INSTITUTE OF THEORETICAL PHYSICS
UNIVERSITY OF WARSAW

Mid-term exam (kolokwium) Statistical Physics B

Monday, 25 November 2024, 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: Classical ideal gases (*25 points*)
Consider N classical particles in a volume V at temperature T. We assume that the particles are non-interacting with Hamiltonian,

$$H(\mathbf{p}^N) = \sum_{i=1}^{N} g(\mathbf{p}_i),$$

where g is an arbitrary function. We used the notation $\mathbf{p}^N = (\mathbf{p}_1, ..., \mathbf{p}_N)$, with $\mathbf{p}_i$ the momentum of particle $i = 1, ..., N$.

(a) *(5 points)* What is the appropriate ensemble for this system? What is the corresponding thermodynamic potential? Compute this thermodynamic potential in the thermodynamic limit.

(b) *(5 points)* Compute the equation of state for this system, i.e., $p(\rho, T)$ with $\rho = N/V$. How does your expression depend on the specific form of g? Explain your answer.

Consider now the specific case where $g(\mathbf{p}) = c|\mathbf{p}|$ with c the speed of light. We consider this so-called ultrarelativistic gas in the grand-canonical ensemble.

(c) *(5 points)* Find the grand canonical partition function for this system and the corresponding thermodynamic potential.

(d) *(10 points)* Determine the average number of particles $\langle N \rangle$. Compute the internal energy, the entropy, and the pressure for this system and express them in terms of $\langle N \rangle$ (i.e., eliminate μ from your expressions). Are the values of these thermodynamic quantities different in the canonical ensemble? Why or why not?

Problem 2: Keesom interactions *(20 points)*
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) *(5 points)* 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, high-temperature result is given by

$$\beta w(r) = -\frac{1}{2}\left(\frac{1}{4\pi}\right)^2 \beta^2 \int d\mathbf{e}_1 \int d\mathbf{e}_2\, v(r, \mathbf{e}_1, \mathbf{e}_2)^2,$$

where we have neglected any radius-independent terms (why can we do this?).

(b) *(10 points)* Evaluate the expression found in (a) explicitly for the dipole-dipole interaction potential. (*Hint: First compute* $\int d\mathbf{e}_i\, \mathbf{e}_i \mathbf{e}_i$.) Show that

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

(c) *(5 points)* 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?

Problem 3: The first Yvon-Born-Green equation (*10 points*)

Consider the potential energy $\Phi(\mathbf{r}^N) = \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) + \sum_{i<j} v(\mathbf{r}_i, \mathbf{r}_j)$. Prove that

$$\nabla\rho(\mathbf{r}) + \beta\rho(\mathbf{r})\nabla V_{\text{ext}}(\mathbf{r}) = -\beta \int d\mathbf{r}'\, \rho^{(2)}(\mathbf{r}, \mathbf{r}')\nabla v(\mathbf{r}, \mathbf{r}').$$

What is the physical interpretation of this equation? As usual, $\rho(\mathbf{r})$ is the one-particle density, and $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ is the ensemble average of the two-body density operator.

Problem 4: The hard-rod fluid in one spatial dimension (*40 points*)

For a one-dimensional hard-rod fluid the intrinsic Helmholtz free energy functional $\mathcal{F}[\rho]$ functional is analytically known. It is given by

$$\beta\mathcal{F}[\rho] = \int_{-\infty}^{\infty} dz\, \rho(z)\left\{\ln\left[\frac{\rho(z)\Lambda}{1 - t(z)}\right] - 1\right\}, \quad t(z) = \int_{z-\sigma}^{z} dz'\, \rho(z').$$

Here $\rho(z)$ is the one-body density profile and Λ is the thermal wavelength.

(a) *(5 points)* Derive from $\mathcal{F}[\rho]$ the Helmholtz free energy density and pressure for the homogeneous hard-rod fluid. Express your result in terms of the one-dimensional packing fraction $\eta = \rho\sigma$, with ρ the number density and σ the length of the rods. Interpret the result for the pressure in terms of the free volume available to the centres of the rods.

(b) *(5 points)* Derive an expression for the isothermal compressibility $\kappa_{\text{T}} = -L^{-1}(\partial L/\partial p)_{N,T}$ for the homogeneous hard-rod fluid. What happens to κ_T when $\eta \to 1$? Give a physical interpretation of your results.

The excess functional can be expressed in terms of weighted densities $\{n_\alpha | \alpha = 0, 1\}$,

$$\beta\mathcal{F}_{\text{ex}}[\rho] = \int_{-\infty}^{\infty} dz\, \Phi(\{n_\alpha(z)\}), \quad \Phi(\{n_\alpha\}) = -n_0(z)\ln[1 - n_1(z)].$$

This relation is exact. The weighted densities are defined by

$$n_\alpha(z) = \int_{-\infty}^{\infty} dz'\, \rho(z') w^{(\alpha)}(z - z'), \quad \alpha \in \{0, 1\},$$

with weight functions

$$w^{(0)}(z) = \frac{1}{2}[\delta(z - R) + \delta(z + R)], \quad w^{(1)}(z) = \Theta(R - |z|),$$

with Θ the Heaviside step function and $R = \sigma/2$.

(c) *(5 points)* Consider $V_{\text{ext}}(z) = 0$. In this case, show that $\Phi(\{n_\alpha\})$ is the excess Helmholtz free energy density (per $k_{\text{B}}T$) for a homogeneous fluid.

(d) *(10 points)* Prove for general $V_{\text{ext}}(z)$ that

$$c^{(2)}(z_1, z_2) = -\int_{-\infty}^{\infty} dz \sum_{\alpha,\beta=0,1} \frac{\partial^2 \Phi}{\partial n_\alpha(z) n_\beta(z)} \omega^{(\alpha)}(z - z_1)\omega^{(\beta)}(z - z_2),$$

Evaluate this expression explicitly in terms of $n_0(z)$ and $n_1(z)$ and the weight functions.

(e) *(5 points)* Prove that

$$\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz'\, w^{(\alpha)}(z')w^{(\beta)}(z' - z)e^{-ikz} = \tilde{w}^{(\alpha)}(k)\tilde{w}^{(\beta)}(k), \quad \alpha, \beta \in \{0, 1\}.$$

where we defined the Fourier transform of a function f as $\tilde{f}(k) = \int_{-\infty}^{\infty} dz\, f(z)e^{-ikz}$.

(f) *(10 points)* Consider the case where $V_{\text{ext}}(z) = 0$. Show that the structure factor is given by

$$S(k) = \left[1 + \frac{2\eta}{1 - \eta}\left(\frac{\sin q}{q} + \frac{\eta}{1 - \eta}\frac{1 - \cos q}{q^2}\right)\right]^{-1}, \quad q = k\sigma.$$

(*Hint: Use the result from (e).*)

(g) *(5 points)* Show that this expression for $S(k)$ reproduces the result in (b). Give representative sketches of $S(k)$ for some values of η. Do you observe crystallisation? Explain.

◡̈ END OF EXAM ◡̈