Hand-in sheet 3 – Statistical Physics B

- *Please hand in your solution before Thursday 5 December 2024, 16:15.*
- *You can hand in your solutions in digital format as a pdf-file. Make sure to provide a file name which contains the hand-in number, your name, and your student number. You can send your solution to jeffrey.everts AT fuw.edu.pl. Also include your name and student number in the pdf file.*
- *In case of paper format, please do not forget to write your name and student number.*
- *Make sure to answer every question as completely as possible. When you do calculations, provide sufficient explanation for all steps.*
- *In total 100 points can be earned.*

Effective interactions of charged surfaces in an electrolyte

Consider an external charge distribution $eQ(\mathbf{r})$ consisting of particles/external surfaces with center of mass positions $\{\mathbf{R}^N\}$ and an ionic charge distribution $eq(\mathbf{r})$ consisting of monovalent ions, i.e. $q(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r})$. We are interested in the effective interactions that can occur between the various bodies that constitute $Q(\mathbf{r})$. We connect the system to a reservoir where the external charge distribution is absent, characterized by ionic chemical potentials $\mu_\pm$ and bulk ion concentrations ρ_b. The external surfaces exert external potentials $V_\pm^{\mathrm{ext}}(\mathbf{r})$ on the ions. Furthermore, the ions reside in a solvent that is modeled as a dielectric continuum with relative permittivity ϵ_r. Non-Coulombic interactions between ions are neglected.

(a) (*10 points*) Write down the grand potential functional $\Omega_\mathrm{V}[\rho_\pm;\mathbf{R}^N]$ of this system within the mean-field approximation and explain in detail what the various terms represent.

(b) (*15 points*) Introduce the dimensionless electrostatic potential $\phi(\mathbf{r}) = \beta e\psi(\mathbf{r})$, given by

$$\phi(\mathbf{r}) = \ell_\mathrm{B}\int d\mathbf{r}'\,\frac{Q(\mathbf{r}')+q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},$$

with ℓ_B the Bjerrum length. Give an expression for ℓ_B and discuss what it physically represents. show that

$$\beta\Omega_\mathrm{V}[\rho_\pm;\mathbf{R}^N] = \sum_{\alpha=\pm}\int d\mathbf{r}\,\rho_\alpha(\mathbf{r})\left[\ln\frac{\rho_\alpha(\mathbf{r})}{\rho_\mathrm{b}} - 1\right] + \frac{1}{2}\int d\mathbf{r}\,\phi(\mathbf{r})[Q(\mathbf{r})+q(\mathbf{r})].$$

(c) (*15 points*) Derive from $\Omega_\mathrm{V}[\rho_\pm;\mathbf{R}^N]$ the Poisson-Boltzmann equation

$$\nabla^2\phi(\mathbf{r}) = \kappa^2\sinh[\phi(\mathbf{r})] - 4\pi\ell_\mathrm{B}Q(\mathbf{r}).$$

Give an expression for κ and discuss what it physically represents.

(d) (*15 points*) Define $W(\mathbf{R}^N) = \min_{\rho_\pm}\Omega_\mathrm{V}[\rho_\pm;\mathbf{R}^N]$ and show that

$$\beta W(\mathbf{R}^N) = \rho_\mathrm{b}\int d\mathbf{r}\,[\phi(\mathbf{r})\sinh\phi(\mathbf{r}) - 2\cosh\phi(\mathbf{r})] + \frac{1}{2}\int d\mathbf{r}\,Q(\mathbf{r})\phi(\mathbf{r})$$

What is the physical meaning of $W(\mathbf{R}^N)$?

(e) (*10 points*) Determine $W(\mathbf{R}^N)/V$ for $N = 0$ (no external surfaces), with V being the system volume. How do you interpret this quantity?

(f) (*15 points*) Take $Q(\mathbf{r}) = \sigma\delta(z - H/2) + \sigma\delta(z + H/2)$. Write down the relevant Poisson-Boltzmann equation and derive the corresponding boundary conditions. Assuming σ to be small, linearise the corresponding Poisson-Boltzmann equation (i.e., $|\phi(\mathbf{r})| \ll 1$) and show that

$$\phi(z) = \frac{y \cosh(\kappa z)}{\sinh(\kappa H/2)},$$

with $y = 4\pi\ell_{\mathrm{D}}\ell_{\mathrm{B}}\sigma$.

(g) (*20 points*) Derive the disjoining pressure from $W(H)$ for $\kappa H \gg 1$,

$$\beta P(H) = 8\pi\ell_{\mathrm{B}}\sigma^2 \exp(-\kappa H).$$

Is $P(H)$ an osmotic pressure? Motivate your answer.