INSTITUTE OF THEORETICAL PHYSICS
UNIVERSITY OF WARSAW

Final exam Topics in Modern Statistical Physics

Wednesday, 7 February 2024, 9:00-12:00

- *Read every question carefully before answering. The exam consists of three problems, and a total of 100 points can be earned.*
- *Make sure to answer every question as completely as possible. When you do calculations, provide sufficient explanation for all steps.*
- *Write clearly and structured; unreadable work cannot be corrected.*
- *Make sure to divide your time into the problems equally, considering the number of points you can earn for each question. If you think you made a calculational mistake somewhere, point it out in words, and do not spend too much time correcting, e.g. minus signs.*

Problem 1: Depletion interactions (*25 points*)
Consider two hard planar walls with thickness d and surface area A, where the surface areas A are aligned parallel to each other. The walls have center-of-mass positions $\mathbf{R}_1 = -[(H+d)/2]\hat{\mathbf{z}}$ and $\mathbf{R}_2 = [(H+d)/2]\hat{\mathbf{z}}$. Besides the solvent, the medium consists of N_2 polymer blobs with characteristic diameter σ and positional degrees of freedom $\mathbf{r}^{N_2} = (\mathbf{r}_1, ..., \mathbf{r}_{N_2})$. For the potential energy of the system, we assume that the polymers behave as an ideal gas amongst each other, but they do interact with the planar walls, i.e.,

$$\Phi(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}^{N_2}) = \phi_{11}(H) + \Phi_{12}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}^{N_2}),$$

with wall-wall potential $\phi_{11}(H)$. The solvent is not explicitly considered because solvent particles do not interact with polymers or the walls. The canonical partition function of the system is

$$Z(N_1 = 2, N_2, V, T) = \frac{1}{2!\mathcal{V}^2} \int d\mathbf{R}_1 \int d\mathbf{R}_2 \int \frac{d\mathbf{r}_2^N}{N_2!\Lambda_2^{3N_2}} \exp[-\beta\Phi(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}^{N_2})],$$

with Λ_2 the thermal de Broglie wavelength of a polymer blob, neglecting any internal degrees of freedom. The semi-grand partition function is $\Xi(N_1, \mu_2, V_2) = \sum_{N_2=0}^{\infty} \exp(\beta\mu_2 N_2) Z(N_1, N_2, V, T)$ with thermodynamic potential $\beta\Omega = -\ln \Xi(N_1, \mu_2, V, T)$.

(a) (*5 points*) We define the effective interaction potential $\Phi_{\text{eff}}(H)$ as

$$\exp[-\beta\Omega(N_1 = 2, \mu_2, V, T)] = \frac{1}{2!\mathcal{V}^2} \int d\mathbf{R}_1 \int d\mathbf{R}_2 \exp[-\beta\Phi_{\text{eff}}(H; \mu_2, T)],$$

with $\mathcal{V}$ an irrelevant constant with dimension volume. Derive a formal expression for $\Phi_{\text{eff}}(H)$ in terms of μ_2, $\phi_{11}(H)$, and $\Phi_{12}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}^{N_2})$.

(b) (*10 points*) We assume that the interaction potential between wall and particles is pair-wise additive $\Phi_{12}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}^{N_2}) = \sum_{i=1}^{2} \sum_{j=1}^{N_2} \phi_{12}(|\mathbf{R}_i - \mathbf{r}_j|)$, with a hard sphere-wall potential

$$\phi_{12}(z) = \begin{cases} \infty, & z < (d+\sigma)/2, \\ 0, & z > (d+\sigma)/2, \end{cases}$$

with z, the separation from the centerline of the wall to the centre of a polymer blob. Show by explicit computation that $\Phi_{\text{eff}}(H) = -\Pi A(\sigma - H)$ for $0 < H < \sigma$ and $\Phi_{\text{eff}}(H) = 0$ for $H > \sigma$. Here, Π is the osmotic pressure of a bulk system of polymer blobs, i.e. the excess pressure over a reservoir with pure solvent.

(c) (*5 points*) Explain the occurrence of the attraction in the so-called depletion potential $\Phi_{\text{eff}}(H)$ for $0 < H < \sigma$ in terms of the entropy of the polymer blobs.

(d) (*5 points*) We replace the two flat plates by two hard spherocylinders with arbitrary orientations. Describe in words how you would compute the depletion potential as a function of centre-to-centre separation and orientations of the spherocylinders. For which orientations do you expect the largest attraction as a function of separation? Explain your answer.

