Course on "Statistical Physics of Fields In and Out of Equilibrium"
Spring Semester (2016)
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Homework #5: Hubbard-Stratonovich Transformation (II): Coulomb fluids Due: April 19, 2016

1: *Inhomogeneous Coulomb fluids.* The general form of the field "action" (or Hamiltonian) for an inhomogeneous (confined), classical Coulomb fluid, consisting of point-like mobile "counterions" of charge valency q in equilibrium with a thermal bath at temperature T, can be written as

$$S[\varphi] = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\, \varphi(\mathbf{r})G^{-1}(\mathbf{r},\mathbf{r}')\varphi(\mathbf{r}') + i\int d\mathbf{r}\,\rho_0(\mathbf{r})\varphi(\mathbf{r}) - \tilde{\lambda}k_BT\int d\mathbf{r}\,\Omega(\mathbf{r})e^{-i\beta q e_0\varphi(\mathbf{r})}, \tag{1}$$

where $\varphi(\mathbf{r})$ is a fluctuating potential field, $\beta = 1/(k_BT)$, e_0 is the elementary charge, $\rho_0(\mathbf{r})$ is the fixed charge distribution in the system (or on the confining boundaries due to the presence of macroscopic and/or mesoscopic objects) that interact with the counterions, and $G(\mathbf{r},\mathbf{r}')$ is the general "Coulomb" kernel satisfying

$$-\varepsilon_0\nabla\cdot[\varepsilon(\mathbf{r})\nabla G(\mathbf{r},\mathbf{r}')] = \delta(\mathbf{r}-\mathbf{r}') \tag{2}$$

in a three-dimensional system with an arbitrary dielectric-constant profile $\varepsilon(\mathbf{r})$ and with ε_0 being the permittivity of vacuum. Here, $\Omega(\mathbf{r})$ is the "blip" function identifying the spatial region accessible to counterions (see Fig. 1).

The grand-canonical partition function of this system can be written as

$$\mathcal{Z}_{\tilde{\lambda}} = e^{-\frac{1}{2}\mathrm{tr}\ln G(\mathbf{r},\mathbf{r}')}\int \mathcal{D}\varphi\, e^{-\beta S[\varphi]}, \tag{3}$$

where $\tilde{\lambda}$ is the rescaled fugacity. This problem generalizes the case of a dielectrically homogeneous Coulomb fluid, with $\varepsilon(\mathbf{r}) = \varepsilon$ and $G(\mathbf{r},\mathbf{r}') = G_0(\mathbf{r},\mathbf{r}') \equiv 1/(4\pi\varepsilon\varepsilon_0|\mathbf{r}-\mathbf{r}'|)$ that was discussed in class, by accounting for the dielectric polarization (or the so-called "image-charge") effects generated by the dielectric contrast between the macroscopic bodies and the fluid medium, where mobile ions are present.

(i) Derive the above expression for the partition function of a grand-canonical system of counterions in equilibrium with a bulk reservoir of particles with fugacity λ by starting from the Hamiltonian of a canonical system comprising N counterions, i.e.,

$$\mathcal{H}_N = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\; [\hat{\rho}_c(\mathbf{r}) + \rho_0(\mathbf{r})]\, G(\mathbf{r},\mathbf{r}')\, [\hat{\rho}_c(\mathbf{r}') + \rho_0(\mathbf{r}')] - \frac{q^2e_0^2}{2}NG_0(\mathbf{r},\mathbf{r}'), \tag{4}$$

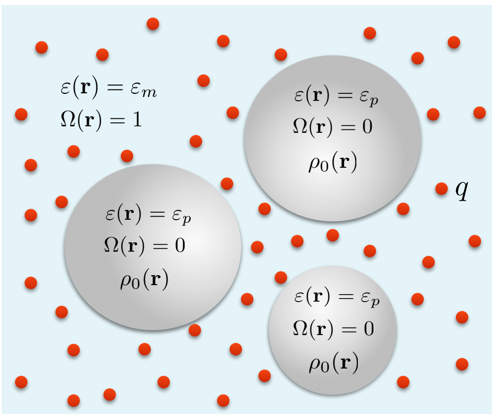

Figure 1. Schematic view of an inhomogeneous Coulomb fluid consisting of impenetrable, fixed, charged objects (such as charged macromolecules) carrying the charge distribution $\rho_0(\mathbf{r})$ and their neutralizing, point-like, mobile counterions of charge valency q. The fixed objects can have a different dielectric constant (e.g., a uniform dielectric constant of ε_p) as compared with the fluid medium (e.g., a solvent such as water with $\varepsilon_m \simeq 80$ at room temperature). In regions accessible to counterions, we have $\Omega(\mathbf{r}) = 1$, and elsewhere $\Omega(\mathbf{r}) = 0$. See Problem 1.

