Institute of Theoretical Physics
University of Warsaw

Retake exam Statistical Physics B

Monday, 17 February 2025, 9:00-13:00

- *Read every question carefully before answering. The exam consists of four problems and a total of 100 points can be earned.*
- *Make sure to answer every question as complete as possible. When you do calculations, make sure to provide sufficient explanation for all steps.*
- *Write clearly and structured, unreadable work cannot be corrected.*
- *Make sure to divide your time on the problems equally, considering the amount of points you can earn for each question. If you think you made somewhere a calculational mistake, point it out in words, and do not spend too much time on correcting e.g. minus signs.*
- *You are allowed to use a hand-written single-sided sheet of notes during this exam.*

Problem 1: Velocity correlations within the Langevin equation (*40 points*)

The Langevin equation is given by

$$v(t) = \dot{x}(t), \quad m\dot{v}(t) = -\zeta v(t) + f(t),$$

with ζ a constant friction constant, and we consider white noise $\langle f(t)\rangle = 0$ and $\langle f(t)f(t')\rangle = \Gamma\delta(t-t')$, with Γ a constant. Here $\langle ...\rangle$ is defined as the average over a subensemble with the same initial velocity $v_0 = v(0)$ but a different realisation of the noise.

(a) *(5 points)* What kind of physical situation does the Langevin equation describe? Give sufficient details.

(b) *(5 points)* Determine explicitly $v(t)$ for a given v_0. What is $\langle v(t)\rangle$? Conclude from your expression why the Brownian particle is out of equilibrium.

(c) *(15 points)* Determine the equal-time correlation function $\langle v^2(t)\rangle$. The limit $\lim_{t\to\infty}\langle v^2(t)\rangle$ is well defined. What is the corresponding value? From it, determine the constant Γ and relate your result to the fluctuation-dissipation theorem.

(d) *(5 points)* Determine the correlator $\langle v(t)f(t)\rangle$ for $t > 0$.

(e) *(10 points)* Show that $\langle v^2(t)\rangle$ satisfies the differential equation

$$m\frac{d}{dt}\langle v^2(t)\rangle = -2\zeta\langle v^2(t)\rangle + 2\langle v(t)f(t)\rangle.$$

Show that your answers in (c) and (e) are consistent with this differential equation.

Problem 2: Zwanzig model *(30 points)*

Consider a system of rectangular cuboidal particles with length L and a square base of size D by D. We only allow discrete orientations for these particles: the long axes can only point in the $\hat{\mathbf{x}}_1 = \hat{\mathbf{x}}$, $\hat{\mathbf{x}}_2 = \hat{\mathbf{y}}$, or $\hat{\mathbf{x}}_3 = \hat{\mathbf{z}}$ direction as measured from the laboratory frame. A particle with orientation α has its long axis pointed in direction $\hat{\mathbf{x}}_\alpha$, with $\alpha = 1, 2, 3$. Within the second-virial approximation the Helmholtz free energy F of the system is given by

$$f = \frac{\beta F}{V} = \sum_{\alpha=1}^{3}\rho_\alpha[\ln(\rho_\alpha\mathcal{V}) - 1] + \sum_{\alpha,\alpha'=1}^{3} B_{\alpha\alpha'}\rho_\alpha\rho_{\alpha'},$$

with ρ_α the density of particles with orientation α, $B_{\alpha\alpha'} = (1/2)\int d\mathbf{r}\,[1 - e^{-\beta\phi_{\alpha\alpha'}(\mathbf{r})}]$ the second virial coefficient for a particle with orientation α interacting with a particle of orientation α' with interaction potential $\phi_{\alpha\alpha'}(\mathbf{r})$. Furthermore, $\mathcal{V}$ is the (irrelevant) thermal volume.

(a) *(5 points)* We assume that the particles interact via hard interactions, i.e., no overlap between particles are allowed. There are only two independent virial coefficients $B_{\parallel} := B_{\alpha\alpha}$ (parallel particles) and $B_{\perp} := B_{\alpha\bar{\alpha}}$ with $\bar{\alpha} \neq \alpha$ (perpendicular particles). Compute $B_{\parallel}$ and $B_{\perp}$ explicitly.

(b) *(5 points)* Consider the dimensionless free energy $\psi = fL^2D$ and the dimensionless density $c_\alpha = L^2D\rho_\alpha$. Show that in the needle limit $L/D \to \infty$ we find

$$\psi = \sum_{\alpha=1}^{3} c_\alpha(\log c_\alpha - 1) + \sum_{\alpha\neq\alpha'} c_\alpha c_{\alpha'}.$$

We introduce the nematic order parameter S via $c_3 = c(1+2S)/3$ and $c_1 = c_2 = c(1-S)/3$, with $c = \sum_{\alpha=1}^{3} c_\alpha$.

