FLUCTUATIONS IN MULTICOMPONENT SYSTEMS*

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I give a brief review of particle and charge fluctuations in multicomponent systems. The long range nature of the Coulomb forces greatly reduce the fluctuations of the net charge Q_Λ in a domain $\Lambda \subset \mathbb{R}^d$. In particular, while the variance of particle numbers in Λ grows like the volume, $\langle Q_\Lambda^2 \rangle$ grows only like the surface area of Λ.

The basic building blocks of matter are charged particles, so the behavior of electric charge fluctuations in space is a problem of some conceptual interest. To be specific I will consider fluctuations in a domain Λ contained inside a very large, spatially homogeneous and overall neutral system in d-dimensions. I shall later take Λ itself to be of macroscopic size but always such that the volume of Λ, denoted by $|\Lambda|$, is very small compared to the size of the whole system. This situation is idealized by taking the system to be infinitely extended from the beginning with Λ some regular domain in $\mathbb{R}^d$.

The microscopic configuration of the full system is specified by $X = \{\mathbf{x}_i\}, i = 1,2,3,\ldots$, $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$, $\mathbf{r}_i \in \mathbb{R}^d$, representing the coordinates of the particles and $\sigma_i \in \{1,\ldots,k\}$ the species of the particle at position $\mathbf{r}_i$. Statistical properties of relevant observables or functions on the phase space, $f(X)$, will be obtained from a translation invariant (extremal) probability measure $\mu(dX)$. For a classical system in equilibrium, at temperature β^{-1} and uniform densities n_γ, $\gamma = 1,\ldots,k$, μ will be an infinite volume Gibbs measure obtained as the thermodynamic limit from some sequence of finite boxes. For an equilibrium quantum system μ will be the infinite volume limit of the diagonal elements of the density matrix $\hat{\mu}$ in the position or X representation.[1] The existence of such a limit measure can be proven under suitable assumptions on the potential; Coulomb interactions require extra care, see [2,3].

To appreciate the "peculiar" behavior of charge fluctuations in equilibrium systems (both classical and quantum), I will first consider fluctuations of particle numbers of the individual species. Let $\rho_\gamma(\mathbf{r};X)$ be the microscopic particle density of species γ at $\mathbf{r} \in \mathbb{R}^d$

$$\rho_\gamma(\mathbf{r};X) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta\sigma_i,\gamma, \qquad \gamma = 1,2,\ldots,k. \tag{1}$$

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The number of particles of species γ in Λ will then be the integral of the random variables $\rho_\gamma(\mathbf{r};X)$ over Λ

$$N_\Lambda^{(\gamma)}(X) = \int_\Lambda \rho_\gamma(\mathbf{r};X)d\mathbf{r}. \tag{2}$$

Their expectations and covariances, with respect to the measure μ, will be given by

$$\langle N_\Lambda^{(\gamma)}\rangle = n_\gamma|\Lambda|, \tag{3}$$

$$B_\Lambda^{(\gamma\delta)} = \langle (N_\Lambda^{(\gamma)} - \langle N_\Lambda^{(\gamma)}\rangle)(N_\Lambda^{(\delta)} - \langle N_\Lambda^{(\delta)}\rangle)\rangle = \int_\Lambda\int_\Lambda d\mathbf{r}_1 d\mathbf{r}_2 \hat{G}_{\gamma\delta}(\mathbf{r}_1 - \mathbf{r}_2) \tag{4}$$

Here $n_\gamma = \langle\rho_\gamma(\mathbf{r};X)\rangle$ is the density of species γ and

$$\hat{G}_{\gamma\alpha}(\mathbf{r}_1 - \mathbf{r}_2) = \langle\rho_\gamma(\mathbf{r}_1;X)\rho_\alpha(\mathbf{r}_2;X)\rangle - n_\gamma n_\alpha = n_{\gamma\alpha}(\mathbf{r}_1 - \mathbf{r}_2) - n_\gamma n_\alpha + n_\gamma\delta(\mathbf{r}_1 - \mathbf{r}_2)\delta_{\gamma\alpha} \tag{5}$$

where $n_{\gamma\alpha}$ is the usual pair density, see [1,4].

