Sheet 02

Discussion: Thursday 16.05.2024 (in two weeks!)

Exercise 1 Fluctuations and entropy

In Chapter 26 we have discussed fluctuations and entropy. The assumption was that all subsystems α remain in *changing equilibrium*, i.e. we can introduce entropy also for the fluctuating subsystems

$$S_\alpha = S_\alpha^{\text{eq}} + \delta S_\alpha.$$

1. Expand $S_{\mathcal{S}} = \sum_\alpha S_\alpha$ with
$$S_{\mathcal{S}} = S_{\mathcal{S}}^{\text{eq}} + \delta_f^{(1)} S_{\mathcal{S}} + \delta_f^{(2)} S_{\mathcal{S}}$$
in the fluctuations δX_α^i up to second order using the Gibbs form of subsystems in entropy representation.
Argue why $\delta_f^{(1)} S_{\mathcal{S}} = 0$.
2. Show that
$$\delta_f^{(2)} S_{\mathcal{S}} = -\frac{1}{2T_{\mathcal{S}}} \sum_\alpha \left(\delta T_\alpha \delta S_\alpha + \sum_{i=1}^n \delta \left(\frac{\gamma_\alpha^i}{T\alpha} \right) \delta X_\alpha^i \right).$$
3. Derive $\delta_f^{(2)} S_{\mathcal{S}}$ for a simple fluid. Note that for a fluid in (local) equilibrium only three of the six variables can be independent, e.g. (T, P, N). Use
$$C_{P\alpha} = T_\alpha \left. \frac{\partial S_\alpha}{\partial T_\alpha} \right|_P, \quad \kappa_{T\alpha} = -\frac{1}{V_\alpha} \left. \frac{\partial V_\alpha}{\partial P_\alpha} \right|_T, \quad \alpha = \frac{1}{V_\alpha} \left. \frac{\partial V_\alpha}{\partial T_\alpha} \right|_P$$
and the Maxwell relations.

Exercise 2 Thermodynamic potentials and equilibrium

In chapter 9 it is shown that the free energy F is the appropriate thermodynamic potential, which becomes minimal at equilibrium if we keep T constant through a reservoir. Perform a corresponding argument for the Gibbs energy

$$G(T, P, \mu),$$

as well as the enthalpy

$$H(S, P, \mu).$$

Derive the condition for the extremum and show that these are minima.

Exercise 3 Helmholtz equation

One can derive the Helmholtz equation for $\frac{\partial E}{\partial V}\big|_T$ in a different way without using Maxwell relations. To do this, consider $\mathrm{d}S$ and express $\mathrm{d}E$ in other variables. Note: You will need other second derivatives.

Exercise 4 Exercise 3: Reversible work

Our system S does reversible work $-\xi dX$. How much heat do you have to add to S to keep the temperature T constant?