Coulomb Systems: Thermodynamics, Fluctuations, Large Deviations and Rigidity

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Dedicated to the memory of Janco.
Friend, colleague and teacher
The properties of macroscopic matter are almost entirely determined by the Coulomb interactions between electrons and nuclei, satisfying appropriate quantum statistics. While the real world is 3 dimensional it is useful to consider such systems also in other dimensions and as classical systems. The Coulomb interaction between charges $e_i, e_j$ at positions $r_i, r_j$ in $\mathbb{R}^d$ is, with $r = |r_i - r_j|$, 

$$v_d(r) = \begin{cases} 
-e_i e_j r & d = 1 \\
-e_i e_j \log(r) & d = 2 \\
+e_i e_j r^{2-d} & d \geq 3
\end{cases}$$ (1)
I shall also consider the Jellium or one-component-plasma (OCP) model (introduced by Wigner) in which particles with a positive charge $e$ move in a uniform background of negative charge with density $-\rho e$. The background produces an external potential proportional to $\rho e r_i^2$; $r_i$ the distance from the center of rotational symmetry.
My concern here will be primarily with effects due to the long range nature of the Coulomb potential. When necessary, we can think of the charges as being smeared out in little balls or having hard cores to take care of the singular contact interactions in $d \geq 2$. 
To treat such systems via the Gibbs formalism of statistical mechanics we consider globally neutral systems, \( \sum N_{\alpha,j} e_\alpha = 0 \) in a sequence of regular domains \( V_j \subset \mathbb{R}^d \), such that \( V_j \to \mathbb{R}^d \) as \( j \to \infty \) while the densities \( \frac{N_{\alpha,j}}{|V_j|} \to \rho_\alpha \).

For the OCP \( \frac{N_j}{|V_j|} = \rho \), the background density in an interval, disc, ball.
In each such box $V_j$ the properties of the system will be determined by the canonical measure (density matrix)

$$
\mu_j = \frac{\exp \left[ -\beta H_j \right]}{Z(\beta, \{N_j\}, V_j)}
$$

(2)

where $H_j$ is the Hamiltonian of the system, including both Coulomb and other short range interactions.
We take the “$j \to \infty$ limit” of the sequence,

$$f_j \equiv - (\beta V_j)^{-1} \log Z(\beta, \{N_j\}, V_j) \to f(\beta, \rho) \quad (3)$$

and identify $f(\beta, \rho)$ with the Helmholtz free energy of the macroscopic system. To make this connection with thermodynamics work we have to show that the limit $f_j \to f(\beta, \rho)$ exists and has the right (convexity) properties.
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When there are excess charges $Q_j$ in the $V_j$ they will go to the surface of the $V_j$ and the limit may or may not exist. When it does exist the bulk properties will be the same, in the thermodynamic limit, $j \to \infty$, as they are for neutral systems. I shall not consider that case here.
Correlations

Taking the thermodynamic limit, $j \to \infty$, we expect to obtain also infinite volume measures $\mu$, at least along sub-sequences. I shall assume the existence of such measures and that they have a unique decomposition into extremal measures which are either translation invariant or periodic. I shall further assume that the latter have correlation functions with decent (at least integrable) clustering properties.
Taking the thermodynamic limit, $j \rightarrow \infty$, we expect to obtain also infinite volume measures $\mu$, at least along sub-sequences. I shall assume the existence of such measures and that they have a unique decomposition into extremal measures which are either translation invariant or periodic. I shall further assume that the latter have correlation functions with decent (at least integrable) clustering properties. This can be proven for symmetric charges (Frohlich-Park) and at high temperature or low density. (This will be discussed further later). They can also be explicitly determined in some exactly soluble models.
In $d = 1$, both the OCP model and the two component model are exactly solvable (Lenard, Baxter, Kunz, ... ) and one finds that the OCP (but not the two component) system has a periodic structure i.e. a Wigner crystal with period $\rho^{-1}$. In these systems the correlations decay exponentially.
For the OCP in $d = 2$, one has an exact expression for the correlation functions at one particular temperature $\beta = 2$. These correlations have super good clustering properties (Ginibre, Jancovici) with the truncated pair correlation function

