Charge fluctuations in Coulomb systems

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It was shown by Martin and Yalcin that the mean-square fluctuation $\langle Q_\Lambda^2 \rangle$ in the net electric charge Q_Λ contained in a subregion Λ of an infinitely extended equilibrium Coulomb system (plasma, electrolytes, etc.) grows only as the *surface area* S_Λ *(not the volume)* of Λ and that $Q_\Lambda/\sqrt{S_\Lambda}$ has a Gaussian distribution as $\Lambda \to \infty$. We extend these results to joint charge fluctuations in different spatial regions: Let space be divided into disjoint regions Λ_i, $i=1,2,\ldots$, say, cubes of length L. We show that as $L \to \infty$, the covariance in Q_{Λ_i}/L behaves as $L^{-2}\langle Q_{\Lambda_i} Q_{\Lambda_j} \rangle = -\frac{1}{6} L^{-2} \langle Q_{\Lambda_i}^2 \rangle = -\frac{1}{6} K$ *if* Λ_i and Λ_j are adjacent, and is zero if they do not have a common face. Furthermore, the variables Q_Λ/L approach, as $L \to \infty$, a jointly Gaussian distribution. These results can be proven rigorously whenever the correlations in the system decay faster than the fourth power of the distance, which is known to happen in many cases. This behavior of charge fluctuations is shown to be required for the consistency of the usual statistical-mechanical treatment of neutral-molecular systems.

I. INTRODUCTION

The properties of macroscopic matter are almost entirely determined by the Coulomb interactions between electrons and nuclei, satisfying appropriate quantum statistics. In many investigations of macroscopic systems, however, one starts instead with an "effective" short-range microscopic Hamiltonian, e.g., we describe inert fluids as a collection of neutral atoms represented by point masses interacting via Lennard-Jones pair potentials. This description completely ignores charge fluctuations and its validity must therefore require (at the minimum) that these be small. In fact, if all the charges are bound into neutral atoms or molecules then the fluctuations in the net charge Q_Λ in a region Λ will be due entirely to the surface of Λ cutting these entities in a "random" way. $\langle Q_\Lambda^2 \rangle$ may then be expected to be proportional to the surface area of Λ and this is indeed small compared to typical variances, which are proportional to the volume of Λ.

The question naturally arises as to whether this implicit assumption is indeed a consequence, in some or all situations, of the true Coulomb interactions. In particular, is it true for charge fluctuations in plasmas, molten salts, metals, etc., where bare Coulomb interactions are part of the effective Hamiltonian? Fluctuations in these systems play an important role in determining shifts and broadenings of spectral lines[1] and are therefore of practical interest. We shall show here that this is, in fact, the case; charge fluctuations in systems containing free charges are qualitatively similar to those implicitly assumed for systems composed of neutral atoms or molecules. This (at first sight) somewhat surprising fact is brought about by the very long range of the Coulomb force which produces effective strong coupling among charges no matter how high the temperature (or weak the bare coupling) is. Indeed, the reduced growth of charge fluctuations is a direct consequence of screening—the fundamental fact of life in Coulomb systems. Screening makes free charges behave, on a macroscopic scale, as if they were effectively grouped into neutral entities. For this reason, also, fluctuations in adjacent (and only in adjacent) regions will have a strong (negative) correlation.

Our results extend those of Martin and Yalcin[2] for fluctuations in a single region and the proof, like theirs, is based on the existence of a generalized charge screening in Coulomb systems. This can be proven rigorously[3] for systems whose spatial correlation functions satisfy the usual equilibrium classical Born-Green-Yvon hierarchy and decay faster than r^{-4}. While the restriction to classical systems is almost certainly not essential, the integrable decay of charge correlations is necessary for our proof. The result is presumably valid, however, also in crystals where such a decay is not expected. Whether it also remains valid at "critical points" of charged systems is an open question. It presumably holds in the Kosterlitz-Thouless transition region in two dimensions where the charges are tightly bound into neutral entities.

