

# Intermediate exam T4

## Thermodynamics and Statistical Physics 2019-2020

Friday 29-11-2019; 19:00-21:00

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:  $a+b+c+d+e+f=4+6+6+4+5+5=30$

Consider a crystal of  $N$  molecules. The molecules do not interact with each other and are identical but distinguishable by their location in the crystal. Each molecule has a ground state that is two-fold and an excited state that is three-fold degenerate. The energy of the ground state is zero; the energy of the excited state is  $\varepsilon$ .

- a) If  $n$  of the  $N$  molecules are in the excited state, argue that the number of microstates  $\Omega(n)$  is given by:

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

- b) Calculate the energy  $E$  of this system (in terms of  $\varepsilon$ ,  $k$ ,  $T$  and  $N$ ) using the expression from a). In this problem you may assume that both  $n$  and  $N$  are large numbers and that the use of Stirling's approximation is justified.

We now assume that the crystal is in equilibrium with a heat bath at temperature  $T$ .

- c) Write down the partition function for one of these molecules and show that the mean energy  $\langle E \rangle$  for a single molecule is:

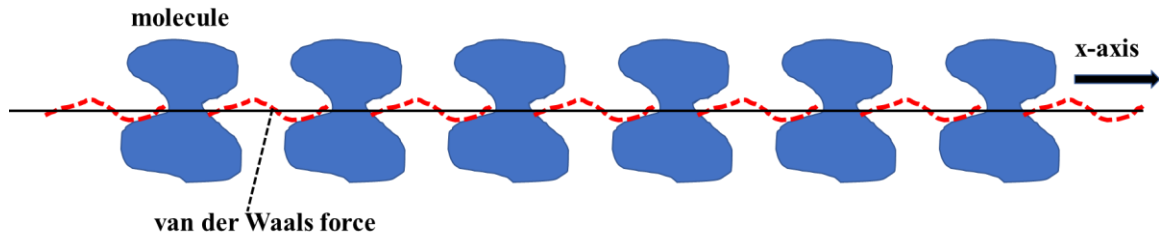
$$\langle E \rangle = \varepsilon \frac{1}{1 + \frac{2}{3} e^{\frac{\varepsilon}{kT}}}$$

What is the relation with the answer in b)?

- d) Give the partition function of the crystal of  $N$  molecules. Motivate your answer.  
e) Calculate the heat capacity  $C_V$  of this crystal of  $N$  molecules as a function of temperature.  
f) Calculate the heat capacity in limiting situations the  $T \rightarrow 0$  (very low temperature) and  $T \rightarrow \infty$  (very high temperature).

PROBLEM 2 *Score:  $a+b+c+d=8+7+7+8=30$*

The figure below shows a 1D-crystal of  $N$  identical molecules of mass  $M$  that are bound together by van der Waals forces. The crystal is in equilibrium with a heat bath at temperature  $T$ .



The van der Waals forces in this crystal lead to a quadratic dependence of the potential energy on the coordinate that describes the displacement of the molecule in the  $x$ -direction (relative to its equilibrium position). This leads to the following expression for the total energy  $E_{molecule}$  of a molecule,

$$E_{molecule} = \frac{1}{2} M v_x^2 + \alpha x^2$$

with  $v_x$  the velocity of the molecule and  $\alpha$  a positive constant quantifying the strength of the van der Waals interaction.

- Use the Boltzmann distribution to show that the contribution to the mean energy of a molecule of the potential energy term is given by:  $\langle \alpha x^2 \rangle = \frac{1}{2} kT$ .
- State the equipartition theorem.
- Give an expression for the mean total energy  $\langle E_{crystal} \rangle$  of the 1D-crystal.

Suppose the molecules also have an internal structure that allows rotation along *one* principal axis and vibration in the  $y$ -direction. The rotation mode is excited above temperature  $T_r$  and the vibration mode above temperature  $T_v > T_r$ .

- Calculate the heat capacity  $C_V$  of the 1D-crystal of molecules with internal structure for each of the following three temperature ranges  $T < T_r$ ;  $T_r < T < T_v$ ; and  $T > T_v$  and make a plot of the temperature dependence of this heat capacity. Take into account the third law for the situation at  $T = 0$ .

PROBLEM 3 Score:  $a+b+c+d=8+7+7+8=30$

Consider a spinless *diatomic* molecule with mass  $m$  that is enclosed in a volume  $V$ . The atom is in equilibrium with a heat bath at temperature  $T$ .