$$\rho_2(r) - \rho^2 = -\rho^2 e^{-\pi \rho r^2}, \quad r = |r_1 - r_2|$$

Higher order truncated correlations also decay like $\sim e^{-\gamma D^2}$, $D$ the distance between groups of particles.
To fluctuate is normal and in most cases fluctuations are themselves normal, by which I mean that in a region $\Lambda$ with volume $|\Lambda|$, they grow like the square root of $|\Lambda|$ as in a Poisson process (or faster as at critical points). There are however many very interesting cases where the fluctuations are subnormal. This includes local charge fluctuations in globally neutral macroscopic systems, the case I shall now discuss.
To get a feeling for what such fluctuations might look like we note that in many situations, such as those involving fluids at low and moderate temperatures, we usually consider macroscopic systems as made up of neutral atoms or molecules interacting via effective short range Lennard-Jones type potentials. In such cases, the fluctuations in the net charge $Q_\Lambda$ in a region $\Lambda$ will be due entirely to the surface of $\Lambda$ cutting these entities in a “random” way. $\langle Q^2_\Lambda \rangle$ may then be expected to be proportional to the surface area of $\Lambda$. 
The question naturally arises as to whether this type of behavior 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?
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To simplify matters I shall consider the classical OCP (with $e = 1$) whose structure is of interest also in other contexts, such as the distribution of eigenvalues of random matrices. I will indicate the difference with multi-component systems when relevant.
Now, while for systems with short range interactions one can prove (Ginibre) that the variance in particle number \( N_\Lambda \) in a region \( \Lambda \subset \mathbb{R}^d \) grows at least as fast as the volume |\( \Lambda \)|

\[
\mathcal{V}_\Lambda = \langle (N_\Lambda - \langle N_\Lambda \rangle)^2 \rangle \geq c|\Lambda|, \quad c > 0,
\]

(5)

this does not hold for Coulomb interactions. Fluctuations in the charge \( Q_\Lambda \), which for the OCP is the same as fluctuations in \( N_\Lambda \) with \( \langle N_\Lambda \rangle = \rho|\Lambda| \), will, as already noted, only grow as the surface area \( \langle Q^2_\Lambda \rangle \sim |\partial \Lambda| \). This is in fact what one can prove, under reasonable assumptions on clustering.
To see how this comes about we note that the variance $\mathcal{V}_\Lambda$ is expressible in terms of the pair correlation function of the infinite system. For a translation invariant system we have,

$$\mathcal{V}_\Lambda = \int_\Lambda \int_\Lambda d\mathbf{r}_1 d\mathbf{r}_2 G(\mathbf{r}_1 - \mathbf{r}_2)$$

$$= |\Lambda| \int_{\mathbb{R}^d} G(\mathbf{r}) d\mathbf{r} - \int_{\mathbb{R}^d} G(\mathbf{r}) \alpha_\Lambda(\mathbf{r}) d\mathbf{r},$$

where

$$G(\mathbf{r}_1 - \mathbf{r}_2) = \left\langle \sum_{i,j} \delta(\mathbf{r}_1 - \mathbf{x}_i) \delta(\mathbf{r}_2 - \mathbf{x}_j) \right\rangle - \rho^2,$$

$$= \rho \delta(\mathbf{r}_1 - \mathbf{r}_2) + \rho_2 (\mathbf{r}_1 - \mathbf{r}_2) - \rho^2,$$

$$\alpha_\Lambda(\mathbf{r}) = \int \chi_\Lambda(\mathbf{r} + \mathbf{r}_1) [1 - \chi_\Lambda(\mathbf{r}_1)] d\mathbf{r}_1$$

$$\chi_\Lambda(\mathbf{y}) = \begin{cases} 1 & \mathbf{y} \in \Lambda \\ 0 & \mathbf{y} \notin \Lambda \end{cases}$$
This is modified in a simple way for a periodic system. For charge fluctuations in multi-charge systems $G(r)$ corresponds to the charge-charge correlations.
When $\Lambda \uparrow \mathbb{R}^d$ in a self similar way $\alpha_\Lambda$ will grow like the surface area $|\partial \Lambda| \sim |\Lambda|^{(d-1)/d}$ with $|\partial \Lambda| = 2$ for $d = 1$. Averaging $\alpha_\Lambda(r)/|\partial \Lambda|$ over rotations we obtain

