6 Thermodynamics (2) and canonical ensemble

6.1: Heat engine

Exercise 5.23 from Reif's book

6.2: Adiabats and Isotherms

Can isotherms and adiabats for a simple gas or liquid cross more than once?

6.3: Paramagnet

As a model of a paramagnet, one can consider a system of $N \gg 1$ localized particles with spin 1/2. We neglect magnetic interactions between the spins. The only contribution to the energy is the Zeeman energy in an applied magnetic field,

$$E = -2 \sum_{j=1}^{N} s_i \mu_B H,$$

where H is the magnetic field strength, μ_B is the Bohr magneton, and s_i takes the values $\pm 1/2$, $i = 1, \ldots, N$.

(a) Calculate the number of microstates $\Omega(E)$ in which the total energy of the N spins is between E and $E + \delta E$. Use the fact that the number of spins, N, is large and take the energy uncertainty δE large in comparison to the microscopic energy scale $\mu_B H$ but small in comparison to $N \mu_B H$.

(b) Use your answer to (a) to calculate the temperature T of the system of spins.

(c) Express the energy E, the entropy S, and the Helmholtz free energy F in terms of T.

(d) Calculate the canonical partition function $Z(T)$ for the same system of spins.

(e) Use your answer to (d) to calculate the energy E, the entropy S, and the Helmholtz free energy F.

Suggested problems for further study:

6.4: Heat engine

At low temperatures, the heat capacity of liquid ^{3}He is proportional to the absolute temperature, $C = \alpha T$, where α is a proportionality constant. Two reservoirs of liquid ^{3}He of equal size are used as a source and a sink for a heat engine. Initially, their temperatures are T_1 and T_2, respectively. Finally, as a result of the operation of the heat engine, the two reservoirs attain a common temperature T_f.

(a) What is the total amount of work done by the heat engine. Express your answer in terms of α, T_1, T_2, and T_f.

(c) Use arguments based on entropy considerations to derive an inequality relating T_f to the initial temperatures T_1 and T_2.

(d) For given initial temperatures T_1 and T_2, what is the maximum amount of work obtainable from the heat engine?

6.5: Piezoelectricity

If an elastic rod subject to a tension force f is placed in an electric field $\mathcal{E}$, work done by the rod has two contributions: Work done against tension, $dW_{\text{tension}} = -f dL$, and work done against the electric field, $dW_{\text{field}} = -EdP$. Here L is the length of the rod and P is its polarization. Hence, for a quasi-static process where the length and the polarization the rod are changed, the change dE of the rod's energy is written

$$dE = TdS + f dL + \mathcal{E}dP.$$

(a) Typically we are interested in a setup where not the entropy S, the length L, and the polarization P are specified, but the temperature T, the tension f and the electric field $\mathcal{E}$. Derive a thermodynamic potential G that is a function of these three variables and express dG in terms of dT, df and $d\mathcal{E}$. This thermodynamic potential is sometimes called the "piezoelectric Gibbs function".

(b) Derive the Maxwell relations

$$\left(\frac{\partial S}{\partial f}\right)_{\mathcal{E},T} = \left(\frac{\partial L}{\partial T}\right)_{\mathcal{E},f}, \quad \left(\frac{\partial S}{\partial \mathcal{E}}\right)_{f,T} = \left(\frac{\partial P}{\partial T}\right)_{\mathcal{E},f}, \quad \left(\frac{\partial L}{\partial \mathcal{E}}\right)_{f,T} = \left(\frac{\partial P}{\partial f}\right)_{\mathcal{E},T}.$$

(c) If the tension f is changed at constant electric field and temperature, heat is exchanged between the rod and its environment. Show that the corresponding heat capacity $(dQ/df)_{\mathcal{E},T}$ is equal to

$$\left(\frac{dQ}{df}\right)_{\mathcal{E},T} = LT\alpha_{f,\mathcal{E}},$$

where $\alpha_{f,\mathcal{E}}$ is the linear expansion coefficient at constant tension and electric field.

(d) Similarly, derive an equation for $(dQ/d\mathcal{E})_{f,T}$, the amount of heat exchanged when the electric field $\mathcal{E}$ is changed at constant tension and temperature. Express your answer in terms of the electric susceptibility χ_e and its derivative to temperature.

(e) Finally, express $(\partial L/\partial\mathcal{E})_{T,f}$ in terms of the derivative $\partial\chi_e/\partial f$.

The fact that piezoelectric materials couple electrical and mechanical degrees of freedom allow for many applications. Piezoelectric materials can be used to transform small mechanical changes into an electrical signal, or they can use mechanical properties (e.g., vibration of quartz plates) into an oscillating electrical signal with a very precise frequency.