2.18}$$

3. If $\alpha > 3$, i.e., if $Q/Q_0 \to +\infty$, (2.16) behaves like $Q^2/2R$ (the dominant contribution now is the self-energy of the sphere of radius R), and

$$P(\xi_\alpha;\, R) \sim \exp(-\beta Q^2/2R) = \exp[-(1/2)\,\beta R^{2\alpha-1}\xi_\alpha^2] \tag{2.19}$$

Thus, the very tail of the probability law is Gaussian again, as in the regime $1 \leqslant \alpha < 2$ described by (2.15), but now with another rate of decay.

3. TWO-COMPONENT PLASMA

3.1. General Picture

Another Coulomb system of interest is the two-component plasma, made up of two species of particles of charges e and $-e$. We may address the same problem: study the fluctuations of the charge Q inside a large spherical (circular) subregion Λ of radius R. However, for a classical two-component plasma to be well-behaved, the Coulomb interaction must be regularized in some way at short distance, and the probability law for the charge fluctuations, especially the large ones, is expected to depend on the detail of this regularization.

In the three-dimensional case, in the regime $1 \leqslant \alpha \leqslant 2$, Eq. (2.14) and its limiting form (2.2) for $\alpha < 2$ also apply to the two-component plasma. In the two-dimensional case, some microscopic results are available, as follows.

3.2. Two-Dimensional Solvable Model

Equation (2.1) also applies to a two-dimensional two-component plasma, with a Coulomb interaction $\pm e^2 \ln(r/L)$ between the particles. This model also is exactly solvable[12] at the temperature such that $\beta e^2 = 2$, and an exact expression for the free energy density f in (2.1) is available. Thus, we can describe the following regimes:

$\alpha = 1$. In ref. 12, in terms of the bulk fugacity z and of the length scale L of the logarithmic interaction, a rescaled fugacity $m = 2\pi L z$ is defined (m is an inverse length and it turns out that m^{-1} is of the order of the correlation length). This parameter m controls the bulk density. The free energy density $f(e\sigma)$ of a double electrical layer with a linear charge density $e\sigma$ was computed (polarizable interface problem of ref. 12) in terms of an auxiliary parameter $\Delta\phi$, the potential difference across the interface (it happens that f remains finite even in the limit of no short-distance cutoff in the Coulomb interaction, and this is the case which is considered here). The result was for the function $f(e\sigma)$ the parametric representation

$$\beta f = -\frac{m}{2}\left(\cosh\frac{\Delta\phi}{e} - 1\right) + \beta e\sigma\,\Delta\phi$$

$$\sigma = \frac{m}{4}\sinh\frac{\Delta\phi}{e}$$

(in the notation of ref. 12, our f is $\Omega/A = \gamma + e\sigma\,\Delta\phi$). Therefore, more explicitly,

$$\beta f(e\sigma) = -\frac{m}{2}\left\{\left[1 + \left(\frac{4\sigma}{m}\right)^2\right]^{1/2} - 1\right\} + 2\sigma\sinh^{-1}\frac{4\sigma}{m} \tag{3.1}$$

Using (3.1) in (2.1) and (1.7) gives the probability law when $\alpha = 1$ for an arbitrary value of $e\sigma = Q/2\pi R = \xi_1/2\pi$.

$\alpha < 1$. In the limit $\sigma \to 0$, i.e., when $\alpha < 1$, one recovers the Gaussian law of Martin and Yalcin.[3] Indeed, (3.1) gives

$$f \sim \frac{4\sigma^2}{\beta m} = \frac{2}{m}\left(\frac{Q}{2\pi R}\right)^2$$

and (1.7) becomes

$$P(\xi_\alpha; R) \sim \exp\left(-\frac{2\beta}{m}\frac{Q^2}{2\pi R}\right) = \exp[-\beta(\pi m)^{-1} R^{2\alpha-1}\xi_\alpha^2] \tag{3.2}$$

The charge–charge correlation function is exactly known,[12]

$$rs(r) = -2e^2\left(\frac{m^2}{2\pi}\right)^2 r\{[K_0(mr)]^2 + [K_1(mr)]^2\}$$

where K_0 and K_1 are modified Bessel functions, and it can be checked that the variance in (3.2) is in agreement with the general formula (1.2).

$\alpha > 1$. In the limit $\sigma \to \infty$, (3.1) has the behavior

$$\beta f \sim 2\,|\sigma| \left(\ln \frac{8\,|\sigma|}{m} - 1 \right) \sim \beta e^2\,|\sigma| \ln |\sigma| \tag{3.3}$$

and (1.7) becomes

$$P(\xi_\alpha; R) \sim \exp(-\beta e\,|Q| \ln |Q|) \sim \exp[-\beta e R^\alpha\,|\xi_\alpha| \ln(R^\alpha\,|\xi_\alpha|)] \tag{3.4}$$

These results (3.3) and (3.4) for the two-dimensional two-component plasma are to be compared with the results (2.11) and (2.6) for the two-dimensional one-component plasma. As $|\sigma|$ increases, the thickness of the double electrical layer decreases in the two-component case, while it increases in the one-component case. This is why the free energy is smaller in the two-component case.