$$\lim_{|\Lambda| \to \infty} \frac{\alpha_\Lambda(r)}{|\partial \Lambda|} = \alpha_d |r|,$$

where

$$\alpha_d = \begin{cases} 
1/2 & d = 1 \\
1/\pi & d = 2 \\
\ldots & 
\end{cases}$$
In Coulomb systems

\[
\lim_{|\Lambda|} \frac{1}{V_\Lambda} = \int_{\mathbb{R}^d} G(r) dr = 0, \tag{6}
\]

due to Debye screening. This is known as the “first sum rule”. Systems satisfying (6) are also known as superhomogeneous.
In Coulomb systems

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due to Debye screening. This is known as the “first sum rule”. Systems satisfying (6) are also known as superhomogeneous. We then have, for systems satisfying (6),

\[ \frac{\nu_\Lambda}{|\partial \Lambda|} \to -\alpha_d \int_0^\infty r^d G(r)dr, \]  

(7)
where we have sphericalized \( G \). Equation (7) is called the Stillinger-Lovett relation. When (6) holds but (7) is infinite the variance will grow faster than the surface area but slower than the volume.
Question Can the variance grow slower than $|\partial \Lambda|$. The answer by J. Beck is “no” if the distribution is rotational invariant (or $\Lambda$ is a sphere). It is still an open question how small this variance can be and whether it attains its minimum value for a regular lattice.
Going beyond the variance, we also have that for Coulomb systems in $d \geq 2$ the charge fluctuation satisfy a central limit theorem: deviation from the average divided by the square root of the variance gives

$$\frac{(N_\Lambda - \langle N_\Lambda \rangle)}{\sqrt{\mathcal{V}_\Lambda}} \rightarrow \xi,$$

a standard Gaussian random variable. This was proven by Martin-Yalcin.
In fact the following is true: let $\mathbb{R}^2$ (generally $\mathbb{R}^d$) be divided into squares $\Gamma_j$ of area $L^2$ whose centers are located $L\mathbb{Z}^2$. Setting

$$\xi_j = Q(\Gamma_j)/\sigma(\Gamma_j), \quad \sigma(\Gamma_j) = KL^{1/2}$$

we find that the joint distribution of the $\{\xi_j\}$ approaches as $L \to \infty$ a Gaussian measure with covariance

$$C_{j,k} = \left[ \delta_{j,k} - \frac{1}{4} \sum_e \delta_{j-k,e} \right] = \frac{1}{4} [\Delta]_{j,k}, \quad (\ast)$$

where $e$ is the unit lattice vector and $\Delta$ is the discrete Laplacian.
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$$C_{j,k} = \left[ \delta_{j,k} - \frac{1}{4} \sum_e \delta_{j-k,e} \right] = \frac{1}{4} [ -\Delta ]_{j,k}, \quad (*)$$

where $e$ is the unit lattice vector and $\Delta$ is the discrete Laplacian. This means that the charge fluctuations in $\Gamma_{j,L}$ are compensated by the opposite charges in neighboring (cubes). This is exactly what one would expect when the charges are bound together in neutral molecules.

The same holds for $d > 2$. In $d = 1$, $|\partial\Lambda| = 2$ and as shown by M-Y the charge (particle in OCP) fluctuations are bounded and have a well-defined non Gaussian distribution as $|\Lambda| \to \infty$. 
Large Deviations