Problem 2: Nematic liquid crystals (*35 points*)
An inhomogeneous nematic liquid crystal is modelled by the Landau-de Gennes free energy $F_{\text{LdG}}[\mathcal{Q}] = \int d\mathbf{r} f(\mathcal{Q}(\mathbf{r}))$. The form of the free energy density within the one-constant approximation at a given temperature T is

$$f(\mathcal{Q}(\mathbf{r})) = \frac{L_1}{2}\partial_\alpha \mathcal{Q}_{\beta\gamma}(\mathbf{r})\partial_\alpha \mathcal{Q}_{\beta\gamma}(\mathbf{r}) + A(T-T^*)\text{Tr}[\mathcal{Q}(\mathbf{r})^2] - B\text{Tr}[\mathcal{Q}(\mathbf{r})^3] + C\{\text{Tr}[\mathcal{Q}(\mathbf{r})^2]\}^2,$$

with Einstein summation convention implied and constants $A, B, C, L_1, T^* > 0$. The symmetric traceless tensorial order-parameter *density* $[\mathcal{Q}]_{\alpha\beta} =: \mathcal{Q}_{\alpha\beta}$ is given by the ensemble average

$$\mathcal{Q}_{\alpha\beta}(\mathbf{r}) = \left\langle \frac{3}{2N}\sum_{i=1}^{N}\left(\hat{u}_{i\alpha}\hat{u}_{i\beta} - \frac{1}{3}\delta_{\alpha\beta}\right)\delta(\mathbf{r}-\mathbf{r}_i)\right\rangle,$$

with $(\mathbf{r}_1, ..., \mathbf{r}_N)$ and $(\hat{\mathbf{u}}_1, ..., \hat{\mathbf{u}}_N)$ the centre-of-mass positions and orientations of the particles in the liquid crystal (the mesogens), respectively, and N the number of particles. Tr(...) denotes the trace of a tensor, e.g, $\text{Tr}[\mathcal{Q}(\mathbf{r})^2] = \mathcal{Q}_{\alpha\beta}(\mathbf{r})\mathcal{Q}_{\beta\alpha}(\mathbf{r})$.

(a) (*5 points*) Within the uniaxial approximation, the order parameter is given by

$$\mathcal{Q}_{\alpha\beta}(\mathbf{r}) = \frac{3}{2}S(\mathbf{r})\left(\hat{n}_\alpha(\mathbf{r})\hat{n}_\beta(\mathbf{r}) - \frac{1}{3}\delta_{\alpha\beta}\right),$$

with $S(\mathbf{r})$ the scalar order parameter and $\hat{\mathbf{n}}(\mathbf{r})$ the director with $|\hat{\mathbf{n}}(\mathbf{r})|^2 = \hat{n}_\alpha(\mathbf{r})\hat{n}_\alpha(\mathbf{r}) = 1$. What do these quantities physically represent? Derive an expression for $S(\mathbf{r})$ that connects this quantity to the one-body distribution function $\rho(\mathbf{r}, \hat{\mathbf{u}}) = \langle\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\hat{\mathbf{u}}-\hat{\mathbf{u}}_i)\rangle$.

(b) (*5 points*) Show that within the uniaxial approximation and under the assumption of a spatially constant director field that $F_{\text{LdG}}[\mathcal{Q}]$ reduces to

$$F_{\text{LdG}}[S] = \int d\mathbf{r}\left[\frac{m}{2}|\nabla S(\mathbf{r})|^2 + a(T-T^*)S(\mathbf{r})^2 - bS(\mathbf{r})^3 + cS(\mathbf{r})^4\right],$$

and give the expressions for m, a, b, and c. Why is the cubic term absent for a ferromagnet?

(c) (*5 points*) Consider the case where $S(\mathbf{r})$ =constant. The free energy in (b) describes a phase transition at $T = T_{\text{IN}}$. What is the order of this phase transition? Sketch how a system of 15-20 mesogens looks like for $T < T_{\text{IN}}$ and $T > T_{\text{IN}}$. Explain your sketches.

(d) (*5 points*) Determine T_{IN} and the *non-trivial* value of the order parameter $S_{\text{IN}} := S(T_{\text{IN}})$.

(e) (*5 points*) What is the difference when we quench a system at $T > T_{\text{IN}}$ to a temperature $T_* < T < T_{\text{IN}}$ compared to $T < T_*$?

(f) (*10 points*) Take the inhomogeneous system at coexistence $T = T_{\text{IN}}$ with $S(\mathbf{r}) = S(z)$ and boundary conditions $S(z \to \infty) = S_{\text{IN}}$ and $S(z \to -\infty) = 0$. Show from the Euler-Lagrange equation $\delta F_{\text{LdG}}[S]/\delta S(\mathbf{r}) = 0$ that the order-parameter profile is determined by,

$$S(z) = \frac{S_{\text{IN}}}{2}\left[1 - \tanh\left(\frac{z}{2\xi}\right)\right].$$

You may fix the order-parameter profile such that $S(z = 0) = S_{\text{IN}}/2$. Give the expression for ξ and explain the physical meaning of this quantity.