where $\hat{\rho}_c(\mathbf{r}) = \sum_{i=1}^{N} qe_0\delta(\mathbf{r}-\mathbf{r}_i)$ is the counterion *charge density* operator and, in the last term of the above Hamiltonian, we have subtracted the formation energy of individual counterions (*why?*). Note also that λ is the bare fugacity, which is a given parameter, while the field-theoretic "action" contains a rescaled fugacity, $\tilde{\lambda}$. How is the latter parameter related to the former one?

(ii) Show that the *density profile* of counterions, which builds up in response to their interactions with the fixed charge distribution $\rho_0(\mathbf{r})$ and the polarization charges on the dielectric boundaries, is given by:

$$n_c(\mathbf{r}) \equiv \langle \hat{n}_c(\mathbf{r})\rangle = \tilde{\lambda}\Omega(\mathbf{r})\left\langle e^{-i\beta qe_0\varphi(\mathbf{r})}\right\rangle, \tag{5}$$

where $\hat{n}_c(\mathbf{r}) = \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)$ is the counterion *number density* operator. Show that the expression on the right-hand side of the above equation is real-valued and independent of the choice of the reference value for the potential field.

(iii) How is the density profile of counterions expressed in canonical ensemble with N counterions? In order to answer this question, you can start by explaining how $\tilde{\lambda}$ should be calculated as a function of the average number of counterions. Then, consider the thermodynamic limit $N\to\infty$ and note also that the system must be *globally electroneutral* in this limit, i.e., in a canonical system, we must have $Nqe_0 + \int d\mathbf{r}\,\rho_0(\mathbf{r}) = 0$.

(iv) Using Schwinger-Dyson equations discussed in class show that:

$$-\varepsilon_0\nabla\cdot[\varepsilon(\mathbf{r})\nabla\langle\varphi(\mathbf{r})\rangle] = -i\rho_0(\mathbf{r}) - iqe_0\tilde{\lambda}\Omega(\mathbf{r})\left\langle e^{-i\beta qe_0\varphi(\mathbf{r})}\right\rangle. \tag{6}$$

Interpret this result by expressing it in terms of the Wick-rotated potential field $\psi = i\varphi$. Expand the exponential term on the right-hand side of the equation and show that this equation relates different field correlation functions.

(v) Assuming that the field correlations can be ignored, derive the following closed-form partial differential equation, known as the Poisson-Boltzmann equation, governing the mean field $\bar{\psi}(\mathbf{r}) = \langle\psi(\mathbf{r})\rangle$:

$$-\varepsilon_0\nabla\cdot\left[\varepsilon(\mathbf{r})\nabla\bar{\psi}(\mathbf{r})\right] = \rho_0(\mathbf{r}) + qe_0\bar{n}_c(\mathbf{r}), \tag{7}$$

$$\bar{n}_c(\mathbf{r}) \equiv \tilde{\lambda}\Omega(\mathbf{r})e^{-\beta qe_0\bar{\psi}(\mathbf{r})}. \tag{8}$$

Recall the Poisson equation from the standard electrostatics of fixed charges and discuss its similarities and differences with the above equation. What is the fundamental origin of the differences here?

2: *Lattice Coulomb-gas model: From ionic liquids to sine-Gordon field theory.* In order to describe the behavior of Coulomb fluids containing positively and negatively charged mobile ions dispersed in a neutral background (e.g., a solvent such as water), one is required to account for the finite size of ions and their excluded-volume repulsions, especially when the ionic concentration is very large as, for instance, is the case in ionic liquids. This can be done by dividing the volume of the system, V, into small equal-size cells ("lattice sites") and allowing only a single ion in each cell. The ions are thus placed on a three-dimensional cubic lattice with unit-cell volume a^3, representative of the volume ("size") of a single ion (see Fig. 2).

