Problem Set 12 – Statistical Physics B

Problem 1: Free energy minimisation

In the lecture, we discussed that for an isolated system the internal energy is minimal. Show that for a system that can only exchange energy with its surroundings, that the Helmholtz free energy is minimal in equilibrium.

Problem 2: Heat equation

(a) Empirically it is known that the heat or energy current density is related to temperature gradients via the law of Fourier $\mathbf{J}_\epsilon = -k\nabla T$, with k the thermal conductivity. Connect the kinetic coefficient $L_{\epsilon\epsilon}$ to k.

(b) The heat equation is

$$\frac{\partial}{\partial t}T(\mathbf{r},t) = \kappa\nabla^2 T(\mathbf{r},t),$$

with κ the thermal diffusivity. Express κ in terms of the number density ρ, isobaric heat capacity per particle c_P, and $L_{\epsilon\epsilon}$. You may assume that the material is a solid or liquid.

(c) Consider now a system that is translationally invariant in the (x, y) plane, i.e. $T(\mathbf{r}, t) = T(z, t)$. We impose boundary conditions $\lim_{z\to\pm\infty} T(z, t) = T_\pm$, $\forall t > 0$. As the initial condition, we take $T(z, 0) = T_- + \Theta(z)(T_+ - T_-)$. Determine $T(z, t)$. In particular show that $T(z, t) = T(z/\xi)$, and give an expression for ξ. How do you interpret this result?

(d) Show that for $|z/\xi| \ll 1$, we find

$$T(z,t) \sim \frac{1}{2}(T_+ + T_-) + \frac{T_+ - T_-}{\sqrt{\pi}\xi(t)}z,$$

and give a physical interpretation for $\xi(t)$.

(e) Determine the entropy production density $\sigma(\mathbf{r}, t)$ and plot this quantity for several values of $\xi(t)$. What do you conclude? How does the total entropy production $\int d\mathbf{r}\,\sigma$ evolve as a function of t?

Problem 3: Entropy fluctuations

(a) Use the Einstein fluctuation theory to prove that

$$\left\langle \frac{\partial \Delta S}{\partial \alpha_i}\alpha_j \right\rangle = -k_\mathrm{B}\delta_{ij},$$

where $\Delta S = S(E, \boldsymbol{\rho}) - S(E, \boldsymbol{\rho}_\mathrm{eq})$ and $\boldsymbol{\alpha} = \boldsymbol{\rho} - \boldsymbol{\rho}_\mathrm{eq}$, with $\boldsymbol{\rho}$ the generalised density vector. What are examples of components of $\boldsymbol{\rho}$?

(b) Use the result of the previous question to show that

$$\langle \boldsymbol{\alpha}\boldsymbol{\alpha}\rangle = k_\mathrm{B}\mathbf{g}^{-1},$$

with $g_{ij} = \partial^2 S/\partial\rho_i\partial\rho_j|_{\boldsymbol{\rho}=\boldsymbol{\rho}_\mathrm{eq}}$.

Problem 4: Principle of minimum entropy production

The principle of minimum entropy production shows that under certain circumstances the total entropy production is minimised for a stationary state, where the state of the system does not evolve in time.

(a) Is a stationary state necessarily an equilibrium state? If not, what is the difference?

(b) Consider a one-component solid with some fixed temperature distribution on the walls in which the system is enclosed. Write down the equation for the temperature distribution assuming that the kinetic coefficient $L_{\epsilon\epsilon}$ is a constant. What is the equation for the stationary state?

(c) Write down an expression for $P = \int_V d\mathbf{r}\,\sigma$. What temperature distributions minimize this functional?

(d) Prove that

$$\frac{\partial P}{\partial t} = -2 \int_V d\mathbf{r}\, \frac{c_{\mathrm{V}}}{T^2} \left(\frac{\partial T}{\partial t} \right)^2 \leq 0.$$

with c_{V} the heat capacity per particle at constant volume. What do you conclude for stationary states in this example?