

## 1 Basic Thermodynamics and Statphysics

### 1.1 Thermodynamic properties

The entropy of a classical ideal gas is given by

$$S(U, V, N) = k_B N \log \left[ \frac{V}{N} \left( \frac{4\pi m U}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} k_B N. \quad (1)$$

From this expression, calculate:

- the transformed potentials  $F(T, V, N)$  and  $G(p, T, N)$ .
- the specific heat at a constant volume,  $C_V \equiv \frac{1}{N} \left( \frac{\partial U}{\partial T} \right)_V$ .
- the coefficient of thermal expansion,  $\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$ .
- the isothermal compressibility,  $\kappa_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$ .

### 1.2 Maximal work

Find the maximal work one can extract connecting two equal volumes  $V_1 = V_2 = V$  containing equal numbers of ideal gas particles  $N_1 = N_2 = N$  that were before connection at different temperatures  $T_1 \neq T_2$ .

### 1.3 Two level system with degeneracy

Consider a system of  $N$  distinguishable particles, in which the energy of each particle can assume one of two distinct values, 0 or  $\epsilon$  (with  $\epsilon > 0$ ). The higher energy level has a  $g$ -fold degeneracy. The total energy in the system is  $E$ . Assume  $N, E \gg 1$ .

- Find the entropy of the system.
- Find the temperature as a function of  $E$ , and show that it can be negative. What happens when a system of negative temperature is allowed to exchange heat with a system of positive temperature?
- Find the occupation number of the lower energy state in terms of the temperature.
- Consider for example a system with  $E = 3N\epsilon/4$  in contact with a heat bath at temperature  $T = 500K$ , with  $g = 2$ . In what direction does the heat flow?
- The original system (uncoupled from a heat bath) is brought into contact with a similar system (with the same  $N$ ,  $E$  and  $\epsilon$ ), whereby the two systems can exchange both energy and particles. In the second system both energy levels are non-degenerate. Obtain the change in entropy of the two systems before and after they were brought together by considering the combined system within the microcanonical ensemble. Is this a reversible process?

## 1.4 Random chain model

Recent experiments permit measurement of forces on single DNA molecules or on individual polypeptide chains. In these experiments one of the endpoints of the polymer is held fixed. We can analyze these force-stretching experiments by considering a simple ideal polymer model. In this model the polymer is a chain of  $N$  rod-like monomers of length 1, which can turn in space. For simplicity restrict ourselves here to a two-dimensional system, where these turns are of 90, 180 or 270 degrees. The chain is held fixed between the points  $(0, 0)$  and  $(L, 0)$ . It has an elastic energy of  $E = -fL$ .

- (a) First consider the one-dimensional case where the chain can turn only in 180 degrees. Within a micro-canonical ensemble, calculate the entropy  $S(L, N)$  as a function of the distance  $L$  between the endpoints. Verify that in the large  $N$  limit the entropy is extensive, namely  $S(L, N) = Ns(\ell)$ , with  $\ell = L/N$ .
- (b) Repeat (a) for the two-dimensional case by allowing the chain to make turns of 90, 180 or 270 degrees.
- (c) Plot the distance  $L$  as a function of the temperature of the chain for (a) and (b). How does confining the polymer to move only in one dimension affect its length at given temperature? Elasticity in nature can either arise from entropic effects such as in polymers or from molecular forces in crystalline materials such as metals. Based on the plot, propose an experimental method to determine between the two types of materials.