Institute of Theoretical Physics
University of Warsaw

Final exam Statistical Physics B

Monday, 27 January 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: Stationary solution of the Langevin equation (*40 points*)

Consider a stochastic process described by the real causal variable $\xi(t)$ for which $C_\xi(t) = \langle \xi(\tau)\xi(\tau+t)\rangle$ depends only on time t, where the brackets define an equilibrium ensemble average. This is called a wide-sense stationary stochastic process. We define the power spectral density as

$$S_\xi(\omega) = \lim_{T\to\infty} \frac{1}{T} \left\langle \left| \int_{-T/2}^{T/2} dt\, \xi(t) e^{i\omega t} \right|^2 \right\rangle.$$

Furthermore, we define the Fourier transform $\tilde{F}$ of a function F as

$$\tilde{F}(\omega) = \int_{-\infty}^{\infty} dt\, F(t) e^{i\omega t}, \quad F(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, \tilde{F}(\omega) e^{-i\omega t}.$$

(a) *(5 points)* Prove that

$$S_\xi(\omega) = \int_{-\infty}^{\infty} dt\, C_\xi(t) e^{i\omega t} = \int_0^{\infty} dt\, C_\xi(t) \cos(\omega t).$$

We will apply this result to the Langevin equation in the stationary limit. 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.

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

(c) *(5 points)* Prove that the velocity response is given by $\tilde{v}(\omega) = \tilde{\chi}(\omega)\tilde{f}(\omega)$ and determine $\tilde{\chi}(\omega)$. What is $\chi(t)$ for $t < 0$? Give a short derivation.

(d) *(10 points)* Derive a differential equation for the quantity $v_T(t)$ which equals $v(t)$ for $-T/2 < t < T/2$ and is zero otherwise. Use this result to prove that

$$S_v(\omega) = \frac{S_f(\omega)}{(m\omega)^2 + \zeta^2}.$$

(e) *(10 points)* Determine $\langle v(\tau)v(\tau+t)\rangle$ in the stationary limit by applying the expression derived in (a). Use this result to determine Γ by invoking the equipartition theorem. Why is the latter relation sometimes called the second fluctuation-dissipation theorem?

(f) *(5 points)* Do we have in this case that $\tilde{\chi}''(\omega) = (\beta\omega/2)S_v(\omega)$? What is the underlying (physical) reason? Explain clearly your answer.

Problem 2: Phase transitions (*25 points*)

Consider the Flory-type free energy

$$\beta a^3 \mathcal{F}[\phi] = \int d\mathbf{r}\ \left\{\kappa|\nabla\phi(\mathbf{r})|^2 + \phi(\mathbf{r})\ln\phi(\mathbf{r}) + [1-\phi(\mathbf{r})]\ln[1-\phi(\mathbf{r})] + \chi\phi(\mathbf{r})[1-\phi(\mathbf{r})]\right\},$$

with a an (irrelevant) length scale parameter, κ a stiffness parameter, $\phi(\mathbf{r})$ a local volume fraction, and χ an energetic parameter.

(a) *(5 points)* Explain in words how you would derive such a free energy from first principles and what kind of approximations you need to employ.

(b) *(10 points)* Derive the spinodal for the free energy above for a bulk system. Explain why χ^{-1} plays the role of temperature and plot the spinodal as function of ϕ and χ^{-1}. Mark important points in your plot, such as possible critical points. What does a spinodal physically represent?

(c) *(5 points)* What kind of phase transition does the above free energy describe? Are such phase transitions within this model an example of spontaneous symmetry breaking? If so what kind of symmetry is broken?

(d) *(5 points)* Does the given free energy allow for the existence of Goldstone modes? Explain your answer.

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.

(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 $\mathbf{C}(k)$. 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? You may use the following result for $\alpha \in \mathbb{R}$:

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

Problem 4: Onsager reciprocal relations (*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)* Suppose the fluxes are linearly dependent $\sum_{i=1}^{n} a_i J_i = 0$ with $a_n \neq 0$. Prove that in this case Onsager reciprocity $L_{ik} = L_{ki}$ is still valid for $i, k = 1, ..., n$.

◡̈ END OF EXAM ◡̈