Note that in (3) and (4) we have used the fact that μ is translation invariant. This permits also to rewrite (4) in the form

$$B_\Lambda^{\gamma\delta} = |\Lambda|\int_{\mathbb{R}^d} \hat{G}_{\gamma\delta}(\mathbf{r})d\mathbf{r} - \int_{\mathbb{R}^d} \hat{G}_{\gamma\delta}(\mathbf{r})\alpha_\Lambda(\mathbf{r})d\mathbf{r}, \tag{6}$$

where

$$\alpha_\Lambda(\mathbf{r}) = \int_{\mathbb{R}^d} \chi_\Lambda(\mathbf{r}+\mathbf{r}_1)[1 - \chi_\Lambda(\mathbf{r}_1)]d\mathbf{r}_1, \tag{7}$$

In (7) χ_Λ is the characteristic function of the set $\Lambda \subset \mathbb{R}^d$

$$\chi_\Lambda(\mathbf{y}) = \begin{cases} 1, & \mathbf{y}\in\Lambda \\ 0, & \mathbf{y}\notin\Lambda \end{cases}$$

The existence of the separate integrals in (6) requires that $\hat{G}_{\gamma\delta}(\mathbf{r})$ be integrable, e.g., decay faster than $|r|^{-(d+\epsilon)}$ for some $\epsilon > 0$. This is expected to be the case for pure phases away from critical points. It can generally be proven rigorously only at high temperatures and low densities.[1,3]

To find out what happens to $B_\Lambda^{\gamma\delta}$ when Λ is large, formally when $|\Lambda| \to \infty$, we observe[5-7] that when $\Lambda \to \mathbb{R}^d$ in a self-similar way then $\alpha_\Lambda(\mathbf{r})$ will grow like $|\partial\Lambda|$, the $d-1$ dimensional "surface area" of Λ. ($|\partial\Lambda| \equiv 2$ for $d = 1$.) Averaging $|\partial\Lambda|^{-1}\alpha_\Lambda(\mathbf{r})$ over rotations yields,[5]

$$lim_{|\Lambda|\to\infty}|\partial\Lambda|^{-1}\overline{\alpha_\Lambda(\mathbf{r})} = \alpha_d r. \tag{8}$$

with α_d a constant and $r = |\mathbf{r}|$,

$$\alpha_d = \begin{cases} \frac{1}{2}, & d = 1 \\ \pi^{-1}, & d = 2 \\ \frac{1}{4}, & d = 3. \end{cases}$$

Hence, dividing (6) by the volume, the second term on the rhs will vanish when $\Lambda \nearrow \mathbb{R}^d$, to give

$$lim_{|\Lambda|\to\infty}|\Lambda|^{-1}B_\Lambda^{\gamma\delta} = b_{\gamma\delta} = \int_{\mathbb{R}^d} \hat{G}_{\gamma\delta}(\mathbf{r})d\mathbf{r}. \tag{9}$$

For systems in equilibrium the right hand side of (9) can be identified, under general conditions involving equivalence of ensembles, with thermodynamic susceptibilities or compressibilities, that is

$$b_{\gamma\delta} = \frac{\partial n_\gamma}{\partial\lambda_\delta} = \frac{\partial^2\Pi}{\partial\lambda_\gamma\partial\lambda_\delta}, \tag{10}$$

where λ_δ is the chemical potential of species δ and Π is the Gibbs free energy or grand canonical pressure (each multiplied by β).

The covariance matrix per unit volume, $\mathbf{b}$, is expected to be *strictly* positive for systems with short range interactions — it was proven by Ginibre for some model classical systems.[1] This implies in particular that if we look at the covariance of the fluctuations in some linear combination of the $N_\Lambda^{(\gamma)}$, say $T_\Lambda = \sum_\gamma c_\gamma N_\Lambda^{(\gamma)}(X)$ with $\sum|c_\gamma| > 0$ then $\langle(T_\Lambda - \langle T_\Lambda\rangle)^2\rangle/|\Lambda|$ will remain strictly positive as $|\Lambda| \to \infty$.

