

# Test exam for T4

## Thermodynamics and Statistical Physics 2018-2019

**Read these instructions carefully before making the exam!**

- Write your name and student number on *every* sheet.
- *Make sure to write readable for other people than yourself. Points will NOT be given for answers in illegible writing.*
- *Language; your answers have to be in English.*
- Use a *separate* sheet for each problem (see figure below).
- Use of a (graphing) calculator is allowed.
- This exam consists of 3 problems.
- The weight of the problems is Problem 1 (P1=30 pts); Problem 2 (P2=30 pts); Problem 3 (P3=30 pts). Weights of the various subproblems are indicated at the beginning of each problem.
- The grade of the exam is calculated as  $(P1+P2+P3+10)/10$ .
- For all problems you have to write down your arguments and the intermediate steps in your calculation, *else the answer will be considered as incomplete and points will be deducted.*

PROBLEM 1 Name S-number		PROBLEM 2 Name S-number		PROBLEM 3 Name S-number	
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PROBLEM 1 Score:  $a+b+c+d+e=7+7+6+5+5=30$

Suppose we have a 3D classical gas consisting of  $N$  identical molecules that are trapped in a potential well. The gas is in equilibrium with a heat bath with temperature  $T$ . The molecules have some internal structure leading to three principal rotation axes. This leads to the following expression for the total energy of one molecule,

$$E = E_{kin} + E_{pot} + E_{rot}$$

with  $E_{kin} = \frac{1}{2}M(v_x^2 + v_y^2 + v_z^2)$ ;  $E_{pot} = \alpha(x^4 + y^4 + z^4)$  and  $E_{rot} = \frac{1}{2} \frac{L_1^2}{I_1} + \frac{1}{2} \frac{L_2^2}{I_2} + \frac{1}{2} \frac{L_3^2}{I_3}$ ,

and  $M$  the mass of the molecule,  $\vec{v} = (v_x, v_y, v_z)$  its velocity,  $\vec{x} = (x, y, z)$  its position,  $\alpha$  a constant describing the strength of the potential well,  $L_1, L_2, L_3$  the angular momenta along the three principal rotation axes and  $I_1, I_2, I_3$  the corresponding moments of inertia.

- Use the Boltzmann distribution to show that the mean energy of a molecule due to its  $x$ -component of the velocity is given by:  $\langle \frac{1}{2} M v_x^2 \rangle = \frac{1}{2} kT$ .
- State the equipartition theorem.
- Use the Boltzmann distribution to show that the mean potential energy of a molecule is given by  $\langle E_{pot} \rangle = \frac{3}{4} kT$ .
- Give an expression for the mean total energy  $\langle E \rangle$  of the gas.
- Give an expression for the heat capacity  $C_V$  of the gas.

PROBLEM 2 *Score:  $a+b+c+d+e+f=5+5+5+5+5+5=30$*

Consider a system of  $N$  molecules in equilibrium with a heat bath at temperature  $T$ . The (excitation) energy levels of a molecule are given by:

$$E_n = n\varepsilon \text{ with } n = 0, 1, 2, \dots, M - 1$$

a) Show that the partition function of a single molecule related to the excitations is:

$$Z_1 = \frac{1 - e^{-\beta\varepsilon M}}{1 - e^{-\beta\varepsilon}}$$

b) Give the probability  $P_n$  for a single molecule to be in its  $n^{\text{th}}$  excited state.

c) Show that the mean energy  $\langle E \rangle$  for a single molecule is:

$$\langle E \rangle = \varepsilon \left( \frac{1}{e^{\beta\varepsilon} - 1} - \frac{M}{e^{\beta\varepsilon M} - 1} \right)$$

d) Show that the entropy  $S$  for a single molecule is:

$$S = k \left[ \left( \frac{\varepsilon\beta}{e^{\beta\varepsilon} - 1} - \frac{M\varepsilon\beta}{e^{\beta\varepsilon M} - 1} \right) + \ln \left( \frac{1 - e^{-\beta\varepsilon M}}{1 - e^{-\beta\varepsilon}} \right) \right]$$

e) In case you may neglect interactions between the molecules and the molecules are distinguishable (e.g. they are part of a crystal with a localized position for each molecule) what would be the total energy and total entropy of the system of  $N$  molecules?

f) Give expressions for the total energy and total entropy in the limit  $T \rightarrow \infty$ .