As might be expected from the reduction of fluctuations, the probability of large deviations from charge neutrality, for multi-component or OCP system, will be smaller for Coulomb systems than those for systems with short range interactions. This problem was studied by Jancovici, L., and Manificat (JLM) in (1993), using electrostatic type arguments. They found that this is indeed the case in all dimensions and all $\beta$. 
For the 2d OCP with density $\rho = 1$, the probability of having $n(R)$ particles in a disc of radius $R$, corresponding to a charge $|Q| = |n(R) - \pi R^2|$, behaves as

$$\text{Prob} \left\{ |n(R) - \pi R^2| > R^\alpha \right\} \sim \exp \left[ -c_\alpha R^{\phi(\alpha)} \right],$$

with

$$\phi(\alpha) = \begin{cases} 
2\alpha - 1 & , \quad \frac{1}{2} < \alpha \leq 1 \\
3\alpha - 2 & , \quad 1 \leq \alpha \leq 2 \\
2\alpha & , \quad \alpha \geq 2 
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This probability is much smaller than the large deviations for systems with short range interactions where, e.g. for $\alpha = 2$ one would get $e^{-cR^2}$ instead of $e^{-cR^4}$. As usual the symbol $\sim$ means that taking the logarithm of both sides and dividing by $R^{\phi(\alpha)}$ we get a finite limit when $R \to \infty$. 
Interestingly the behavior of the probability for $|Q| < R$, $\frac{1}{2} \leq \alpha < 1$ is of the form

$$P_r(Q) \sim \exp \left[ -\frac{Q^2}{2\sigma R} \right]$$

(8)

where $\sigma = \lim_{R \to \infty} \frac{\langle Q^2 \rangle}{R} = -\int_{0}^{\infty} r^2 G(r) \, dr$. 
These “macroscopic” results can be checked and confirmed at $\beta = 2$ where we have explicit solutions for the correlation functions. We can get then additional information such as the charge density outside the disc of radius $R$ conditioned on there being no particles inside. In particular the density at $r = R^+$ is given by $\rho(R^+) \sim \frac{1}{2} \pi \rho^2 R$. 
It turns out that the large deviation function we obtained is of the same form, in its dependence on $\alpha$ as that of a point process generated by the zeroes of a Gaussian Entire Function, $f = \sum \frac{\xi_k}{\sqrt{k!}} z^k$, with the $\xi_k$ i.i.d standard complex Gaussians (Nazonov, Sodin, Volberg).
The Jancovici–Lebowitz–Manificat Law for Large Fluctuations of Random Complex Zeroes

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Abstract: Consider a Gaussian Entire Function

\[ f(z) = \sum_{k=0}^{\infty} \frac{\zeta_k}{\sqrt{k!}} z^k, \]

where \( \zeta_0, \zeta_1, \ldots \) are Gaussian i.i.d. complex random variables. The zero set of this function is distribution invariant with respect to the isometries of the complex plane. Let \( n(R) \) be the number of zeroes of \( f \) in the disk of radius \( R \). It is easy to see that \( \mathbb{E} n(R) = R^2 \), and it is known that the variance of \( n(R) \) grows linearly with \( R \) (Forrester and Honner). We prove that, for every \( \alpha > 1/2 \), the tail probability \( \mathbb{P} \left\{ |n(R) - R^2| > R^\alpha \right\} \) behaves as \( \exp \left[ -R^{\varphi(\alpha)} \right] \) with some explicit piecewise linear function \( \varphi(\alpha) \). For some special values of the parameter \( \alpha \), this law was found earlier by Sodin and Tsirelson, and by Krishnapur.

In the context of charge fluctuations of a one-component Coulomb system of particles of one sign embedded into a uniform background of another sign, a similar law was discovered some time ago by Jancovici, Lebowitz and Manificat.
For \( d = 1 \), we have, as already noted, the probability of having the charge going to infinity in any interval of length \( L \) goes to zero independent of how \( L \to \infty \), i.e, the \( \phi(\alpha) \) is infinite for \( \alpha > 0 \). (It may be interesting to note here that this fact is not a consequence of having bounded variance in any interval as can be shown by a counter-example (Goldstein, Lebowitz, Speer).) The situation in \( d = 3 \) is similar to that in \( d = 2 \) although the details differ.
So far we have discussed fluctuations and large deviations of the charge in a region $\Lambda$ without saying anything about the configuration of particles/charges outside $\Lambda$, i.e. in $\Lambda^c = \mathbb{R}^d \setminus \Lambda$. We ask now: what can we say about the distribution of points (charge) inside $\Lambda$ given the configuration in $\Lambda^c$, i.e, we want the conditional probability $\mu_\Lambda (dX_\Lambda | X_{\Lambda^c})$ of a configuration in $dX_\Lambda$ given $X_{\Lambda^c}$. 