HINT: The density of states due to translational motion for a *spinless* particle confined to an enclosure with volume  $V$  is (expressed as a function of the particle's momentum  $p$ ):

$$f(p)dp = \frac{V}{h^3} 4\pi p^2 dp$$

- a) Show that the single molecule partition function  $Z_1^{trans}$  for the translational modes of the molecule is given by,

$$Z_1^{trans} = V \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}}$$

Suppose for the diatomic molecule the vibrational and rotational modes are independent and their energy levels are given by  $E_{i,j} = E_i^{vib} + E_j^{rot}$ , in which  $E_i^{vib}$  is the  $i$ -th ( $i = 1, 2, 3, \dots$ ) energy level due to vibrational motion and  $E_j^{rot}$  the  $j$ -th ( $j = 1, 2, 3, \dots$ ) energy level due to rotational motion.

- b) Show that the total single molecule partition function of the diatomic molecule can be written as:

$$Z_1 = Z_1^{trans} Z_1^{int} \text{ with } Z_1^{int} = Z_1^{vib} Z_1^{rot}$$

with  $Z_1^{vib}$  and  $Z_1^{rot}$  the single molecule partition function for vibrational and rotational motion, respectively.

- c) Suppose we have a classical ideal gas of  $N$  of these molecules enclosed in a volume  $V$ . What are the two assumptions that justify writing the  $N$ -molecule partition function as:

$$Z_N = \frac{1}{N!} (Z_1)^N$$

- d) Use  $Z_N$  to calculate the pressure  $p$  of this classical ideal gas of  $N$  diatomic molecules. Does the vibrational and rotational motion of the molecules contribute to this pressure? Explain your answer.

Solutions

PROBLEM 1

a)

There are  $\frac{N!}{(N-n)!n!}$  ways to pick  $n$  molecules out of  $N$ . The factors  $2^{N-n}$  and  $3^n$  account for the 2- and 3-fold degeneracy of the ground state and the excited state, so for each molecule in these states there are 2 and 3 possibilities, respectively.

b)

The entropy  $S$  is given by,

$$S = k \ln \Omega(n) = k \ln \left( 3^n 2^{N-n} \frac{N!}{n!(N-n)!} \right)$$

Using Stirling's approximation this can be written as:

$$S = k(n \ln 3 + (N-n) \ln 2 + N \ln N - N - n \ln n + n - (N-n) \ln(N-n) + (N-n))$$

The temperature is given by,

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial n} \frac{\partial n}{\partial E}$$

With  $E = n\varepsilon$  we find,

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial n} \frac{\partial n}{\partial E} = \frac{1}{\varepsilon} \frac{\partial S}{\partial n} = \frac{k}{\varepsilon} (\ln 3 - \ln 2 - 1 - \ln n + 1 + \ln(N-n) + 1 - 1) \\ &= \frac{k}{\varepsilon} \left( \ln \frac{3}{2} - \ln n + \ln(N-n) \right) = \frac{k}{\varepsilon} \ln \left( \frac{3(N-n)}{2n} \right) \Rightarrow \end{aligned}$$

$$\frac{\varepsilon}{kT} = \ln \left( \frac{3(N-n)}{2n} \right) \Rightarrow e^{\frac{\varepsilon}{kT}} = \frac{3}{2} \left( \frac{N}{n} - 1 \right) \Rightarrow n = \frac{N}{1 + \frac{2}{3} e^{\frac{\varepsilon}{kT}}}$$

And

$$E = n\varepsilon = \frac{N\varepsilon}{1 + \frac{2}{3} e^{\frac{\varepsilon}{kT}}}$$

c)

The single molecule partition function is:

$$Z_1 = 2 + 3e^{-\beta\varepsilon}$$

$$\langle E \rangle = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{3\varepsilon e^{-\beta\varepsilon}}{2 + 3e^{-\beta\varepsilon}} = \frac{\varepsilon}{1 + \frac{2}{3}e^{\frac{\varepsilon}{kT}}}$$

Relation with b); in b) we have the energy of  $n$  molecules. For 1 molecule the energy will be  $1/n$  which is the mean energy found in c)

d)

$$Z_N = Z_1^N = (2 + 3e^{-\beta\varepsilon})^N$$

Motivation: the molecules are distinguishable (by their location in the crystal) and do not interact with each other and can thus be considered as independent systems (see also B&B equation 20.42 and text before).

e)

Because,  $\ln Z_N = N \ln Z_1$   
we have,

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = -N \frac{\partial \ln Z_1}{\partial \beta} = N \langle E \rangle = \frac{N\varepsilon}{1 + \frac{2}{3}e^{\frac{\varepsilon}{kT}}}$$

And

$$C_V = \frac{\partial U}{\partial T} = \frac{-N\varepsilon}{\left(1 + \frac{2}{3}e^{\frac{\varepsilon}{kT}}\right)^2} \times \frac{2}{3}e^{\frac{\varepsilon}{kT}} \times \frac{-\varepsilon}{kT^2} = \frac{2}{3}Nk \frac{\left(\frac{\varepsilon}{kT}\right)^2 e^{\frac{\varepsilon}{kT}}}{\left(1 + \frac{2}{3}e^{\frac{\varepsilon}{kT}}\right)^2}$$

f)