We note that $N_\Lambda^{(\gamma)}$ can be thought of as a sum of $|\Lambda|$ random variables, each variable representing the number of particles of species γ in a unit cell inside Λ. When these variables are "approximately" independent, as in systems with short range interactions away from critical points, then the variance will grow like $|\Lambda|$ and the right side of (9) will be bounded away from both zero and infinity. The deviation of $N_\Lambda^{(\gamma)}$ from its average, divided by $\sqrt{|\Lambda|}$, will then also converge to a Gaussian random variable. This is 'normal' behavior. At a critical temperature there may be long range positive correlations between the densities in different regions and some of the fluctuations will then grow like $|\Lambda|^\nu$, $\nu > 1$. This represents 'super-normal' fluctuations corresponding to infinite susceptibilities. We do not expect to find, in systems with short range interactions, 'subnormal' fluctuations or zero susceptibilities.

The situation is however very different when there are free charges in the system, i.e., charged particles which can move about without restraints. These interact with the Coulombic potential,

$$\phi(r_i, r_j : \sigma_i, \sigma_j) = e_{\sigma_i} e_{\sigma_j} \phi_d(r_{ij}), \tag{11}$$

$$\phi_d(r) = \begin{cases} -r, & d = 1 \\ -\log r, & d = 2 \\ r^{-1}, & d = 3 \end{cases},$$

which are now included explicitly in the Hamiltonian. In such cases, with the system overall neutral, $\sum e_\gamma n_\gamma = 0$, the variance of $Q_\Lambda = \sum e_\gamma N_\Lambda^\gamma(X)$, the net charge in Λ, is sub-normal, growing more slowly than $|\Lambda|$.[5] More precisely, while $b_{\gamma\delta}$ is strictly positive, for each γ and δ, $|\Lambda|^{-1}\langle Q_\Lambda^2\rangle \to 0$. This is a direct consequence of "complete charge screening"[5,8] corresponding to

$$\int_{\mathbb{R}^d} S(\mathbf{r})d\mathbf{r} = 0 \tag{12}$$

where $S(\mathbf{r})$ is the charge–charge correlation

$$S(\mathbf{r}_1 - \mathbf{r}_2) = \langle q(\mathbf{r}_1; X) q(\mathbf{r}_2; X)\rangle$$

with

$$q(\mathbf{r} : X) = \sum e_\gamma \rho_\gamma(\mathbf{r}; X)$$

What we have instead is that the fluctuations grow only like the surface of Λ

$$lim_{|\Lambda|\to\infty} |\partial\Lambda|^{-1}\langle Q_\Lambda^2\rangle = -\alpha_d \int_{\mathbb{R}^d} rS(r)d\mathbf{r} = \mathcal{K}_d(\beta) \tag{13}$$

with α_d defined in (8). This behavior of $\langle Q_\Lambda^2\rangle$ implies that the determinant of the matrix $\mathbf{b}$ vanishes, which is consistent with the independence of the thermodynamic pressure from certain components of the chemical potentials.[2,3]

In writing (13) we have assumed that the infinite system is isotropic and the integral (13) exists, e.g., that $S(r)$ decays faster than $r^{-(d+1+\epsilon)}$. There are also interesting situations corresponding to $(d+1)$-dimensional charges (points, lines, $d = 2, 1$) confined to $\mathbb{R}^d$ when $S(r) \sim r^{-(d+1)}$ in which case $\langle Q_\Lambda^2\rangle$ grows like $|\partial\Lambda| \log|\Lambda|$. (These have been much studied

for the one component system of 'charges' in $d = 1$, where the statistics of the charges corresponds, after suitable scaling, to the distribution of eigenvalues of the Gaussian Orthogonal, Unitary, or Symplectic Random Matrices.[9])

Eq. (12) is the first of an infinite set of moment conditions or sum rules which can be shown to hold for systems with Coulomb interactions under certain assumptions on the decay of correlations; the latter can be proven to hold for classical systems at high temperatures and low densities and for various exactly solvable special cases, see [5, 6, 8, 10] and references there. The sum rule in (12) is expected to always hold for both classical and quantum systems. Hence, starting with the formula analogous to (7)

$$\langle Q_\Lambda^2 \rangle = |\Lambda| \int S(\mathbf{r}) d\mathbf{r} - \int S(\mathbf{r}) \alpha_\Lambda(\mathbf{r}) d\mathbf{r}. \tag{14}$$

and using (12) and (8) leads directly to (13).