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II. RESULTS

We consider an infinite, equilibrium, classical m-component system of particles with charges e_α, $\alpha=1,\ldots,m$. We denote by $q_i=(\alpha_i,r_i)$ the species and position of the ith particle $i=1,\ldots$. The particles interact via pair potentials $v(q_1,q_2)$ which are Coulombic for distances beyond some fixed R. In ν dimensions,

$$v(q_i,q_j)=e_{\alpha_i}e_{\alpha_j}r^{2-\nu}\,,\quad r=|\vec{r}_i-\vec{r}_j|>R \tag{2.1}$$

($-\ln r$ for $\nu=2$). The exact form of v for small r is unimportant for our considerations. In particular, it can, to insure stability, contain a hard core or a quantum cutoff.[4] We can also deal with smeared charges and with Jellium, where there is a uniform background charge.

The equilibrium state of the system, taken (for simplicity) to be uniform in space, will be described by correlation functions, $\rho(q)=\rho_\alpha,\rho(q_1,q_2)=\rho_{\alpha_1\alpha_2}(\vec{r}_1-\vec{r}_2)$, etc. These are assumed to satisfy the usual stationary Born-Green-Yvon hierarchy equations.[3] We also introduce explicitly the symmetric n-point truncated total charge-density correlation functions $S_n(\vec{r}_i,\ldots,\vec{r}_n)$,

$$S_1(\vec{r}_1)=\langle\sigma(\vec{r}_1)\rangle=\sum e_\alpha\rho_\alpha=0\,, \tag{2.2}$$

$$S_2(\vec{r}_1,\vec{r}_2)=S(\vec{r}_1-\vec{r}_2)=\langle\sigma(\vec{r}_1)\sigma(\vec{r}_2)\rangle-\langle\sigma(\vec{r}_j)\rangle\langle\sigma(\vec{r}_2)\rangle$$
$$=\sum e_{\alpha_1}e_{\alpha_2}[\rho(q_1,q_2)+\rho(q_i)\delta_{\alpha_1\alpha_2}\delta(\vec{r}_1-\vec{r}_2)-\rho(q_1)\rho(q_2)]\,, \tag{2.3}$$

where

$$\sigma(\vec{r})=\sum e_{\alpha_i}\delta(\vec{r}-\vec{r}_i) \tag{2.4}$$

is the microscopic charge density.

The S_n are directly related to charge fluctuations: Let Q_{Λ_t} be the net microscopic charge in Λ_t. Then by definition the nth cumulant of the random variables (Q_{Λ_t}) is given by

$$\langle Q_{\Lambda_{t_1}},\ldots,Q_{\Lambda_{t_n}}\rangle^c=\int\cdots\int S_n(\vec{r}_1,\ldots,\vec{r}_n)\times\prod_{i=1}^{n}\chi_{\Lambda_{t_i}}(\vec{r}_i)d\vec{r}_i\,, \tag{2.5}$$

where $\chi_\Lambda(\vec{r})$ is the characteristic function of the region Λ. In particular,

$$\langle Q_{\Lambda_1}Q_{\Lambda_2}\rangle=\int\int S_2(\vec{r}_1,\vec{r}_2)\chi_{\Lambda_1}(\vec{r}_1)\chi_{\Lambda_2}(\vec{r}_2)d\vec{r}_2d\vec{r}_2=\int d\vec{r}\,S(\vec{r})\gamma_{\Lambda_1\Lambda_2}(\vec{r})\,, \tag{2.6}$$

where

$$\gamma_{\Lambda_1\Lambda_2}(\vec{r})=\int d\vec{y}\,\chi_{\Lambda_1}(\vec{r}+\vec{y})\chi_{\Lambda_2}(\vec{y})\,. \tag{2.7}$$

Noting that $\chi_\Lambda(\vec{r})=1-\chi_{\overline{\Lambda}}(\vec{r})$, where $\overline{\Lambda}$ is the complement of Λ in $\mathbf{R}^\nu$, we may rewrite (2.6) for $\Lambda_1=\Lambda_2=\Lambda$ as

$$\langle Q_\Lambda^2\rangle=|\Lambda|\int S(\vec{r})d\vec{r}-\int d\vec{r}\,S(\vec{r})\gamma_{\Lambda\overline{\Lambda}}(\vec{r})\,. \tag{2.8}$$

Equation (2.10) is the square of the charge fluctuation in a fixed region Λ contained in a translation invariant infinite system where $|\Lambda|$ is the volume of Λ.