PROBLEM 3 *Score:  $a+b+c+d=8+8+7+7$*

Consider a classical two-dimensional monoatomic gas that consists of  $N$  atoms with mass  $m$ . The ‘volume’ of this gas is given by a square with side  $L$  (and surface area  $A = L^2$ ). In this problem you only have to consider the translational motion of the atoms.

- a) Show that for an atom confined to this surface  $A$ , the number of states in which the atom has a momentum with its magnitude between  $p$  and  $p + dp$  is given by:

$$f(p)dp = \frac{2\pi A}{h^2} p dp$$

- b) Show that the single atom partition function is given by,

$$Z_1 = \frac{A2\pi mkT}{h^2}$$

- c) Give an expression for the  $N$ -atom partition function and use this to show that the Helmholtz free energy  $F$  of the 2-dimensional gas is,

$$F = -NkT \left[ \ln \left( \frac{A2\pi mkT}{Nh^2} \right) + 1 \right]$$

- d) Calculate the surface tension  $\tau$  of the 2-dimensional gas by using the expression of the Helmholtz free energy and the fundamental thermodynamic equation in two dimensions ( $dE = TdS - \tau dA$ ).

Solutions  
PROBLEM 1

a)

$$\langle \frac{1}{2} m v_x^2 \rangle = \frac{\int_{-\infty}^{\infty} \frac{1}{2} M v_x^2 e^{-\beta E} dx dy dz dv_x dv_y dv_z dL_1 dL_2 dL_3}{\int_{-\infty}^{\infty} e^{-\beta E} dx dx dy dz dv_x dv_y dv_z dL_1 dL_2 dL_3} \Rightarrow$$

$$\langle \frac{1}{2} m v_x^2 \rangle = \frac{\int_{-\infty}^{\infty} \frac{1}{2} M v_x^2 e^{-\frac{1}{2}\beta M v_x^2} dv_x \int_{-\infty}^{\infty} e^{-\beta \dot{E}} dx dx dy dz dv_y dv_z dL_1 dL_2 dL_3}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta M v_x^2} dv_x \int_{-\infty}^{\infty} e^{-\beta \dot{E}} dx dx dy dz dv_y dv_z dL_1 dL_2 dL_3} \Rightarrow$$

$$\langle \frac{1}{2} M v_x^2 \rangle = \frac{\int_{-\infty}^{\infty} \frac{1}{2} M v_x^2 e^{-\frac{1}{2}\beta M v_x^2} dv_x}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta M v_x^2} dv_x} = -\frac{\partial \ln I}{\partial \beta}$$

Where we have defined  $I = \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta M v_x^2} dv_x$ . Substitute  $z^2 = \beta v_x^2$  then  $z = \sqrt{\beta} v_x$  and  $dv_x = \frac{dz}{\sqrt{\beta}}$  and the integral becomes,

$$I = \frac{1}{\sqrt{\beta}} \int_{-\infty}^{\infty} e^{-\frac{1}{2} M z^2} dz$$

And

$$\langle \frac{1}{2} M v_x^2 \rangle = -\frac{\partial \ln I}{\partial \beta} = -\frac{\partial}{\partial \beta} \left[ \ln \frac{1}{\sqrt{\beta}} + \ln \left\{ \int_{-\infty}^{\infty} e^{-\frac{1}{2} M z^2} dz \right\} \right] = -\left[ \sqrt{\beta} \left( -\frac{1}{2} \frac{1}{\beta^{\frac{3}{2}}} \right) + 0 \right] \Rightarrow$$

$$\langle \frac{1}{2} M v_x^2 \rangle = \frac{1}{2\beta} = \frac{1}{2} kT$$

b)

For a classical system in equilibrium with a heat bath at temperature  $T$  every term in the Hamiltonian (energy) that is quadratic in one of the systems (independent) coordinates will contribute  $\frac{1}{2} kT$  to the mean energy of the system.

c)

Idem as under a) we arrive at:

$$\langle \alpha x^4 \rangle = \frac{\int_{-\infty}^{\infty} \alpha x^4 e^{-\beta \alpha x^4} dx}{\int_{-\infty}^{\infty} e^{-\beta \alpha x^4} dx} = -\frac{\partial \ln I}{\partial \beta}$$

