UNIVERSAL CRITICAL-LIKE FEATURES OF COULOMB SYSTEMS

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ABSTRACT

From the laws of macroscopic electrostatics of conductors, one can deduce universal properties for the thermal fluctuations in a conducting classical Coulomb system at equilibrium; the correlations of the electric potential are long-ranged, like in a critical system. There are finite-size corrections to the free energy, which are universal, like in a critical system. The universal features can be checked on solvable models.

1. Introduction

A Coulomb system is a system of particles interacting through the Coulomb potential, plus perhaps some short-range interaction; there may also be a continuous charged background. This review is about some universal (i.e. independent of the microscopic detail) equilibrium properties of classical (i.e. non-quantum) Coulomb systems. This universality is closely related to the universality of the macroscopic electrostatics of conductors. Therefore, the systems under consideration are assumed to be conductors; this excludes for instance a two-dimensional Coulomb gas below the Kosterlitz-Thouless transition temperature.

The universal properties of Coulomb systems closely resemble, at any temperature (provided the system is a conductor), the universal properties of a system with short-range forces, at its critical temperature. At first sight, this might be surprising: an essential feature of critical systems is the existence of long-range correlations, while conducting Coulomb systems are known to have short-range particle-particle correlations (of the Debye-Hückel type for instance) dominated by the screening effect. However, in a Coulomb system, the correlations of the electric potential or electric field are long-ranged, and therefore critical-like (this is not

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always appreciated, although this has been established for some time). Section 2 describes this critical-like universality of the correlations in Coulomb systems.

It is known that there are universal finite-size corrections to the free energy of critical systems, especially in two dimensions. Similar universal corrections occur in Coulomb systems. They are discussed in Section 3.

An extreme case of finite-size effects is provided by Coulomb systems of “restricted dimension”, for instance particles interacting through the usual three-dimensional Coulomb potential $1/r$ but confined in a two-dimensional manifold such as a plane. The universal properties of some systems of this type are discussed in Section 4.

Exactly solvable models of Coulomb systems are available in two dimensions. They can be used for checking the generic universal features.

2. Universal Correlations

2.1. Inside a Coulomb System

Inside a conducting Coulomb system of macroscopic size, the charge correlations are short-ranged; for instance, within the Debye-Hückel approximation, the charge correlation function is proportional to $-\exp(-r/\lambda)/r$ and has a characteristic range $\lambda$, the Debye length. However, the electric potential correlation function is long-ranged, with an algebraic decay; for distances $|r - r'|$ large compared to the microscopic scale,

$$
\beta < \phi(r) \phi(r') >^T = \frac{1}{|r - r'|},
$$  

(1)

where $\phi(r)$ is the microscopic electric potential at point $r$, $\beta$ the inverse temperature, and $< \cdots >^T$ denotes a truncated statistical average. The power law decay in Eq. 1 is reminiscent of a correlation function at a critical point, and this function is universal in that sense that it is independent of the microscopic detail of the Coulomb system (except for microscopic distances, just as in a critical system).

From Eq. 1, one obtains the electric field correlation function

$$
\beta < E_x(r)E_x(r') > = \frac{1}{|r - r'|},
$$  

(2)

also critical-like and universal.
Eq. 1 can be proven as a consequence of the screening assumption, as follows. Let us put an infinitesimal external point charge $q$ at $r$. The corresponding perturbation Hamiltonian is $\delta H = q\phi(r')$. By linear response theory, the average electric potential at $r'$ is changed by

$$\delta < \phi(r') > = -\beta < \phi(r') > T = -\beta q < \phi(r') > \phi(r) > T.$$  \hspace{1cm} (3)

On the other hand, the screening assumption says that $q$ surrounds itself with a microscopic polarization cloud of charge $-q$; since $\phi$ denotes the potential created by the charges of the system (not the external charge), for $|r-r'|$ large compared to the microscopic scale,

$$\delta < \phi(r') > = -\frac{q}{|r-r'|}.$$  \hspace{1cm} (4)

Together, Eqs. 3 and 4 lead to Eq. 1.

