Problem Set 2 – Statistical Physics B

Problem 1: Thermodynamics

Consider a closed system with fixed internal energy E, particle number N, and volume V.

(a) Combine the first and second law of thermodynamics to write down an expression for dE. How are the pressure p, temperature T, and chemical potential μ related to $E = E(S, V, N)$?

The Helmholtz free energy is defined as $F(N, V, T) = E(S(T, V, N), V, N) - TS(T, V, N)$.

(b) How are the pressure p, entropy S, and chemical potential μ related to $F = F(N, V, T)$?

(c) Derive the three Maxwell relations for a system at fixed (N, V, T).

We now wish to describe the system in terms of the independent variables T, p, and N, i.e. the volume is no longer an independent variable.

(d) Write down the relevant thermodynamic potential $G(N, p, T)$ for this system in terms of $F(N, V, T)$. This is called the Gibbs free energy.

(e) How are μ, V, and S related to G?

(f) From extensivity we can write $G(N, p, T) = Ng(p, T)$. What is the physical interpration of $g(p, T)$?

(g) Show that $(\partial\mu/\partial p)_T = v$, where $v = V/N$ being the specific volume.

Problem 2: The Euler form of the internal energy

(a) Let f be a homogeneous function of degree 1. That is

$$f(u_1, ..., u_n) = \lambda f(x_1, ..., x_n),$$

for all $\lambda \in \mathbb{R}$ and $u_i = \lambda x_i$. Prove Euler's theorem

$$f(x_1, ..., x_n) = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right)_{\{x_j\}\neq x_i} x_i.$$

(b) Consider the internal energy $E(S, V, N)$ with $dE = TdS - pdV + \mu dN$. Use the result in (a) to find the Euler form of the internal energy

$$E(S, V, N) = TS - pV + \mu N.$$

(c) Derive the Gibbs-Duhem relation

$$d\mu = -sdT + vdp,$$

where $s = S/N$ and $v = V/N$.

Problem 3: The classical limit of the quantum harmonic oscillator

Consider a one-dimensional harmonic oscillator with energy states $\epsilon_n = \hbar\omega(n + 1/2)$, with $n = 0, 1, 2, ...$ the quantum number enumerating the energy levels, ω the angular frequency, and $h = 2\pi\hbar$ the Planck constant.

(a) Explicitly compute the (quantum-mechanical) canonical partition function $Z_q(T)$ for this system. What is the high-temperature limit for this quantity, where $T \gg \hbar\omega/k_B$?

A classical harmonic oscillator is described by the Hamiltonian $H(x, p_x) = p_x^2/(2m) + m\omega^2 x^2/2$. Here m is the mass, p_x is the linear momentum in the x direction, and x is the amplitude of the oscillator. The classical partition function is given by

$$Z_c(T) = \frac{1}{C} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dx \, \exp[-\beta H(x, p_x)].$$

We will determine the prefactor C by imposing that $Z_c(T)$ equals $Z_q(T)$ in the high-temperature limit.

(b) Compute $Z_c(T)$ explicitly. Does this quantity depend on m? Show that $C = h$.

We conclude that

$$\sum_{n=0}^{\infty} \exp(-\beta\epsilon_n) = \frac{1}{h} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dx \, \exp[-\beta H(x, p_x)]$$

in the classical limit $\beta\hbar\omega \to 0$. In other words, every volume element $dxdp_x$ of magnitude h in the classical phase space accounts for a single quantum state.

(c) Connect this correspondence qualitatively to the Heisenberg uncertainty relation $\Delta x \Delta p_x \geq \hbar/2$.

Problem 4: The mechanical interpretation of temperature

In this problem we derive a relation between the temperature and the ensemble average of the kinetic energy. Consider a general Hamiltonian of the form

$$H(\mathbf{p}^N, \mathbf{r}^N) = K(\mathbf{p}^N) + \Phi(\mathbf{r}^N), \quad \text{with } K = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}.$$

(a) Show that

$$\sum_{i=1}^{N} \left\langle \mathbf{p}_i \cdot \frac{\partial H}{\partial \mathbf{p}_i} \right\rangle = 2\langle K \rangle,$$

where the angular brackets denote the canonical ensemble average.

(b) Show also that

$$\left\langle p_{i\alpha} \frac{\partial H}{\partial p_{i\alpha}} \right\rangle = k_B T,$$

with $\alpha = x, y, z$. Hint: use partial integration.

(c) Combine the previous results, to show that $\langle K \rangle = (3/2)Nk_B T$. What is the generalisation of this expression in D spatial dimensions?

(d) Does your result depend on the form of Φ? Give explanations why.