Problem 3: Sedimentation of charged macroions (*40 points*)
Consider charged spherical particles (macroions) with number density profile $\rho_{\rm p}(\mathbf{r})$. The particles reside in a medium consisting of (i) a solvent modelled as a dielectric continuum with dielectric constant ϵ, and (ii) monovalent cations (+) and anions (-) with density profiles $\rho_\pm(\mathbf{r})$, respectively. Within a density-functional framework, we approximate the intrinsic Helmholtz free energy functional as

$$\beta\mathcal{F}[\rho_{\rm p},\rho_\pm] = \sum_{i={\rm p},\pm}\int d\mathbf{r}\rho_i(\mathbf{r})\{\ln[\rho_i(\mathbf{r})\mathcal{V}_i]-1\} + \frac{\ell_{\rm B}}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{q(\mathbf{r})q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}.$$

Here, $\beta^{-1} = k_{\rm B}T$ is the thermal energy, $\ell_{\rm B} = \beta e^2/(4\pi\epsilon)$ is the Bjerrum length with e the elementary charge unit, $\mathcal{V}_i$ is the thermal volume of species $i = \pm$, p, and $eq(\mathbf{r}) = e[\rho_+(\mathbf{r}) - \rho_-(\mathbf{r}) + Z_{\rm p}\rho_{\rm p}(\mathbf{r})]$ is the total local charge density. Note that each sphere has valency $Z_{\rm p}$.

(a) (*5 points*) Discuss briefly but detailed what the various terms in $\mathcal{F}[\rho_{\rm p},\rho_\pm]$ represent and what approximations underlie this functional.

(b) (*5 points*) Derive the Euler-Lagrange equations that determine the equilibrium density profiles of the charged spheres and the ions for arbitrary external potentials $V_i^{\rm ext}(\mathbf{r})$ ($i = \pm$,p). It is beneficial to treat all types of particles in the grand-canonical ensemble with chemical potentials μ_i ($i = \pm$,p).

(c) (*5 points*) Consider the case where $\rho_\pm(\mathbf{r}) = 0$ (no ions) and $Z_{\rm p} = 0$ (uncharged spheres). We consider the settling of the spherical particles under gravity, i.e., we take $V_{\rm p}^{\rm ext}(\mathbf{r}) = mgz$, for $z > 0$ and $V_{\rm p}^{\rm ext}(\mathbf{r}) = \infty$ for $z < 0$. Here, m is the buoyant mass of the particles, and g is the gravitational acceleration. For these conditions, derive an expression for $\rho_{\rm p}(\mathbf{r})$ in terms of the gravitational length $\ell_{\rm g} = (\beta mg)^{-1}$ given that the system has height H and surface area A. Furthermore, there are N number of particles in the system volume. You may neglect the effects of curved space-time.

(d) (*5 points*) For $\rho_\pm(\mathbf{r}) \neq 0$ and $Z_{\rm p} \neq 0$ it is useful to introduce the electrostatic potential $\psi(\mathbf{r})$,

$$\psi(\mathbf{r}) = \int d\mathbf{r}'\,\frac{eq(\mathbf{r}')}{4\pi\epsilon|\mathbf{r}-\mathbf{r}'|}.$$

Show that the dimensionless electrostatic potential $\phi(\mathbf{r}) = \beta e\psi(\mathbf{r})$ satisfies

$$\nabla^2\phi(\mathbf{r}) = \kappa^2\sinh[\phi(\mathbf{r})] - 4\pi\ell_{\rm B}Z_{\rm p}\rho_{\rm p}(\mathbf{r}).$$

[*Hint*: $\nabla^2 r^{-1} = -4\pi\delta(\mathbf{r})$]. Give an expression for κ in terms of $2\rho_{\rm b}$, which is the *total* bulk ion density in the absence of macroions. Discuss what κ physically represents.

(e) (*5 points*) A bulk system is locally charge neutral, i.e. $\nabla^2\phi(\mathbf{r}) = 0$. Show that the osmotic pressure Π –defined as the excess pressure over a reservoir with just ions– is given by,

$$\beta\Pi(\rho_{\rm p}) = \rho_{\rm p} + 2\rho_{\rm b}\left(\sqrt{1+y^2}-1\right),$$

with $y := Z_{\rm p}\rho_{\rm p}/(2\rho_{\rm b})$. Note that $\psi(\mathbf{r}) = 0$ for a bulk ion reservoir *without* macroions.

(f) (*10 points*) Consider the equation of state in (e) for $y \gg 1$. Assume that ions are not subjected to gravity, i.e., $V_\pm^{\rm ext}(\mathbf{r}) = 0$ for $z > 0$ and $V_\pm^{\rm ext}(\mathbf{r}) = \infty$ for $z < 0$. Use the equation of hydrostatics $\Pi'(\rho_{\rm p}(z)) = -mg\rho_{\rm p}(z)$ to show that $\rho_{\rm p}(z)$ is a barometric distribution with an "inflated" gravitational length due to the charge $Z_{\rm p}$ of the macroions. As usual, a prime denotes differentiation of a function with respect to its argument.

(g) (*5 points*) Where in the system do you expect the solution from (f) to be valid? What do you expect for the form of $\rho_{\rm p}(z)$ far away from the bottom wall?

$\ddot\smile$ END OF EXAM $\ddot\smile$