But now with  $I = \int_{-\infty}^{\infty} e^{-\beta \alpha x^4} dx$ , and with the substitution  $z^4 = \beta x^4$  then  $z = \beta^{\frac{1}{4}} x$  and  $dx = \frac{dz}{\beta^{\frac{1}{4}}}$  and the integral becomes

$$I = \frac{1}{\beta^{\frac{1}{4}}} \int_{-\infty}^{\infty} e^{-\alpha z^4} dz$$

And

$$\langle \alpha x^4 \rangle = -\frac{\partial \ln I}{\partial \beta} = -\frac{\partial}{\partial \beta} \left[ \ln \frac{1}{\beta^{\frac{1}{4}}} + \ln \left\{ \int_{-\infty}^{\infty} e^{-\alpha z^4} dz \right\} \right] = -\left[ \beta^{\frac{1}{4}} \left( -\frac{1}{4} \frac{1}{\beta^{\frac{5}{4}}} \right) + 0 \right] \Rightarrow$$

$$\langle \alpha x^4 \rangle = \frac{1}{4\beta} = \frac{1}{4} kT$$

Consequently:  $\langle E_{pot} \rangle = \langle \alpha(x^4 + y^4 + z^4) \rangle = \langle \alpha x^4 \rangle + \langle \alpha y^4 \rangle + \langle \alpha z^4 \rangle = \frac{3}{4} kT$

d)

For a single molecule we have

$$\langle E_{tot} \rangle = \langle E_{kin} + E_{pot} + E_{rot} \rangle = \langle E_{kin} \rangle + \langle E_{pot} \rangle + \langle E_{rot} \rangle = \frac{3}{2} kT + \frac{3}{4} kT + \frac{3}{2} kT$$

Where we used the results a) and c) and used equipartition for the rotational degrees of freedom.

Thus for  $N$  molecules:

$$\langle E \rangle = N \langle E_{tot} \rangle = 3 \frac{3}{4} NkT$$

e)

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = 3 \frac{3}{4} Nk$$

The answers to problem 1a and 1c can also be obtained by using the integrals on the formula sheet.

$$\left\langle \frac{1}{2} M v_x^2 \right\rangle = \frac{\int_{-\infty}^{\infty} \frac{1}{2} M v_x^2 e^{-\frac{1}{2} \beta M v_x^2} dv_x}{\int_{-\infty}^{\infty} e^{-\frac{1}{2} \beta M v_x^2} dv_x} = \frac{1}{2} M \frac{\left( \frac{1}{2} \sqrt{\frac{\pi}{c^3}} \right)}{\left( \sqrt{\frac{\pi}{c}} \right)} = \frac{1}{4} M \frac{1}{c} = \frac{1}{4} M \frac{1}{\frac{1}{2} \beta M} = \frac{1}{2} kT$$

$$\langle \alpha x^4 \rangle = \frac{\int_{-\infty}^{\infty} \alpha x^4 e^{-\beta \alpha x^4} dx}{\int_{-\infty}^{\infty} e^{-\beta \alpha x^4} dx} = \alpha \frac{\left( \frac{1}{2} \frac{\Gamma\left(\frac{5}{4}\right)}{c^{\frac{5}{4}}} \right)}{\left( \frac{2\Gamma\left(\frac{5}{4}\right)}{c^{\frac{1}{4}}} \right)} = \frac{1}{4} \alpha \frac{1}{c} = \frac{1}{4} \alpha \frac{1}{\beta \alpha} = \frac{1}{4} kT$$

## PROBLEM 2

a) The partition function of a single molecule related to the excitations is:

$$Z_1 = \sum_{n=0}^{M-1} e^{-\beta E_n} = \sum_{n=0}^{M-1} e^{-\beta n \varepsilon} = \sum_{n=0}^{M-1} t^n = \frac{1-t^M}{1-t} = \frac{1-e^{-\beta \varepsilon M}}{1-e^{-\beta \varepsilon}}$$

b)

According to 4.14 or text above 20.11 or lecture 2 (period 1b) we have:

$$P_n = \frac{e^{-\beta E_n}}{Z_1} = \left( \frac{1-e^{-\beta \varepsilon}}{1-e^{-\beta \varepsilon M}} \right) e^{-n\beta \varepsilon}$$

c)

