Advanced statistical mechanics

(WS 12/13, FU Berlin)

Problem sheet 3

Due date: November 14, 2012

Problem 8: Entropy change (1+1+1+1+1)

We want to calculate the change in entropy ΔS as a function of the initial and final volume and temperature of a substance while it performs work according to $\delta A = p\, dV$.

a) Starting from Gibbs' fundamental equation find two functions f, g depending on V, p, and T, such that

$$\mathrm{d}S = f\ \mathrm{d}V + g\ \mathrm{d}T. \tag{1}$$

Hint: Consider the internal energy U as a function of V and T.

Now assume that the substance is an ideal gas of N particles, i.e., $p\,V = N\,k\,T$ and $U = \frac{3}{2} N\,k\,T$. Calculate the change in entropy

b) ΔS_1, during an isothermal ($T = \mathrm{const.}$) expansion from V_- to V_+,

c) ΔS_2, during isochoric ($V = \mathrm{const.}$) heating from T_- to T_+,

d) and ΔS_3, during an isobaric ($p = \mathrm{const.}$) expansion from V_- to V_+ ,

solely as a function of N, k, and the given parameters respectively.

e) Calculate the change of entropy during the isochoric heating of $1\mathrm{mol}$ of an ideal gas from $0°\mathrm{C}$ to $100°\mathrm{C}$.

Problem 9: Maxwell relations (1+2+1)

a) Consider the internal energy U as a functions of its natural variables S and V and derive $(\partial U/\partial S)_V$ from Gibbs' fundamental equation.

b) The free energy F is defined as the negative Legendre transform of U w.r.t. S,

$$F := U - TS. \tag{2}$$

Write its differential $\mathrm{d}F$ in terms of $\mathrm{d}V$ and $\mathrm{d}T$.

c) Conclude that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V . \tag{3}$$

Problem 10: Entropy of an ideal gas (1+2+1+1)

Consider an ideal gas, where

$$pV = NkT, \qquad U = \frac{f}{2} NkT, \tag{4}$$

and where k is a constant defining the temperature scale.

a) Conclude from Gibbs' fundamental equation or from the solution to Problem 8a that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V . \tag{5}$$

and calculate the heat capacity

$$C_V := \left(\frac{\partial U}{\partial T}\right)_V . \tag{6}$$

b) Show that for some curve c from (T_0, V_0) to (T, V)

$$\Delta S := \int_c \mathrm{d}S = Nk \ln\left(\frac{T^{f/2}V}{T_0^{f/2}V_0}\right). \tag{7}$$

Hint: The result from Problem 9 can be used.

c) Argue that there must be a function depending only on N such that

$$S(T, V, N) = Nk \ln\left(\frac{T^{f/2}V}{f(N)}\right) \tag{8}$$

d) From the fact that V and N are extensive variables of S, i.e. $S(T, \lambda V, \lambda N) = \lambda S(T, V, N)$ for any $\lambda > 0$, find that

$$f(N) = \Phi N \tag{9}$$

for some constant Φ (that is independent of all the variables). What is the final result for the entropy of an ideal gas of N particles at temperature T in a volume V?

Problem 11: Mixing entropy of an ideal gas (1+2+1)

We consider two ideal gases of N_1 and N_2 identical particles of volumes V_1 and V_2 separated by a partition wall and coupled to a temperature bath a temperature T. In this problem we want to investigate the entropy ΔS generated by the mixing of the two gases when the partition wall is removed. We denote the pressures of the gases before the mixing by p_1 and p_2 and after the mixing by p.

a) Using the result from Problem 10d write ΔS in terms of p_1, p_2, p, N_1 and N_2.

b) What is ΔS for the special case where $p_1 = p_2$? Is the mixing process reversible in that case? In what sense?

c) Now consider $p_2 = 3p_1$ and one mole, i.e., a total particle number of $N_1 + N_2 = N_A \approx 6 \cdot 10^{23}$. What is the value of ΔS in that case?

Brief information

- The problem sheets will be distributed always on Tuesdays.
- Each problem sheet will allow for earning 16-20 points.
- The solutions can be handed in by groups of two students.
- You are permitted to work together with more students, but then indicate all their names on your completed homework.
- The solution is to be handed in at latest in the tutorial on the due date. If solutions are repeatedly (more than once) handed in late only half of the achieved point will be awarded.
- It is necessary to have achieved at least 60 percent of all points in order to be allowed to participate in the exam.
- The exam will determine the final grade.