Number Rigidity
For equilibrium Gibbs measures of systems with short range interactions the answer to this is given by the DLR (Dobrushin, Lanford, Ruelle) equations.

\[
\mu_\Lambda (x_1, \ldots x_N|X^c_\Lambda) = \frac{\exp \left[ -\beta U(X_\Lambda|X^c_\Lambda) \right]}{\int e^{-\beta U(X_\Lambda|X^c_\Lambda)} dX_\Lambda}
\]

where \( U(X_\Lambda|X^c_\Lambda) \) is the potential energy of a configuration in \( \Lambda \) given the configuration in \( \Lambda^c = \mathbb{R}^d \setminus \Lambda \).
This equation involving $U(X_\Lambda|X_{\Lambda^c})$ holds for all infinite volume Gibbs measures whether these are obtained as limits of finite volume micro-canonical, canonical or grand-canonical ensembles (with the appropriate $\beta$ and $z$ for the first two). It does not however work for systems with long range Coulomb interactions, where $U(X_\Lambda|X_{\Lambda^c})$ may be infinite for many configurations.
Aizenman and Martin (AM 1981), using earlier work by Lenard, gave a characterization of these measures in $d = 1$ via the electric field $E(x)$.

Using this description AM proved that the charge in an interval $[a, b] = \Lambda$, which corresponds for the OCP to the number of particles in $\Lambda$, is uniquely specified by the configuration $X_{\Lambda^c}$ for all typical configurations with respect to infinite volume measure $\mu$. (The set of atypical configurations has measure zero).
This “number rigidity” property, i.e., $N_\Lambda = f(X_{\Lambda^c})$, was recently proven by Ghosh and Peres (GP2012) to hold for the OCP in $d = 2$, at $\beta = 2$. It was also proven by Ghosh (G2012) to hold at $\beta = 2$ for the $d = 1$ Dyson log gas, i.e., for charged particles in one dimension interacting via a $2d$ logarithmic Coulomb potential in a uniform background. The variance of particle number in an interval $[a, b]$ in this system grows like $\log(b - a)$ which is slower than $|\Lambda|$ but greater than $|\partial \Lambda|$.
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GP also showed that while $N_\Lambda$ is fixed by $X_{\Lambda^c}$ the distribution of points inside $\Lambda$ is not rigid: it is in fact absolutely continuous with respect to the Lebesgue measure. The same is true for the 1d Coulomb system studied by MA.
The 2d and 1d cases studied by GP correspond (as is well known) respectively to the distribution of the bulk eigenvalues of the random matrices chosen from the Ginibre ensemble and of the Gaussian Unitary Ensemble (GUE or GCE). In the Ginibre ensemble each of the entries in a $N \times N$ matrix are iid complex Gaussian random variables while the GUE consists of random Gaussian Hermitian matrices whose eigenvalues are real. The infinite volume measure $\mu$ is obtained by letting $N \to \infty$ and scaling to make the density $\rho$ uniform.
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In recent work with Aizenman and Ghosh we were indeed able to prove rigidity for systems (point processes) $d = 1$ and 2 in which $\frac{V}{|\Lambda|} \to 0$, i.e., the variance in the particle number (or charge) grows slower than the volume. These are called superhomogeneous processes. We require in addition that the truncated pair correlation function decays at least as fast as $r^{-2}$ in $d = 1$ and as $r^{-(4+\epsilon)}$ in $d = 2$. This includes all the cases mentioned before as well as the 1$d$ log gas for $\beta \leq 2$, the 2$d$ two component Coulomb system in $d = 2$ for $\beta \leq 2$ using results of Samai, and the 2$d$ OCP for small $\beta$. I believe in fact that this is the case for all $\beta$ in $d = 1$ and 2 but should not hold in $d \geq 3$. 