The mean energy of one molecule is given by,

$$\langle E \rangle = -\frac{\partial \ln Z_1}{\partial \beta} = -\frac{\partial}{\partial \beta} [\ln(1-e^{-\beta \varepsilon M}) - \ln(1-e^{-\beta \varepsilon})] = \frac{-\varepsilon M e^{-\beta \varepsilon M}}{1-e^{-\beta \varepsilon M}} + \frac{\varepsilon e^{-\beta \varepsilon}}{1-e^{-\beta \varepsilon}} \Rightarrow$$

$$\langle E \rangle = \varepsilon \left( \frac{1}{e^{\beta \varepsilon} - 1} - \frac{M}{e^{\beta \varepsilon M} - 1} \right)$$

d)

First calculate the Helmholtz free energy  $F = -kT \ln Z_1$ .

$$F = -kT \ln Z_1 = -kT [\ln(1-e^{-\beta \varepsilon M}) - \ln(1-e^{-\beta \varepsilon})].$$

And then use the definition of  $F$  namely,  $F = U - TS$  to find ( $U = \langle E \rangle$ ):

$$S = \frac{U - F}{T} = \varepsilon k \beta \left( \frac{1}{e^{\beta \varepsilon} - 1} - \frac{M}{e^{\beta \varepsilon M} - 1} \right) + k [\ln(1-e^{-\beta \varepsilon M}) - \ln(1-e^{-\beta \varepsilon})]$$



$$S = k \left[ \left( \frac{\varepsilon\beta}{e^{\beta\varepsilon} - 1} - \frac{M\varepsilon\beta}{e^{\beta\varepsilon M} - 1} \right) + \ln \left( \frac{1 - e^{-\beta\varepsilon M}}{1 - e^{-\beta\varepsilon}} \right) \right]$$

e)

The molecules behave as independent systems because of their weak interaction and the energy and entropy of all molecules can in principle be added (discussion 20.4, combining partition functions). However, we also need the molecules to be distinguishable so that:

$$Z_N = (Z_1)^N \Rightarrow \ln Z_N = N \ln Z_1$$

Thus

$$\langle E_{tot} \rangle = N\varepsilon \left( \frac{1}{e^{\beta\varepsilon} - 1} - \frac{M}{e^{\beta\varepsilon M} - 1} \right)$$

and

$$\langle S_{tot} \rangle = Nk \left[ \left( \frac{\varepsilon\beta}{e^{\beta\varepsilon} - 1} - \frac{M\varepsilon\beta}{e^{\beta\varepsilon M} - 1} \right) + \ln \left( \frac{1 - e^{-\beta\varepsilon M}}{1 - e^{-\beta\varepsilon}} \right) \right]$$

f)

In case  $T \rightarrow \infty$  all energy states for a molecule will be equally probable ( $P_n = \frac{1}{M}$ ). This means that the mean energy for a single molecule at high temperatures will be:

$$\langle E \rangle = \frac{1}{M} \sum_{n=0}^{M-1} n\varepsilon = \frac{\varepsilon}{M} \sum_{n=0}^{M-1} n = \frac{\varepsilon}{M} \sum_{n=1}^{M-1} n = \frac{\varepsilon}{M} \left( \frac{1}{2} M[M-1] \right) = \frac{1}{2} (M-1)\varepsilon$$

And thus:  $\langle E_{tot} \rangle = \frac{1}{2} N(M-1)\varepsilon$

Each molecule has M different equally likely states thus the entropy is  $k \ln M$  per molecule. And for the total entropy we find:  $\langle S_{tot} \rangle = Nk \ln M$ .

