Course on "Statistical Physics of Fields In and Out of Equilibrium"
Spring Semester (2016)
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Homework #8: Field Theory for Coulomb Fluids: Mean-field theory & loop expansion
(*extra-credit problem set*) Due: August 25, 2016

▶ *Primitive model of Coulomb fluids confined by charged boundaries.* Consider the field "action" derived in the class for an inhomogeneous one-component Coulomb fluid, consisting of mobile point-like "counterions" of charge valency q dispersed in a continuum dielectric background ("solvent") of dielectric constant $\varepsilon(\mathbf{r})$ in thermal equilibrium at ambient temperature T (see Fig. 1), i.e.,

$$S[\varphi] = \int d\mathbf{r} \left[\frac{\varepsilon(\mathbf{r})\varepsilon_0}{2}(\nabla\varphi)^2 + i\rho_0(\mathbf{r})\varphi(\mathbf{r}) - \tilde{\lambda} k_B T \Omega(\mathbf{r}) e^{-i\beta q e_0 \varphi(\mathbf{r})} \right], \tag{1}$$

where $\beta = 1/(k_B T)$, $\varphi(\mathbf{r})$ is the fluctuating (electrostatic) potential field, e_0 the elementary charge, ε_0 the permittivity of vacuum, $\rho_0(\mathbf{r})$ the distribution of fixed charged boundaries (or fixed macroscopic and/or mesoscopic charged objects in the medium) and $\tilde{\lambda}$ the rescaled fugacity of counterions. The system is assumed to be globally electroneutral. The fixed charged objects are supposed to be impenetrable to counterions; hence, the "blip" function $\Omega(\mathbf{r}) = 0$ in the regions occupied by these objects and $\Omega(\mathbf{r}) = 1$ elsewhere in space, i.e., in the regions accessible to counterions. In what follows, assume that the system is dielectrically homogeneous, i.e., $\varepsilon(\mathbf{r}) = \varepsilon$ everywhere in space. In this case, all charges including counterions and the fixed charges interact via the standard Coulomb interaction kernel in three dimensions.

Note: See Problem 1 in ***Homework #5: Hubbard-Stratonovich Transformation (II): Coulomb fluids*** of these homework series for further details that may be useful in solving the following problems and also for a more general case of the above model.

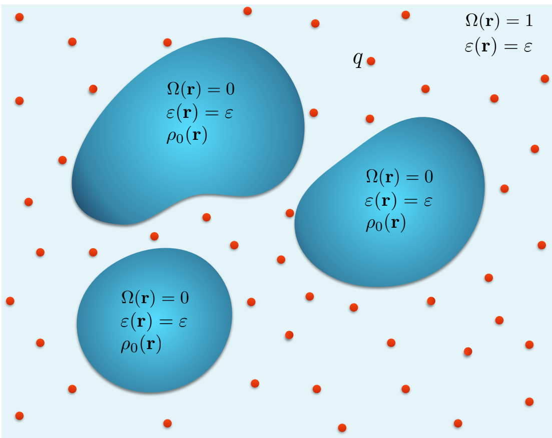

Figure 1. Schematic view of an inhomogeneous Coulomb fluid consisting of impenetrable, fixed, charged objects (such as charged macromolecules, shown here by large dark-blue shapes), carrying the charge distribution $\rho_0(\mathbf{r})$, and their neutralizing, point-like, mobile counterions of charge valency q (shown by small red spheres). The dielectric constant is the same and equal to ε everywhere in space. Counterions can only access the regions outside the fixed objects, where $\Omega(\mathbf{r}) = 1$.

1: *Counterion density next to a planar charged wall.* Consider a special case of the above model in which the space accessible to counterions is restricted by a single planar half-space (wall), whose surface, taken perpendicular to the z-axis, is located at $z = 0$, carrying the neutralizing surface charge density $-\sigma e_0$ (we conventionally assume that $\sigma > 0$ and, hence, $q > 0$). The blip function and the fixed charge distribution in this case read

$$\rho_0(\mathbf{r}) = -\sigma e_0 \delta(z), \qquad \Omega(\mathbf{r}) = \theta(z), \tag{2}$$

where $\delta(\cdot)$ and $\theta(\cdot)$ are the Dirac delta and Heaviside step functions, respectively. The Poisson-Boltzmann equation, which follows from the saddle-point approximation for the field "action" (1), governs the mean potential field, giving the well-known *mean-field* number density of counterions next to the surface, $\bar{n}_c(z)$, as

$$\frac{\bar{n}_c(z)}{2\pi\ell_B\sigma^2} = \frac{1}{(1+z/\mu)^2} \qquad z \geq 0, \tag{3}$$

where $\ell_B = e_0^2/(4\pi\epsilon\epsilon_0 k_B T)$ is the so-called *Bjerrum length*, which measures the strength of electrostatic interaction (repulsion) between two elementary charge relative to the thermal energy k_BT, and $\mu = 1/(2\pi\ell_B q\sigma)$ is the *Gouy-Chapman length*, which measures the strength of electrostatic interaction (attraction) between a counterion and the surface charge relative to the thermal energy.

(i) Construct a systematic loop expansion based on the standard procedure discussed in the class and derive general expressions up to the one-loop order for the field-fluctuation corrections to the average (mean-field) counterion number density next to an arbitrary charge distribution. ***Hint:*** Just to remind you, the counterion number density follows from the formal expression $n_c(\mathbf{r}) = \tilde{\lambda}\Omega(\mathbf{r})\left\langle e^{-i\beta q e_0 \varphi(\mathbf{r})}\right\rangle$, where $\langle\cdots\rangle$ denotes ensemble average over equilibrium field fluctuations. Note also that, for obtaining the one-loop corrections to the counterion mean-field density, the fugacity must be expanded to first order as well, i.e., $\tilde{\lambda} \simeq \tilde{\lambda}^{(0)} + \tilde{\lambda}^{(1)}$!

