

Write your name and student number on each sheet that you hand in.

Problem 1

A spin system has a three-fold degenerate ground state and a two-fold degenerate excited state at energy ε . The interaction between the spins can be neglected. The total number of spins is indicated by N . The number of spins in the excited state is indicated by n .

- a) Make plausible that the number of microstates of the system can be written as

$$\Omega(n) = \frac{N! 3^{N-n} 2^n}{\binom{N-n}{n} n!}$$

- b) Calculate the energy of this system (in terms of ε , k , T and N) using the microcanonical ensemble method.
c) Calculate the heat capacity of the system.

Problem 2

A diatomic molecule may to a good approximation be considered as vibrating in one-dimensional simple harmonic motion with circular frequency ω . According to quantum mechanics such a system possesses an infinite set of non degenerate energy

levels with energies $\varepsilon = \hbar\omega \left(r + \frac{1}{2} \right)$, $r = 0, 1, 2, 3, \dots$

- a) Show that the vibrational partition function is given by

$$Z_{\text{vib}} = \frac{e^{-\frac{\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}}, \quad \text{where } \beta = \frac{1}{kT}.$$

- b) Derive an expression for the average vibrational energy of a molecule.
c) How does the vibrational partition function Z_{vib} , combine with the rotational partition function Z_{rot} and translational partition function Z_{tr} of the molecule to the total partition function Z of the entire gas (with N particles).
d) Derive an expression for the vibrational contribution to the entropy of the gas.

Problem 3

- a) Draw a p - T phase diagram for a normal substance, indicating solid, liquid and gaseous phases as well as the special points in the diagram.

- b) The vapour pressure curve is given by $P = C \exp \left\{ -\frac{\Delta_{\text{vap}} H}{RT} \right\}$

In this expression $\Delta_{\text{vap}} H$ denotes the latent heat of vaporization per mol; R is the gas constant.

Give a derivation of this formula starting from the equation of Clausius-Clapeyron. Determine the constant C in terms of given quantities and the normal boiling point T_b at pressure $P_0 (= 1 \text{ atm.})$

Problem 4

The partition function of a gas can be written as

$Z = \sum_{\{n_1, n_2, n_3, \dots\}} e^{-\beta\{n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \dots\}}$ where the sum goes over all the possible values of the occupation numbers n_i of the single particle states.

- a) Derive, starting from the expression given above, the following relation for the average occupation number of the single particle state with energy ε_i :

$$\bar{n}_i = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \varepsilon_i}$$

- b) Show that the partition function of a photon gas is given by $Z_{\text{ph}} = \prod_{r=1}^{\infty} \frac{1}{1 - e^{-\beta\varepsilon_r}}$

- c) Show that the average number of photons of frequency ω is given by

$$\bar{n}(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

- d) Show that the total number of photons N is given by $N = b \frac{Vk^3 T^3}{\hbar^3 \pi^2 c^3}$

Hint: Remember that the density of states for a particles in a box with volume V is given by $f(p)dp = \frac{4\pi V p^2 dp}{h^3}$.

Problem 5

Consider a gas of N non interacting purely relativistic electrons with single particle energy $\varepsilon = pc$. V denotes the volume of the gas.

- a) Make plausible that the density of states for a free electron gas is given by

$$f(p) = \frac{8\pi V p^2 dp}{h^3}$$

The average occupation number of a single particle state with energy ε is given by:

$$n(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$$

- b) Derive an expression for the Fermi energy ε_F of this gas (in terms of N , V , h and c).
- c) Calculate the total energy of the gas assuming $T = 0$ (in terms of N and ε_F).
- d) Derive an expression for the pressure of this gas assuming $T = 0$ (in terms of N , V , h and c).

Physical constants:

Getal van Avogadro: $N_A = 6,02 \times 10^{23} \text{ mol}^{-1}$

Constante van Planck: $h = 6,626 \times 10^{-34} \text{ Js}$

$$\hbar = \frac{h}{2\pi} = 1,055 \times 10^{-34} \text{ Js}$$

Constante van Boltzmann: $k = 1,381 \times 10^{-23} \text{ J K}^{-1}$

Gasconstante: $R = 8,315 \text{ J mol}^{-1} \text{ K}^{-1}$

Lichtsnelheid: $c = 3 \times 10^8 \text{ m s}^{-1}$

Rustmassa elektron $m_e = 9,11 \times 10^{-31} \text{ kg}$

Rustmassa proton $m_p = 1,67 \times 10^{-27} \text{ kg}$

Bohr magneton $\mu_B = 9,27 \times 10^{-24} \text{ A m}^2$

Integrals:

n	$\int_0^{\infty} dx x^n e^{-ax^2} \quad (a > 0)$	$\int_0^{\infty} \frac{x^n dx}{e^x - 1}$	$\int_0^{\infty} \frac{x^n dx}{e^x + 1}$	$\int_0^{\infty} \frac{x^n e^x}{e^x - 1} dx$	$\int_0^{\infty} x^n \ln(1 - e^{-x}) dx$
0	$\frac{1}{2} \sqrt{\left(\frac{\pi}{a}\right)}$	diverges	ln 2	diverges	$-\frac{\pi^2}{6}$
1/2	$\frac{0,6127}{a^{3/4}}$	$2,612 \frac{\sqrt{\pi}}{2}$	0,6781	diverges	$-1,341 \frac{\sqrt{\pi}}{2}$
1	$\frac{1}{2a}$	$\frac{\pi^2}{6}$	$\frac{\pi^2}{12}$	diverges	-1,202
3/2	$\frac{0,4532}{a^{5/4}}$	$1,341 \frac{3\sqrt{\pi}}{4}$	1,153		$-1,127 \frac{3\sqrt{\pi}}{4}$
2	$\frac{1}{4a} \sqrt{\frac{\pi}{a}}$	2,404	1,803	$\frac{\pi^2}{3}$	$-\frac{\pi^4}{45}$
5/2	$\frac{1,662}{a^{7/4}}$	$1,127 \frac{15\sqrt{\pi}}{8}$	3,083		-3,505
3	$\frac{1}{2a^2}$	$\frac{\pi^4}{15}$	$\frac{7\pi^4}{120}$	7,212	-6,221
7/2	$\frac{0,5665}{a^{9/4}}$	12,268	11,184		
4	$\frac{3\sqrt{\pi}}{8a^{5/2}}$	24,886	23,331	$\frac{4\pi^4}{15}$	