(c) *(5 points)* Describe in words what is meant by nematic order and make a sketch of such an ordered system. Why are nematic systems sometimes called partially ordered systems?

(d) *(5 points)* Show that S is a suitable order parameter for nematic order.

(e) *(5 points)* Determine $\psi(c, S)$. For a given c one needs to determine S such that it minimises ψ. Show that $S = 0$ is a solution of $(\partial\psi/\partial S)_c = 0$ for any c. With which phase do you associate $S = 0$?

(f) *(5 points)* Argue on the basis of $(\partial^2\psi/\partial S^2)_c$ at $S = 0$ that ψ is minimised by $S \neq 0$ at sufficiently high c. Which phase do you associate with $S \neq 0$?

Problem 3: Electrostatic screening (*20 points*)

The Ornstein-Zernike equation for a n-component bulk system is given by

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^{n} \rho_k \int d\mathbf{r}'\, c_{ik}(r')h_{kj}(|\mathbf{r}-\mathbf{r}'|), \quad i,j = 1,...,n.$$

Here, $h_{ij}(r)$ and $c_{ij}(r)$ are the indirect and direct correlation functions between a pair of particles of species i and j. Furthermore, ρ_k is the (bulk) number density of species k.

(a) *(5 points)* Define $H_{ij}(k) = \sqrt{\rho_i\rho_j}\int d\mathbf{r}\, h_{ij}(r)e^{-i\mathbf{k}\cdot\mathbf{r}}$ and $C_{ij}(k) = \sqrt{\rho_i\rho_j}\int d\mathbf{r}\, c_{ij}(r)e^{-i\mathbf{k}\cdot\mathbf{r}}$. Show that

$$\mathbf{H}(k) = [\mathbf{I} - \mathbf{C}(k)]^{-1} \cdot \mathbf{C}(k),$$

where we defined the matrices $[\mathbf{H}]_{ij} = H_{ij}$, $[\mathbf{C}]_{ij} = C_{ij}$ and $\mathbf{I}$ is the identity matrix. Are $\mathbf{H}$ and $\mathbf{C}$ symmetric? Explain why or why not.

As an approximate closure relation, we take the random-phase approximation $c_{ij}(r) = -\beta\phi_{ij}(r)$, with $\phi_{ij}(r)$ the pair potential between species i and j. In the following questions you may use the following result for $\alpha \in \mathbb{R}$:

$$\int \frac{d\mathbf{k}}{(2\pi)^3}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{k^2+\alpha^2} = \frac{1}{4\pi}\frac{e^{-\alpha r}}{r}, \quad \alpha > 0.$$

(b) *(5 points)* Consider a two-component system of monovalent point ions ($i = \pm$) with charges $\pm e$ in a medium with dielectric constant ϵ at temperature T. Furthermore, we have $\rho_+ = \rho_- = \rho$. Determine $\mathsf{C}(k)$. To compute the Fourier transform, one has to do the regularisation procedure $1/r \to e^{-\gamma r}/r$ with $\gamma \downarrow 0$ at the end of the calculation.

(c) *(10 points)* Show that $h_{ij}(r) = D_{ij} \exp(-\kappa r)/r$ and determine expressions for D_{ij} and κ. What does κ physically represent? How does your result compare with Debye-Hückel theory?

Problem 4: Entropy production (*15 points*)

Consider an entropy production of the form

$$\sigma = \sum_{i=1}^{n} J_i X_i,$$

where the thermodynamic fluxes J_i are related to thermodynamic forces X_i with $i = 1, ..., n$ via the linear phenomenological relations

$$J_i = \sum_{k=1}^{n} L_{ik} X_k,$$

with L_{ij} being constant phenomenological coefficients.

(a) *(5 points)* When fluxes and thermodynamic forces form a set of independent variables, the kinetic coefficients satisfy the Onsager reciprocal relations: $L_{ik} = L_{ki}$ for $i, k = 1, ..., n$. What is the physical reason behind these relations?

(b) *(10 points)* Consider a solid with temperature distribution $T = T(\mathbf{r}, t)$ enclosed by isothermal walls. You may neglect any particle transport, convection, and thermal expansion of the solid. Within linear phenemonology we have that the energy flux is given by $\mathbf{J}_\epsilon = L_{\epsilon\epsilon} \nabla(1/T)$, which is associated with the internal energy density ϵ. Show that

$$\frac{\partial}{\partial t} \int d\mathbf{r}\, \sigma = -2 \int d\mathbf{r}\, \rho \frac{c_{\mathrm{V}}}{T^2} \left(\frac{\partial T}{\partial t} \right)^2,$$

with ρ the number density of the solid and c_{V} the specific heat capacity at constant volume. What does this result imply for stationary states?

◡̈ END OF EXAM ◡̈