We now assume that the correlations in our system decay faster than the $(\nu+1)$th power of the distance, i.e., that for some $\epsilon>0$,

$$|r^{\nu+1+\epsilon}\rho^T(q_1,\ldots,q_k)|\le\text{const}\,. \tag{2.9}$$

Here $r=\max\{|\vec{r}_i-\vec{r}_j|;i,j=1,\ldots,k\}$, $k=2,3,\ldots$, and $\rho^T(q_1,\ldots,q_k)$ is the truncated k-particle correlation function. It was shown in Refs. 2 and 3 that Eq. (2.9) implies the generalized charge neutrality sum rule

$$\int S_n(\vec{r}_1,\ldots,\vec{r}_n)d\vec{r}_n=0\,,\quad n=2,3,\ldots\,. \tag{2.10}$$

The physical interpretation of (2.10) is[3] that if we fix particles at positions $\vec{r}_1$ to $\vec{r}_{n-1}$ then there will be a charge cloud surrounding them which will completely balance the net charge of the fixed particles on a scale *independent* of the size of a macroscopic system.

It follows now immediately from (2.10) that the first term on the right-hand side of (2.8), which is proportional to the volume and can be shown to be strictly positive for systems with short-range interactions, becoming infinite at the critical point of a demixing transition, vanishes for a system with Coulomb interactions satisfying (2.9). The charge fluctuations are therefore determined entirely by the second term. This is easily shown[2] to be proportional to the surface area $|S_\Lambda|$ when $\Lambda\to\infty$ in a self-similar way, i.e., if we expand some region Λ_0 uniformly to obtain $\Lambda\to\infty$ then

$$\lim_{\Lambda\to\infty}|S_\Lambda|^{-1}\gamma_{\Lambda\overline{\Lambda}}(\vec{r})=\gamma(\vec{r})=\tfrac{1}{2}|S_{\Lambda_0}|^{-1}\int_{S_{\Lambda_0}}|\vec{r}\cdot d\vec{S}|\,. \tag{2.11}$$

Setting now $q_\Lambda=Q_\Lambda/|S_\Lambda|^{1/2}$ the second term in (2.8) gives, for a rotation invariant system in $\nu=3$, a

shape-independent variance

$$\langle q_\Lambda^2 \rangle \underset{\Lambda\to\infty}{\to} -\tfrac{1}{4}\int d\vec{r}\,|\vec{r}|\,S(\vec{r})\equiv K\ , \qquad (2.12)$$

where $\frac{1}{4}|r|$ is the average of $\gamma(\vec{r})$ over rotations in three dimensions; in $\nu=2$, $\frac{1}{4}$ is replaced by $1/\pi$, etc. Martin and Yalcin further showed that (2.2) implies the vanishing of all higher-order cumulants of q_Λ and hence the probability of q_Λ lying between η and $\eta+d\eta$ converges to a Gaussian distribution.

We can now state our main result.

Theorem: Let the space $\mathbf{R}^\nu$, $\nu\geq 2$ be divided into cubes Γ_j of volume L^ν whose centers X_j are located on a simple cubical lattice. Let

$$q_{j,L}=Q_{j,L}/(2\nu L^{\nu-1})^{1/2}$$

be the appropriately normalized charge in Γ_j. Then, under the assumption (2.9), the joint probability density $\mu_L(\vec{\xi})$ of the $q_{j,L}$, $\vec{\xi}=(\xi_j)$, $j\in Z^\nu$, approaches, as $L\to\infty$, a Gaussian measure with covariance

$$C_{j,l}=K\left[\delta_{j,l}-\frac{1}{2\nu}\delta_{j-l,\pm 1}\right]=\frac{K}{2\nu}(-\Delta)_{j,l}\ , \qquad (2.13)$$

where K is given by (2.12), 1 is the unit lattice vector and Δ is the ν-dimensional finite difference Laplacian.

It is seen from (2.13) that $\sum_l C_{j,l}=0$ as it must be, since otherwise taking "blocks" of cubes, Γ, would lead to charge fluctuations which are "normal," i.e., proportional to the volume. Looking directly at $\mu_L(\xi)$ we see that in the limit $L\to\infty$ it is a Gaussian with a lattice Coulomb Hamiltonian

$$\mu_L(\vec{\xi})\sim\exp\left[-\tfrac{1}{2}\sum\xi_i V_{ij}\xi_j\right]\ ,$$
$$V_{ij}=(2\nu/K)(-\Delta)^{-1}_{ij}\ . \qquad (2.14)$$

The proof of the theorem follows from the evaluation of the covariance (2.6) and the observation that, as in the case considered by Martin and Yalcin, (2.9) implies the vanishing of all higher-order cumulants of $q_{j,L}$ as $L\to\infty$. The first part is simple geometry while the second part makes use of the fact that the nth cumulant has a denominator which grows as $L^{(\nu-1)n/2}$; this is *faster* than the numerator obtained from (2.5) for $n>2$. It is here that we require $\nu\geq 2$. In one dimension the charge density itself converges to a random variable which takes on, for $e_\alpha=\pm 1$, integer values.[2]

III. REMARKS

We note the following.