(ii) Up to the one-loop order, and for counterions next to the planar wall, we can write $n_c(z) \simeq \bar{n}_c(z) + n_c^{(1)}(z)$. Obtain explicit form of the one-loop correction term $n_c^{(1)}(z)$ and show that it behaves asymptotically as

$$\frac{n_c^{(1)}(z)}{2\pi\ell_B\sigma^2} \simeq \begin{cases} -\frac{\pi}{8}\left(\frac{z}{\mu}\right)\ln\left(\frac{z}{\mu}\right) & \frac{z}{\mu} \ll 1, \\ -\left(\frac{\mu}{z}\right)^3 \ln\left(\frac{z}{\mu}\right) & \frac{z}{\mu} \gg 1. \end{cases} \tag{4}$$

2: *Counterion-mediated interaction between two planar charged walls.* Consider two plane-parallel half-spaces (walls) with their inner surfaces located, perpendicular to the z-axis, at $z = \pm D/2$, carrying surface charge densities $\sigma_1 e_0$ and $\sigma_2 e_0$, respectively. The neutralizing counterions are assumed to be distributed only in between the two surface in the region $|z| \leq D/2$. The blip function and the fixed charge distribution in this case are

$$\rho_0(\mathbf{r}) = e_0\left[\sigma_1\delta(z + D/2) + \sigma_2\delta(z - D/2)\right], \tag{5}$$
$$\Omega(\mathbf{r}) = \theta(z + D/2) - \theta(z - D/2). \tag{6}$$

The presence of counterions leads to an effective interaction pressure acting on the two surfaces. This pressure was calculated in the class for the case of two *identically* charged, planar walls with $\sigma_1 = \sigma_2 = -\sigma$ on both the mean-field level (using the Poisson-Boltzmann equation) as well as the one-loop level (accounting for Gaussian field fluctuations). The mean-field interaction pressure, $\bar{P}(D)$, was shown to be repulsive and the subleading one-loop correction to the interaction pressure, $P^{(1)}(D)$, was shown to be attractive; both these contributions and, thus, the net pressure to one-loop order, $P(D) \simeq \bar{P}(D) + P^{(1)}(D)$, turned out to be relatively long-ranged with large-separation ($D/\mu \gg 1$) behaviors given by

$$\frac{\beta\bar{P}(D)}{2\pi\ell_B\sigma^2} \simeq \pi^2\left(\frac{\mu}{D}\right)^2, \tag{7}$$
$$\frac{\beta P^{(1)}(D)}{2\pi\ell_B\sigma^2} \simeq -\pi^2\left(\frac{\mu}{D}\right)^3 \ln\left(\frac{D}{\mu}\right). \tag{8}$$

(i) Argue that in the case of two *asymmetrically* charged walls, one can assume, without loss of generality, that

$$\sigma_1 + \sigma_2 < 0, \quad \text{and} \quad \sigma_2 > \sigma_1, \quad \text{so that} \quad \sigma_1 < 0, \tag{9}$$

where we have conventionally assumed that counterions are positively charged ($q > 0$). It is useful to introduce an *asymmetry parameter* $\zeta = \sigma_2/\sigma_1 > -1$ to quantify the dissimilarity between the two surface charges. Argue that one can focus exclusively on the interval $-1 \leq \zeta \leq 1$ and all other cases can be mapped onto this interval with appropriate rescaling of the parameters. Note that the system must be kept electroneutral, which implies that for the antisymmetric case with $\zeta = -1$, there will be no counterions in the system, while, in other cases, including the symmetric case with $\zeta = 1$, which was mentioned above, there will be a finite number of counterions in the system.

(ii) Write down the Poisson-Boltzmann equation governing the mean potential field and calculate the mean-field pressure acting on the surfaces. Show that a repulsive inter-surface pressure is always possible for any given ζ (excluding the trivial case of $\zeta = -1$), while an attractive interaction pressure between the surfaces is possible only when the surfaces have charges of opposite sign $\zeta < 0$.

(iii) Show that for the particular case of $\zeta \to 0^+$ (one surface being neutral), one obtains the asymptotic ($D/\mu \gg 1$) result

$$\frac{\beta \bar{P}(D)}{2\pi \ell_B \sigma_1^2} \simeq \frac{\pi^2}{4}\left(\frac{\mu}{D}\right)^2 \qquad \zeta \to 0^+, \tag{10}$$

where $\mu \equiv 1/(2\pi \ell_B q |\sigma_1|)$.

(iv) Calculate the one-loop correction to the interaction pressure in the particular case of $\zeta \to 0^+$ and show that it is attractive and given asymptotically by

$$\frac{\beta P^{(1)}(D)}{2\pi \ell_B \sigma_1^2} \simeq -\frac{\pi^2}{8}\left(\frac{\mu}{D}\right)^3 \ln\left(\frac{D}{\mu}\right) \qquad \zeta \to 0^+. \tag{11}$$

(v) The results in parts (iii) and (iv) show that the asymptotic behavior of the mean-field and Gaussian-fluctuation contributions to the effective pressure acting on the surfaces, when *one surface is neutral*, coincide with those shown in Eqs. (7) and (8), when the two surfaces are *identically charged*, provided only that we redefine $D \to D/2$. Can you explain this finding?