Problem Set 8 – Statistical Physics B

Problem 1: An ionic solution in contact with a planar charged wall

Consider a planar charged wall positioned at $z < 0$ with a surface charge density $e\sigma$. Note that σ can be either negative or positive. This surface charge is in contact with an electrolyte consisting of monovalent cations and anions for $z > 0$. The solvent in which the ions reside is modeled as a dielectric continuum with dielectric constant $\epsilon = \epsilon_0\epsilon_{\mathrm{r}}$, with ϵ_0 the vacuum permittivity and ϵ_{r} the relative permittivity. The ions cannot penetrate the wall.

(a) Write down the Poisson-Boltzmann equation for this system and derive the boundary conditions. What is the physical meaning of the boundary conditions? [Hint: Note that the electric field is given by $\mathbf{E}(\mathbf{r}) = -\nabla\psi(\mathbf{r})$.]

(b) The total number density of ions is given by $\rho(z) = \rho_+(z) + \rho_-(z)$. Show that

$$\frac{d}{dz}\left[k_{\mathrm{B}}T\rho(z) - \frac{\epsilon_0\epsilon_{\mathrm{r}}}{2}\mathbf{E}(z)^2\right] = 0.$$

Give a physical interpretation of this equation.

(c) Show that the enhancement of the number density at contact is given by

$$\rho(0^+) - 2\rho_{\mathrm{b}} = \frac{\beta(e\sigma)^2}{2\epsilon_0\epsilon_{\mathrm{r}}}.$$

(d) This geometry allows for an exact solution of the non-linear Poisson-Boltzmann equation. Introduce the dimensionless electrostatic potential $\phi(z) = \beta e\psi(z)$ and show that the first integral is given by

$$\frac{d\phi(z)}{dz} = -2\kappa\sinh[\phi(z)/2].$$

Here $\kappa^2 = 8\pi\ell_{\mathrm{B}}\rho_{\mathrm{b}}$, with ℓ_{B} the Bjerrum length. In deriving this expression, did we make an assumption on the sign of σ?

(e) Show that

$$\frac{1}{\sinh(\phi/2)} = 2\frac{d}{d\phi}\{\ln[\sinh(\phi/4)] - \ln[\cosh(\phi/4)]\},$$

and using this result derive that

$$\phi(z) = 4\,\mathrm{artanh}\left(ge^{-z/\ell_{\mathrm{D}}}\right),$$

where $g = \tanh[\phi(0)/4]$ and $\ell_{\mathrm{D}} = \kappa^{-1}$ is the Debye length.

(f) From the boundary condition, derive the Grahame equation

$$\sigma = \frac{1}{2\pi\ell_{\mathrm{B}}\ell_{\mathrm{D}}}\sinh[\phi(0)/2].$$

(g) We introduce the Gouy-Chapman length as $\ell_{\mathrm{GC}} = (2\pi\ell_{\mathrm{B}}|\sigma|)^{-1}$. Give a physical interpretation of this quantity.

(h) Show that we can express the yet unknown g factor as

$$g = \mathrm{sgn}(\sigma)\frac{\ell_{\mathrm{GC}}}{\ell_{\mathrm{D}}}\left\{\left[1 + \left(\frac{\ell_{\mathrm{D}}}{\ell_{\mathrm{GC}}}\right)^2\right]^{1/2} - 1\right\}$$

(i) Find an expression for $\rho_\pm(z)$ and plot several values of $\rho_\pm(z)/\rho_\mathrm{b}$ for various values of σ. Comment on the various plots.

Problem 2: Keesom interactions

Effective interactions can also be computed by integrating out internal degrees of freedom. We will demonstrate this procedure in the case of orientational degrees of freedom. Consider two fixed classical dipoles ($i = 1, 2$) with dipole moments $\boldsymbol{\mu}_i = \mu_i \mathbf{e}_i$ with $\mu_i = |\boldsymbol{\mu}_i|$ and $\mathbf{e}_i$ a unit vector indicating the orientation of the dipole. The dipole-dipole interaction potential is

$$v(r, \mathbf{e}_1, \mathbf{e}_2) = \frac{\mu_1 \mu_2}{4\pi\epsilon_0 r^3}[\mathbf{e}_1 \cdot \mathbf{e}_2 - 3(\mathbf{e}_1 \cdot \hat{\mathbf{r}})(\mathbf{e}_2 \cdot \hat{\mathbf{r}})].$$

Here $\mathbf{r}$ is the separation vector between the two dipoles with $r = |\mathbf{r}|$ and $\hat{\mathbf{r}} = \mathbf{r}/r$.

(a) Show that the above interaction potential can be written as $v(r, \mathbf{e}_1, \mathbf{e}_2) = -\boldsymbol{\mu}_1 \cdot \mathbf{E}_2 = -\boldsymbol{\mu}_2 \cdot \mathbf{E}_1$, with $\mathbf{E}_i$ the electric field generated by dipole i.

(b) Write down an expression for the potential of mean force $w(r)$ by integrating out the orientational degrees of freedom for the dipoles. Show that the far-field result is given by

$$\beta w(r) = -\frac{1}{3}\beta^2 \left(\frac{\mu_1 \mu_2}{4\pi\epsilon_0}\right)^2 \frac{1}{r^6}.$$

(c) Identifying $w(r)$ as a free energy for dipoles at a fixed separation r, compute the entropy associated with $w(r)$. How do you interpret this result?