(1) The use of cubes in the theorem is unimportant. The covariance between two scaled domains is always proportional to their common surface area. The physical significance of the theorem then is, as already mentioned before, that it clearly shows the origin of the charge fluctuations in an equilibrium system. Even when the charges are free and the system is classical, they behave as if the system were made up of neutral molecules. This fact, embodied in the existence and form of the correlations between adjacent regions, cannot be deduced from Ref. 2. It is also clear from our analysis that while the theorem refers to "infinite" regions, the results will hold approximately whenever the diameters L of adjoining regions are large compared to the charge-charge correlation length λ (the Debye length) in the system. The deviations from (2.13) can be expected to vanish as some power of (λ/L).

The existence of a nontrivial Gaussian limit for the correlated joint distribution of properly normalized macroscopic variables is the first rigorous result of this kind which we are aware of. The fact that V_{ij} in (2.14) is a Coulomb potential shows that, under a "block spin" renormalization-group-type analysis, a suitably scaled Coulomb Hamiltonian remains invariant. This may also have relevance for other types of systems in that there may exist quantities whose fluctuation behave like (2.14) when suitably scaled.

An interesting question which suggests itself is the nature of charge fluctuation in a heterogenous system; e.g., take a metal block in the laboratory and ask for its total charge fluctuations. While other fluctuations, for example, energy, which are proportional to the volume (the proportionality constant is the specific heat) become independent (for macroscopic size systems) of the nature of the interactions of the system with its surroundings, the charge fluctuations, being themselves proportional to the surface area, will never "decouple" entirely. The analysis is complicated by the long-range nature of charge correlations near a surface[5] and requires further study.

(2) Consider the "moments" of the charge correlation

$$m_j=\int d\vec{r}\,|r|^j G(r)\ ,$$
$$G(r)=S(r)-\left[\sum\rho_\alpha e_\alpha^2\right]\delta(\vec{r})\ . \qquad (3.1)$$

By (2.10) and (2.12), $m_0=-\sum e_\alpha^2\rho_\alpha$, $m_1=-4K$, and by the Stillinger-Lovett relation[6] $m_2=-6m_0\lambda_D^2$, where the Debye length

$$\lambda_D=\left[4\pi\beta\sum e_\alpha^2\rho_\alpha\right]^{-1/2}\ .$$

The negativity of these moments suggests that $G(r)$ is "mostly" negative. In fact, $G(r)<0$ in the Debye-Hückel approximation (valid at high temperatures or low densities) and in the exactly soluble

cases, i.e., symmetric charges in $\nu=1$,[4] and the one-component plasma at $\beta e^2=2$ for $\nu=2$.[5] (As pointed out by Stillinger and Lovett,[6] however, such negativity cannot hold when the charges have hard cores and the density is high.) When $G(\vec{r})\leq 0$, then, clearly $m_1^2 \leq 6m_0^2\lambda_D^2$.

(3) As noted by Martin and Yalcin[2] the charge in a region Λ is equal to the integral of the electric field over the surface of Λ

$$Q_\Lambda = \int_{S_\Lambda} \vec{E}(\vec{r})\cdot d\vec{S} \approx \Delta \sum_{n=1}^{M} E_n \ . \tag{3.2}$$

The right-hand side of (3.2) corresponds to the division of S_Λ into M small elements of size Δ with E_n the projection of the field into the nth element. It is clear that good decay properties of the electric field correlations $\langle \vec{E}(\vec{r}_1)\vec{E}(\vec{r}_1+\vec{r})\rangle$ are sufficient for (and in some sense implied by) the results in Ref. 2 and here. The fluctuations in the electric field, usually referred to as the microfield, are of considerable interest in plasmas[1] and we are currently investigating their distribution.

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