A symbolic form of the charge correlation function can be obtained from Eq. 1. Since the electric potential $\phi(r)$ and the charge density $\rho(r)$ are related by the Poisson equation $\Delta \phi(r) = -4\pi \rho(r)$, one obtains for the charge correlation function $S(|r-r'|)

$$\beta S(r-r') := \beta < \rho(r) \rho(r') > T = \frac{\beta}{(4\pi)^2} \Delta \Delta' < \phi(r) \phi(r') > T = -\frac{1}{4\pi} \Delta \delta(r-r').$$  \hspace{1cm} (5)

In Eq. 5, the distribution $\Delta \delta(r-r')$ must of course be understood as spread on some microscopic scale. The detail of this spreading is disregarded. However, Eq. 5 is enough for reproducing the Stillinger-Lovett sum rule

$$\beta \int S(r) r^2 d^3r = -\frac{3}{2\pi}.$$  \hspace{1cm} (6)

There is a universality in the charge correlation, as expressed by Eqs. 5 or 6, but the critical-like aspect is hidden.

2.2. Outside a Coulomb System

If the Coulomb system is confined by some boundary, Eqs. 1 and 2 are still valid when $r$ is inside and $r'$ outside the system (except perhaps for an additional irrelevant constant in Eq. 1).

When both $r$ and $r'$ are outside the Coulomb system, the potential correlation function is determined by the electrostatics of conductors: it depends on the shape
of the Coulomb system, but it is otherwise universal, i.e. independent of the microscopic detail. For instance, consider a Coulomb system occupying the half-space $z < 0$, i.e. bounded by the plane wall $z = 0$. Then for both $r$ and $r'$ in the half-space $z > 0$,

$$\beta < \phi(r) \phi(r') >^T = \frac{1}{|r^* - r'|} , $$  

(7)

where $r^* = (x, y, -z)$ is the image of $r = (x, y, z)$.

The proof of Eq. 7 is similar to the proof of Eq. 1. One puts an external point charge $q$ at $r$, and linear response theory again gives Eq. 3. From elementary electrostatics, the total potential shift at $r'$ is $(q/|r - r'|) - (q/|r^* - r'|)$. The part of it created by the charges of the system (not the external charge $q$) is

$$\delta < \phi(r') > = \frac{-q}{|r^* - r'|} .$$  

(8)

Eqs. 3 and 8 lead to Eq. 7.

By derivation of Eq. 7, one obtains the electric field correlation function.

2.3. Universal Surface Charge Correlations

Near the surface of a Coulomb system, one can define a surface charge density $\sigma$ as the volume charge density integrated on some microscopic depth. The correlation function of $\sigma$ is universal (for non-microscopic distances), depending only on the shape of the surface. For instance, for the plane wall case discussed in the previous Section,

$$\beta < \sigma(r) \sigma(r') >^T = -\frac{1}{8\pi^2 |r - r'|^5} .$$  

(9)

This correlation function is long-ranged.10

For proving Eq. 9, one uses the relation $\sigma(r) = (4\pi)^{-1}\delta E_{z}(r)$, where $\delta E_{z}(r) = E_{z}^{+}(r) - E_{z}^{-}(r)$ is the discontinuity of the electric field $z$ component at $r = (x, y, 0)$, and the electric field correlation functions obtained from Eqs. 1 and 7.

Other surface shapes can be dealt with by similar methods.8

2.4. Solvable Models

The two-dimensional analogs of the above correlation functions can be checked on solvable models.
3. Universal Finite-size Corrections to the Free Energy¹¹–¹³

3.1. Two-dimensional Critical Systems

It has been known for some time that there are universal finite-size corrections to the free energy of two-dimensional critical systems.

For a critical system in a strip of width \(W\), with periodic boundary conditions, the free energy \(F\) per unit length has the large-\(W\) expansion³,⁴

\[
\beta F = AW - \frac{\pi c}{6W} + \cdots. \quad (10)
\]

The correction \(-\pi c/6W\) is universal, depending only on the conformal anomaly number (central charge) of the theory. For a strip with fixed or free boundary conditions,

\[
\beta F = AW + B - \frac{\pi c}{24W} + \cdots. \quad (11)
\]

A special simple case is the massless Gaussian model, with a partition function defined by the functional integral

\[
Z_G = \int \mathcal{D}\phi \ e^{-\frac{1}{\kappa} \int (\nabla \phi)^2 + \phi^2}, \quad (12)
\]

for which \(c = 1\); for that Gaussian model, Eqs. 10 and 11 can be easily generalized to \(d\) dimensions¹¹.