If  $T \rightarrow 0$  then with  $x = \frac{\varepsilon}{kT} \rightarrow \infty$

$$C_V = \frac{2}{3}Nk \frac{x^2 e^x}{\left(1 + \frac{2}{3}e^x\right)^2} \approx \frac{3}{2}Nk x^2 e^{-x} = \frac{3}{2}Nk \lim_{x \rightarrow \infty} x^2 e^{-x} = 0$$

If  $T \rightarrow \infty$  then with  $x = \frac{\varepsilon}{kT} \rightarrow 0$

$$C_V = \frac{2}{3}Nk \frac{x^2 e^x}{\left(1 + \frac{2}{3}e^x\right)^2} \approx \frac{2}{3}Nk \frac{x^2(1+x)}{\left(1 + \frac{2}{3}(1+x)\right)^2} \approx \frac{2}{3}Nk x^2 \frac{1}{\left(\frac{5}{3}\right)^2} \rightarrow 0$$

Problem 2

a)

Using the Boltzmann distribution we find,

$$\langle \alpha x^2 \rangle = \frac{\int_{-\infty}^{\infty} \alpha x^2 e^{-\beta E_{\text{molecule}}} dx dv_x}{\int_{-\infty}^{\infty} e^{-\beta E_{\text{molecule}}} dx dv_x} \Rightarrow$$

$$\langle \alpha x^2 \rangle = \frac{\int_{-\infty}^{\infty} \alpha x^2 e^{-\beta \alpha x^2} dx \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta M v_x^2} dv_x}{\int_{-\infty}^{\infty} e^{-\beta \alpha x^2} dx \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta M v_x^2} dv_x} \Rightarrow$$

$$\langle \alpha x^2 \rangle = \frac{\int_{-\infty}^{\infty} \alpha x^2 e^{-\beta \alpha x^2} dx}{\int_{-\infty}^{\infty} e^{-\beta \alpha x^2} dx} = -\frac{\partial \ln I}{\partial \beta}$$

where we have defined  $I = \int_{-\infty}^{\infty} e^{-\beta \alpha x^2} dx$ . Substitute  $z^2 = \beta \alpha x^2$  then  $z = \sqrt{\beta \alpha} x$  and  $dx = \frac{dz}{\sqrt{\beta \alpha}}$  and the integral becomes,

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

and

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

$$\langle \alpha x^2 \rangle = \frac{1}{2\beta} = \frac{1}{2} kT$$

Or using one of the integrals of the formula sheet (with  $c = \alpha\beta$ )

$$\langle \alpha x^2 \rangle = \frac{\int_{-\infty}^{\infty} \alpha x^2 e^{-\alpha\beta x^2} dx}{\int_{-\infty}^{\infty} e^{-\alpha\beta x^2} dx} = \alpha \frac{\left( \frac{1}{2} \sqrt{\frac{\pi}{c^3}} \right)}{\left( \sqrt{\frac{\pi}{c}} \right)} = \frac{1}{2} \alpha \frac{1}{c} = \frac{1}{2} \alpha \frac{1}{\beta \alpha} = \frac{1}{2} kT$$

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)

$$\langle E_{crystal} \rangle = N \langle E_{molecule} \rangle = N \left\langle \left( \frac{1}{2} M v_x^2 + \alpha x^2 \right) \right\rangle = N \left( 2 \times \frac{1}{2} kT \right) = NkT$$

d)

At temperatures above  $T_r$  the rotational mode is excited, leading to one extra quadratic term in  $E_{molecule}$

$$E_{molecule} = \frac{1}{2} M v_x^2 + \alpha x^2 + \frac{L^2}{2I}$$

with  $L$  the angular momentum of the molecule along its rotational axis and  $I$  its moment of inertia.

At temperatures above  $T_v$  the vibrational mode in the  $y$ -direction is also excited leading to two extra quadratic terms in  $E_{molecule}$

$$E_{molecule} = \frac{1}{2} M v_x^2 + \alpha x^2 + \frac{L^2}{2I} + \frac{1}{2} M v_y^2 + \gamma y^2$$

with  $\gamma$  another positive constant.