Assume that the ions are of only two different types with equal sizes and charges $\pm e_0$, where e_0 is the elementary charge. The occupation number of each lattice site i can be denoted by the spin-like variable s_i taking three different values $s_i = +1$ (when the site is occupied by a positive ion), $s_i = -1$ (when the site is occupied by a negative ion) and $s_i = 0$ when the site is unoccupied (or, for instance, it is occupied by a water molecule). It is clear that this kind of lattice model effectively introduces a short-range (excluded-volume) repulsion between the ions preventing the oppositely charged ones from collapsing onto one another because of their Coulomb attraction.

We proceed by assuming that the system is in equilibrium with a bulk reservoir of positively and negatively charged ions with chemical potentials μ_+ and μ_-, respectively. The microscopic Hamiltonian of the above

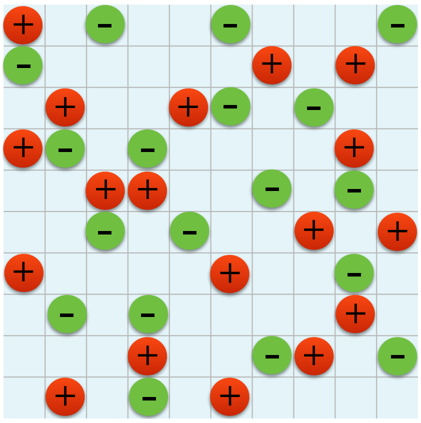

Figure 2. Schematic two-dimensional view of a lattice Coulomb-gas model consisting of equal-size positively and negatively charged ions. For further details, see Problem 2.

lattice Coulomb-gas model can be written as

$$\mathcal{H} = \frac{e_0^2}{4\pi\varepsilon\varepsilon_0}\sum_{i\neq j}\frac{s_i s_j}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \mu_i s_i^2, \tag{9}$$

where ε is the effective dielectric constant of the background medium, ε_0 is the permittivity of vacuum and $\mathbf{r}_i$ is the position of the ion i.

(i) Using the Hubbard-Stratonovich transformation show that the (grand-canonical) partition function of this system is given, in the *continuum limit*, by the following field "action":

$$S[\varphi(\mathbf{r})] = \frac{\varepsilon\varepsilon_0}{2}\int d\mathbf{r}\,(\nabla\varphi)^2 - \frac{k_BT}{a^3}\int_V d\mathbf{r}\ln\left(1 + \lambda_+ e^{-i\beta e_0\varphi(\mathbf{r})} + \lambda_- e^{i\beta e_0\varphi(\mathbf{r})}\right), \tag{10}$$

where the integral in the last term runs only over the volume V available to the ions and $\lambda_\pm = e^{\beta\mu_\pm}$ are the fugacities of the two charge species.

(ii) Express the average total number of positive and negative ions in the system in terms of ensemble averages over the fluctuating potential field $\varphi(\mathbf{r})$.

(iii) The bulk reservoir must be electroneutral and, thus, the total number of positive and negative ions in the bulk must be equal, $N_+ = N_- = N/2$. Note also that the potential field in the bulk can be set equal to zero. Using the result from part (ii), show that the fugacities must be equal, $\lambda_+ = \lambda_- = \lambda$, where

$$\lambda = \frac{1}{2}\frac{\phi_0}{1-\phi_0}, \tag{11}$$

and $\phi_0 = Na^3/V$ is the "volume fraction" occupied by ions. Hence, the field "action" can be re-expressed as

$$S[\varphi(\mathbf{r})] = \frac{\varepsilon\varepsilon_0}{2}\int d\mathbf{r}\,(\nabla\varphi)^2 - \frac{k_BT}{a^3}\int_V d\mathbf{r}\ln\left(1 + 2\lambda\cos(\beta e_0\varphi)\right). \tag{12}$$

(iv) Discuss the limiting forms of the field "action" in the *full-packing* ($\phi_0 \to 1^-$) and in the *infinite-dilution* ($\phi_0 \to 0$) limits. In the latter case, show that the above model reproduces the *sine-Gordon field theory* obtained in class for an off-lattice Coulomb fluid consisting of point-like negative and positive mobile ions whose excluded-volume repulsions (ion-size effects) can be neglected.