Another interesting geometry is a critical system on a finite two-dimensional manifold. The Euler number of the manifold is \(\chi = 2 - 2h - b\), where \(h\) is the number of handles and \(b\) the number of boundaries. In the case there are boundaries \((b \neq 0)\), the boundary conditions are assumed to be either fixed or free. Then, in terms of some characteristic size \(L\) of the manifold, the free energy \(F\) has the large-\(L\) expansion

\[
\beta F = A L^2 + B L - \frac{c \chi}{6} \log L + \cdots \quad (13)
\]

where the last term \(-\frac{c \chi}{6} \log L\) is universal.

3.2. Two-dimensional Coulomb Solvable Models

By explicit calculations performed on the two-dimensional solvable models of Coulomb systems, finite-size corrections very similar to the ones occurring in
Eqs. 10, 11, 13 were found. In a strip of width $W$, with periodic boundary conditions, the free energy $F$ per unit length was found to have the large-$W$ expansion\textsuperscript{12}

$$\beta F = AW + \frac{\pi}{6W} + \cdots .$$  \hspace{1cm} (14)

For Dirichlet boundary conditions for the electric potential\textsuperscript{11} (i.e. the edges of the strip are ideal conductors at zero potential),

$$\beta F = AW + B + \frac{\pi}{24W} .$$  \hspace{1cm} (15)

Thus, Eqs. 14 and 15 for Coulomb systems appear to be identical to Eqs. 10 and 11 for the massless Gaussian model ($c = 1$), except for a change in sign. The nature of the boundary conditions is essential, because, for plain hard walls (the charged particles are confined in the strip, but the electric potential "leaks out"), there is no universal $1/W$ term in the expansion of $\beta F$; instead, the correction is $O(e^{-W})$.

Solvable models of Coulomb systems were also considered on some finite two-dimensional manifolds. On a sphere ($\chi = 2$) of radius $R$, one finds

$$\beta F = AR^2 + \frac{1}{3} \log R + \cdots .$$  \hspace{1cm} (16)

On a disk ($\chi = 1$) of radius $R$, one finds

$$\beta F = AR^2 + BR + \frac{1}{6} \log R + \cdots ,$$  \hspace{1cm} (17)

in both cases of plain hard walls or ideal conductor walls. On an annulus ($\chi = 0$), one finds no log term. Thus, Eqs. 16 and 17 for Coulomb systems also appear to be identical to the general Eq. 13 for the massless Gaussian model ($c = 1$), except again for a change in sign.

Actually, Eqs. 14-17 were found for models solved in the canonical ensemble. When the grand canonical ensemble had to be used, it was the grand potential $\Omega$ rather than the free energy $F$ which was found to have these expansions.

3.3. From Coulomb Systems to the Gaussian Model

Why do Coulomb systems exhibit a free energy finite-size correction which is the same one as for the Gaussian model, except for its sign? A heuristic general
explanation can be given if one assumes that the universal features of Coulomb systems are correctly described by taking for the partition function or grand partition function a functional integral in terms of a charge density field $\rho(r)$:

$$Z_C = \int D\rho e^{-\frac{1}{2} \int \rho(r') \int \rho(r') \frac{\nabla}{r-r'} \rho(r') \, d^3r' \, d^3r}.$$  \hspace{1cm} (18)

(this can be done for an arbitrary dimension; here we use the three-dimensional notation). This expression (18) disregards the microscopic detail. A “change of variable” from the charge density $\rho(r)$ to the electric potential $\phi(r)$ can be made through the Poisson equation $\Delta \phi(r) = -4\pi \rho(r)$, giving

$$Z_C = \int D\phi \frac{D\rho}{D\phi} e^{-\frac{1}{2} \int (\nabla \phi)^2 \, d^3r}.$$  \hspace{1cm} (19)

The Jacobian in (19) is the constant

$$\frac{D\rho}{D\phi} = \text{det}(-\Delta)$$  \hspace{1cm} (20)

which multiplies the Gaussian partition function

$$Z_G = \int D\phi \, e^{-\frac{1}{2} \int (\nabla \phi)^2 \, d^3r} = [\text{det}(-\Delta)]^{-1/2}.$$  \hspace{1cm} (21)

Using Eqs. 20 and 21 in Eq. 19 gives

$$Z_C = \frac{1}{Z_G},$$  \hspace{1cm} (22)

which explains that the universal part of the free energy is the same for the Coulomb system and the Gaussian model, except for the sign:

$$\log Z_C = -\log Z_G.$$  \hspace{1cm} (23)

However, this derivation of Eq. 23 holds only for a Coulomb system with ideal conductor boundary conditions, identical to the fixed boundary conditions for the Gaussian model.
3.4. Direct Approach to Coulomb Systems

A more direct way of establishing the universal finite-size corrections to the free energy of Coulomb systems is to use screening sum rules obeyed by the correlation functions. This method works for a d-dimensional strip with periodic or ideal conductor boundary conditions\textsuperscript{11,12}.