For the mean energy of the crystal in the temperature range  $T_r < T < T_v$  we have, using the equipartition theorem,

$$\langle E_{crystal} \rangle = N \langle E_{molecule} \rangle = N \left\langle \left( \frac{1}{2} M v_x^2 + \alpha x^2 + \frac{L^2}{2I} \right) \right\rangle = \frac{3}{2} NkT$$

and for  $T > T_r$ ,

$$\langle E_{crystal} \rangle = N \langle E_{molecule} \rangle = N \left\langle \left( \frac{1}{2} M v_x^2 + \alpha x^2 + \frac{L^2}{2I} + \frac{1}{2} M v_y^2 + \gamma y^2 \right) \right\rangle = \frac{5}{2} NkT$$

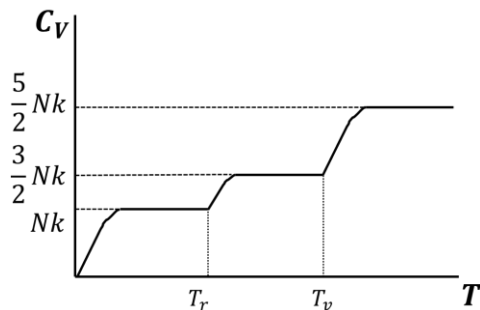
The heat capacities for the different temperature ranges we find with:

$$C_V = \frac{\partial \langle E_{crystal} \rangle}{\partial T}$$

as  $C_V = Nk$ ,  $C_V = \frac{3}{2} Nk$  and  $C_V = \frac{5}{2} Nk$ , respectively.

The consequence of the third law is that  $C_V \rightarrow 0$  when  $T \rightarrow 0$  (see B&B page 205).

This results in the following plot:



PROBLEM 3

a)

Single molecule partition function for translational motion:

$$Z_1 = \int_0^{\infty} f(p) e^{-\beta \frac{p^2}{2m}} dp = \int_0^{\infty} \frac{V}{h^3} 4\pi p^2 e^{-\beta \frac{p^2}{2m}} dp = \frac{4\pi V}{h^3} \int_0^{\infty} p^2 e^{-\beta \frac{p^2}{2m}} dp$$

Use the substitution  $x^2 = \beta \frac{p^2}{2m}$  and thus  $p = \sqrt{\frac{2m}{\beta}} x$  and  $dp = \sqrt{\frac{2m}{\beta}} dx$  to find

$$Z_1 = \frac{4\pi V}{h^3} \left(\frac{2m}{\beta}\right)^{\frac{3}{2}} \int_0^{\infty} x^2 e^{-x^2} dx = \frac{4\pi V}{h^3} \left(\frac{2m}{\beta}\right)^{\frac{3}{2}} \frac{\sqrt{\pi}}{4} = V \left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}$$

The integral was solved using the formula sheet.

b)

$$\begin{aligned} Z_1 &= \int_0^{\infty} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} f(p) e^{-\beta \left(\frac{p^2}{2m} + E_i^{vib} + E_j^{rot}\right)} dp \\ &= \int_0^{\infty} f(p) e^{-\beta \frac{p^2}{2m}} dp \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} e^{-\beta (E_i^{vib} + E_j^{rot})} \\ &= \int_0^{\infty} f(p) e^{-\beta \frac{p^2}{2m}} dp \sum_{i=1}^{\infty} e^{-\beta E_i^{vib}} \sum_{j=1}^{\infty} e^{-\beta E_j^{rot}} \\ &= \int_0^{\infty} f(p) e^{-\beta \frac{p^2}{2m}} dp \sum_{i=1}^{\infty} e^{-\beta E_i^{vib}} \sum_{j=1}^{\infty} e^{-\beta E_j^{rot}} = Z_1^{trans} Z_1^{vib} Z_1^{rot} \\ &= Z_1^{trans} Z_1^{int} \end{aligned}$$

c)

The particles are indistinguishable (3 pts) because it is a gas and situations that have two or more particles occupying the same energy level do not occur (4 pts) because the gas is classical.

d)

Use the  $N$ -atom partition function:

$$\begin{aligned}
Z_N &= \frac{1}{N!} (Z_1)^N = \frac{1}{N!} (Z_1^{trans} Z_1^{int})^N = \frac{1}{N!} \left( V \left( \frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} \right)^N (Z_1^{int})^N \\
&= \frac{V^N}{N!} \left( \frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}N} (Z_1^{int})^N
\end{aligned}$$

and use Helmholtz free energy,

$$F = -kT \ln Z_N$$

To find the pressure,

$$p = - \left( \frac{\partial F}{\partial V} \right)_T = kT \left( \frac{\partial \ln Z_N}{\partial V} \right)_T = kT \left( \frac{\partial (N \ln V)}{\partial V} \right)_T = \frac{NkT}{V}$$

Notice that all the factors in  $\ln Z_N$  can be written as a sum of logarithms of which only the term  $\ln V^N = N \ln V$  depends on the volume. All other terms become zero after the differentiation with respect to  $V$ . The internal motion of the molecule does not depend on the volume so also the term  $\ln(Z_1^{int})^N$  disappears after the differentiation with respect to  $V$ . Consequently, the internal motion does not contribute to the pressure.