Eq. (13) can also be understood and derived by using Gauss' theorem

$$Q_\Lambda = c_d \int_{\partial\Lambda} \mathbf{E}(\mathbf{s}; X) \cdot d\mathbf{s}, \tag{15}$$

where c_d is the inverse of the area of a unit sphere in $\mathbb{R}^d$, $\mathbf{E}$ is the electric field and $d\mathbf{s}$ is an element of the surface area of $\partial\Lambda$. The integral in (15) (like that in (2)) can be treated as a sum of $|\partial\Lambda|$ random variables. It is these random variables, rather than the $q(\mathbf{r}; X)$ which turn out to be "approximately" independent so that the variance of their sum grows like $|\partial\Lambda|$.[11]

A physical interpretation of the charge fluctuations in Λ is that they behave as if the charges in the system were combined into neutral molecules.[7] To see this consider a two component system with charges $\pm e$ which forms neutral dipoles of length l. Then the charge fluctuation in Λ would be due entirely to the boundary, $\partial\Lambda$, "cutting" some of the dipoles. Assuming further that these dipoles had only short range correlations in position and orientation, we would have $\langle Q_\Lambda^2 \rangle = cne^2 l |\partial\Lambda|$, where $n = n_1 = n_2$ is the density of dipoles and c is a constant of order unity. This is of course a caricature of what happens in real systems where, at high temperatures, or if we are treating a classical system with hard cores, then at any temperature, we do not expect any permanent very tightly bound neutral structures. The length l should then be identified with the Debye correlation length $l_D = [4\pi\beta \sum e_\gamma^2 n_\gamma]^{-\frac{1}{2}}$ On the other hand, for quantum systems at not too high temperatures, the charges form neutral atoms and molecules and l would then be characteristic of atomic sizes determined by quantum mechanics, e.g., 1 Bohr radius for Hydrogen, unless the dominant contribution to the charge fluctuations comes form the small fraction of ionized charges. What (13) shows is that the fluctuations exhibit similar behavior at all temperatures even when we deal with plasmas or molten salts.

The above interpretation of the charge fluctuations is strengthened by considering not just the variance but the whole probability distribution of Q_Λ. It was shown by Martin and Yalcin[5] that in dimension $d \geq 2$, $Q_\Lambda / \sqrt{|\partial\Lambda|}$ approaches, as $\Lambda \to \infty$ a Gaussian random variable with variance $\mathcal{K}_d$ given in (12). This result was extended in [7] to show that the distribution of charges in two disjoint domains, Λ_1 and Λ_2 is again Gaussian with a covariance equal to $-\mathcal{K}_d |\partial\Lambda_1 \cap \partial\Lambda_2|$, i.e., it is proportional to the area of their joint boundary. This is exactly what would be expected from fluctuations due to the surface cutting the dipoles and gives, for two adjacent cubes of volume L^d,

$$\frac{\langle Q_1 Q_2 \rangle}{2dL^{d-1}} \to -\mathcal{K}_d. \tag{16}$$

(In one dimension when $|\partial\Lambda|$ doesn't grow with Λ, the charge fluctuations in a given interval L remains bounded and the probability of finding a charge Q_L in a two species system with charges $\pm e$ can be found exactly.[6])

It would be interesting to know the behavior of the charge fluctuations at the critical point (cp) of the liquid–vapor phase transition in a Coulomb system discussed here by Michael Fisher.[12] While the truncated pair correlation functions corresponding to the particle densities become non-integrable at the cp, it is not clear what happens to the charge correlation function $S(r)$ defined in (12). While there is no apriori reason for $S(r)$ to have power law behavior at the cp, it is surely going to be different in the liquid and vapor phases and hence will have some nonanalytic behavior at the cp. This should carry over to $\mathcal{K}(\beta)$ defined in (13), whose behavior as a function of β is very much an open problem.

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