For establishing that $\beta F$ has a $(1/6) \log R$ term for a Coulomb system on a disk with plain hard wall boundary conditions\textsuperscript{13}, we used the stress tensor\textsuperscript{9} to show that $\partial (\beta F)/\partial R = 1/6R$. The difference in sign with the similar term in the Gaussian model was explained by noting that it is the electric potential outside a Coulomb system which approximately obeys Dirichlet boundary conditions on the system boundary (which acts as an ideal conductor on a macroscopic scale); thus, the curvature radius $R$ appears with a different sign when seen from outside rather than from inside. However, a simpler proof based on screening is still to be found.

4. Universality for Coulomb Systems of Restricted Dimension\textsuperscript{14}

Only one example is given here. Consider a two-dimensional system of particles, in the plane $z = W$, interacting through the usual three-dimensional Coulomb potential $1/|r - r'|$, while the plane $z = 0$ is an ideal conductor on which the electric potential is constrained to vanish. Thus, the effective interaction between the particles, including the particle-image interaction, is

$$v(r, r') = \frac{1}{|r - r'|} - \frac{1}{|r^* - r'|}$$ \hspace{1cm} (24)

where $r^*$ is the image of $r$. Such a system has universal charge correlations and a universal $W$-dependence of its free energy.

Let $\sigma(r)$ be the microscopic surface charge density at $r$ ($r$ being in the plane $z = W$). The charge correlation function has the universal form

$$\beta < \sigma(r) \sigma(r') >^T = -\frac{1}{4\pi^2} \sum_{n=0}^{\infty} \frac{(r - r')^2 - 2(nW)^2}{((r - r')^2 + (2nW)^2)^{3/2}}$$

$$\sim -\frac{1}{4\pi^2 |r - r'|^3} \quad \text{if } |r - r'| \ll W$$

$$\sim -\frac{1}{8\pi^2 |r - r'|^3} \quad \text{if } |r - r'| \gg W \quad .$$ \hspace{1cm} (25)
For proving Eq. 25, one uses linear response theory and macroscopic electrostatics for deriving the electric field correlation function, and one relates $< \sigma(r) \sigma(r') >$ to the discontinuities of $< E_x(r) E_x(r') >$ on the conducting plane $z = W$.

The free energy per unit area has a universal finite-$W$ correction:

$$\beta F(W) = \beta F(\infty) - \frac{\zeta(3)}{16\pi W^2}$$  (26)

where $\zeta(3) = 1.202 \ldots$ is a value of the Riemann zeta function. For proving Eq. 25, one uses the electric field correlation function for computing the Maxwell stress tensor which gives $\partial F/\partial W$.

Eqs. 25 and 26 have two-dimensional analogs which can be checked on a solvable model.

5. Conclusion

In the sense described above, conducting classical Coulomb systems are critical-like at any temperature. This similarity with critical systems should not be confused with the possible occurrence of a "true" liquid-vapor critical point in the phase diagram of a Coulomb fluid; this true criticality is another story, about which there is presently a very interesting intense activity.

6. References

15. Y. Levin and M. E. Fisher, to be published, and references quoted there.

The free energy of exciton-exciton Coulombic interactions and vortex interactions is given by

\[ W(\alpha_0) = \frac{1}{2} \alpha_0^2 + \alpha_0 \ln(1 + \alpha_0) \]

for a one-dimensional strip with periodic or ideal Dirichlet boundary conditions. \[ W(\alpha_0) = \frac{1}{2} \alpha_0^2 + \alpha_0 \ln(1 + \alpha_0) \]

It was established that \( W \) has a \( (1/6) \log R \) term for a Coulomb system on a disk with a fixed number of points, a \( 1/3 \) term for a charged medium, and an \( (1/6) \log R \) term for a charged medium with fixed density. The results were extended to \( n \) dimensions using a computer simulation. The insulator model was explained by noting that it is the electric potential at the interior, which is a physical quantity, that determines the effective potential at the surface, which acts as an ideal conductor on a macroscopic scale. This effective potential arises from a difference in sign when viewed from outside rather than from inside. However, a simpler proof based on screening is still to be found.