These expressions can also be derived by letting  $T \rightarrow \infty$  in the results from d)

$$\langle E_{tot} \rangle = N\varepsilon \left( \frac{1}{e^{\beta\varepsilon} - 1} - \frac{M}{e^{\beta\varepsilon M} - 1} \right) \approx N\varepsilon \left( \frac{1}{\beta\varepsilon + \frac{1}{2}(\beta\varepsilon)^2} - \frac{M}{M\beta\varepsilon + \frac{1}{2}(M\beta\varepsilon)^2} \right) \Rightarrow$$

$$\langle E_{tot} \rangle \approx N\varepsilon \left( \frac{M\beta\varepsilon + \frac{1}{2}(M\beta\varepsilon)^2 - M\left(\beta\varepsilon + \frac{1}{2}(\beta\varepsilon)^2\right)}{\left(\beta\varepsilon + \frac{1}{2}(\beta\varepsilon)^2\right)\left(M\beta\varepsilon + \frac{1}{2}(M\beta\varepsilon)^2\right)} \right) \approx N\varepsilon \left( \frac{\frac{1}{2}(\beta\varepsilon)^2(M(M-1))}{(\beta\varepsilon)^2(M)} \right)$$

$$= \frac{1}{2}N(M-1)\varepsilon$$

$$\langle S_{tot} \rangle = Nk \left[ \left( \frac{\varepsilon\beta}{e^{\beta\varepsilon} - 1} - \frac{M\varepsilon\beta}{e^{\beta\varepsilon M} - 1} \right) + \ln \left( \frac{1 - e^{-\beta\varepsilon M}}{1 - e^{-\beta\varepsilon}} \right) \right] \approx Nk \left[ (1-1) + \ln \left( \frac{\beta\varepsilon M}{\beta\varepsilon} \right) \right]$$

$$= Nk \ln M$$

### PROBLEM 3

a)

From the solution of the 2D-wave equation:  $\varphi = A \sin k_x x \sin k_y y$  and taking this function to vanish at  $x = y = 0$  and at  $x = y = L$  results in,

$$k_x = \frac{n_x \pi}{L} \text{ and } k_y = \frac{n_y \pi}{L} \text{ with } n_x \text{ and } n_y \text{ non-zero positive integers.}$$

The total number of states with  $|\vec{k}| < k$  is then given by, (the area of a quarter circle because we have only positive integers, with radius  $k$  divided by the area of the unit surface e.g. the surface of one state, in  $k$ -space).

$$\Gamma(k) = \frac{\frac{1}{4}\pi k^2}{\left(\frac{\pi}{L}\right)^2} = \frac{1}{4} \frac{L^2 k^2}{\pi}$$

The number of states between  $k + dk$  and  $k$  is:

$$f(k)dk = \Gamma(k + dk) - \Gamma(k) = \frac{\partial \Gamma}{\partial k} dk = \frac{1}{2} \frac{L^2 k}{\pi} dk = \frac{1}{2} \frac{Ak}{\pi} dk$$

Converting to momentum  $p = \hbar k = \frac{h}{2\pi} k$  we find,

$$f(p)dp = \left(\frac{2\pi}{h}\right)^2 \frac{1}{2} \frac{Ap}{\pi} dp = \frac{2\pi A}{h^2} p dp$$

b)

Single atom partition function (use substitution  $p = x\sqrt{2mkT}$ ):

$$Z_1 = \int_0^{\infty} \frac{2\pi p A}{h^2} e^{-\beta \frac{p^2}{2m}} dp = \frac{2\pi A}{h^2} \int_0^{\infty} p e^{-\beta \frac{p^2}{2m}} dp = \frac{4mkT\pi A}{h^2} \int_0^{\infty} x e^{-x^2} dx = \frac{4mkT\pi A}{h^2} \frac{1}{2}$$

$$= \frac{A2\pi mkT}{h^2}$$

c)

$N$ -atom partition function:

$$Z_N = \frac{1}{N!} (Z_1)^N = \frac{1}{N!} \left( \frac{A2\pi mkT}{h^2} \right)^N$$

The Helmholtz free energy is:

$$F = -kT \ln Z_N = -kT \ln \frac{1}{N!} (Z_1)^N = -NkT \ln Z_1 - kT \ln N! \Rightarrow$$

$$F = -NkT \ln \left( \frac{A2\pi mkT}{h^2} \right) - NkT (\ln N - 1) = -NkT \left[ \ln \left( \frac{A2\pi mkT}{Nh^2} \right) + 1 \right]$$

d)

From  $F = E - TS \Rightarrow dF = dE - TdS - SdT$  and the fundamental equation for the 2-dimensional gas we find:

$$dF = -SdT - \tau dA$$

And thus,

$$\tau = - \left( \frac{\partial F}{\partial A} \right)_T = \frac{NkT}{A}$$