4. CONCLUSION

We have estimated the probability $P_R(Q)$ that a charge fluctuation Q occurs in a large spherical (circular) subregion Λ of radius R in an infinite three-dimensional (two-dimensional) Coulomb system.

It had been previously proven that when Q and $\sqrt{S}$ (S is the surface area of Λ) both go to infinity with a fixed ratio $q = Q/\sqrt{S}$, $P_R(Q)$ becomes a Gaussian function of q, with a variance related to the first moment of the charge–charge correlation function.

In the present paper, we have shown that the asymptotic behavior of $P_R(Q)$ is given by that same Gaussian as long as Q is of an order smaller than S. When Q is of the order of S, the asymptotic behavior of $P_R(Q)$ is determined by some function (not simple in general) $f(Q/S)$, which is the free energy per unit area of a plane double electrical layer with surface charge densities $\pm Q/S$ on each side of an interface impermeable to the particles. Finally, in the special case of a one-component plasma, when Q is of an order larger than S, the asymptotic behavior of $P_R(Q)$ can be explicitly computed by macroscopic electrostatics.

The above results can be checked in the two-dimensional case by exact microscopic calculations which are feasible at a special value of the temperature. It is then possible to compute explicitly the two-dimensional analog of the free energy density $f(Q/S)$, both for the one-component and the two-component plasmas. For the one-component plasma, some of the results obtained by macroscopic electrostatics have been checked by explicit microscopic calculations.

APPENDIX

At the temperature such that $\beta e^2 = 2$, we consider a two-dimensional one-component plasma subjected to the constraint that there is no particle within the disk of radius R centered at the origin. The background, however, fills the whole plane with a constant charge density $-e\rho$. We want to compute the particle number density $\rho(R)$ at a point infinitely close to the circle of radius R, on the external side.

The method used in refs. 9 and 13 gives for the particle number density $\rho(r)$, $r \geqslant R$,

$$\rho(\tau) = \sum_{n=0}^{\infty} \frac{e^{-\pi\rho r^2} r^{2n}}{\int_R^\infty e^{-\pi\rho s^2} s^{2n} 2\pi s \, ds} \tag{A.1}$$

The integrals in (A.1) can be expressed in terms of the incomplete gamma function

$$\Gamma(n+1, N) = \int_N^\infty e^{-t} t^n \, dt \tag{A.2}$$

where $N = \pi\rho R^2$. That gives

$$\rho(r) = \rho e^{-\pi\rho r^2} \sum_{n=0}^{\infty} \frac{(\pi\rho r^2)^n}{\Gamma(n+1, N)}$$

and in particular

$$\rho(R) = \rho e^{-N} \sum_{n=0}^{\infty} \frac{N^n}{\Gamma(n+1, N)} \tag{A.3}$$

For $N \gg 1$, the dominant values of n in (A.3) will turn out to be such that $N - n = \mathcal{O}(\sqrt{N})$. In that case, an asymptotic expression for $\Gamma(n+1, N)$ can be obtained by rewriting (A.2) as

$$\Gamma(n+1, N) = \int_N^\infty e^{-t + n \ln t} \, dt$$

expanding the argument of the exponential around its maximum at $t = n$ to second order in $t - n$, and performing the integral, with the result

$$\Gamma(n+1, N) \sim e^{-n + n \ln n} \left(\frac{\pi n}{2}\right)^{1/2} \left[1 + \Phi\left(\frac{n - N}{(2n)^{1/2}}\right)\right] \tag{A.4}$$

where Φ is the error function. Using (A.4) in (A.3) gives

$$\rho(R) = \rho e^{-N} \sum_{n=0}^{\infty} e^{n \ln N + n - n \ln n} \left(\frac{2}{\pi n}\right)^{1/2} \left[1 + \Phi\left(\frac{n-N}{(2n)^{1/2}}\right)\right]^{-1} \tag{A.5}$$

Expanding the argument of the exponential around its maximum at $n = N$ to second order in $n - N$, discarding terms of order $1/\sqrt{N}$, and replacing the sum on n by an integral on $t = (n-N)/(2N)^{1/2}$, one finds

$$\begin{aligned} \frac{\rho(R)}{\rho} &= \frac{2}{\sqrt{\pi}} \int_{-(N/2)^{1/2}}^{\infty} dt \, \frac{e^{-t^2}}{1+\Phi(t)} = \ln \frac{2}{1-\Phi((N/2)^{1/2})} \\ &\sim \frac{N}{2} = \frac{1}{2} \pi \rho R^2 \end{aligned} \tag{A.6}$$

This is (2.13).

One may note that $\rho(R)$ would be unchanged if the uniform background inside the disk was replaced by a linear charge density $-e\sigma$ along its circular boundary, with the same total charge, i.e., such that $\sigma 2\pi R = \pi \rho R^2$. Indeed, $\rho(R)$ as given by (A.5) is the same as the density at contact with a charged hard wall carrying $-e\sigma$, as computed in ref. 9.

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