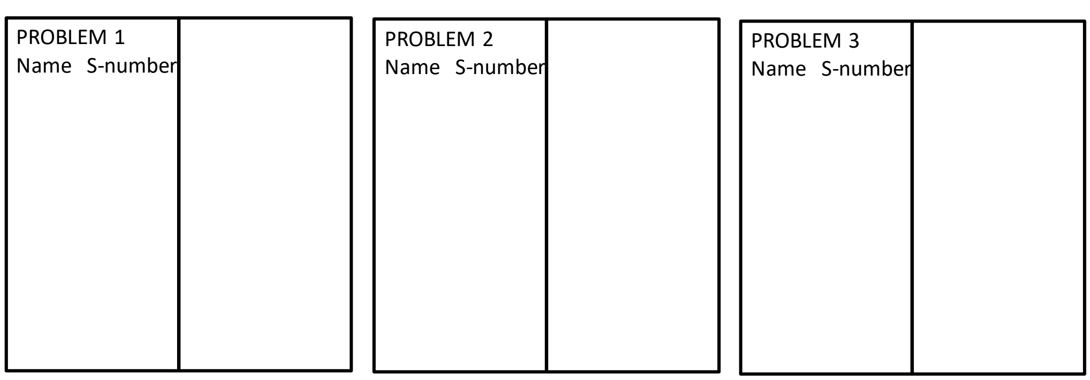
Intermediate exam T4

Thermodynamics and Statistical Physics 2018-2019

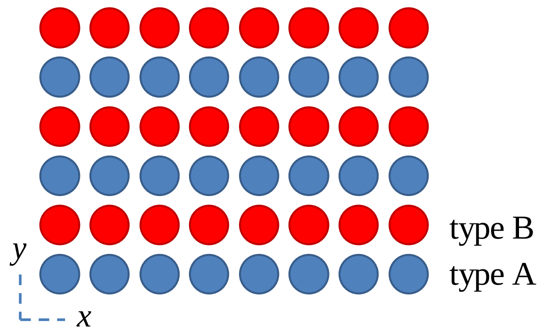
Friday 30-11-2018; 9:00-11:00

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 *Score: a+b+c+d+e=7+7+6+5+5=30*



Suppose we have a 2D crystal consisting of two types of atoms (A and B) that are arranged in rows of alternating type A and type B (see figure above). In total we have $N \times N$ atoms. The crystal is in equilibrium with a heat bath with temperature *T*. The atoms have bonds with their neighbours that lead to a quadratic dependence of the potential energy on the coordinate that describes the displacement from the equilibrium position in the *x*-direction. For the *y*-direction this dependence is more complicated due to the bonds between atoms of different types but can be described by a sum of power 2 and power 4 terms. This leads to the following expressions for the total energy of atoms of type A (E_A) and type B (E_B),

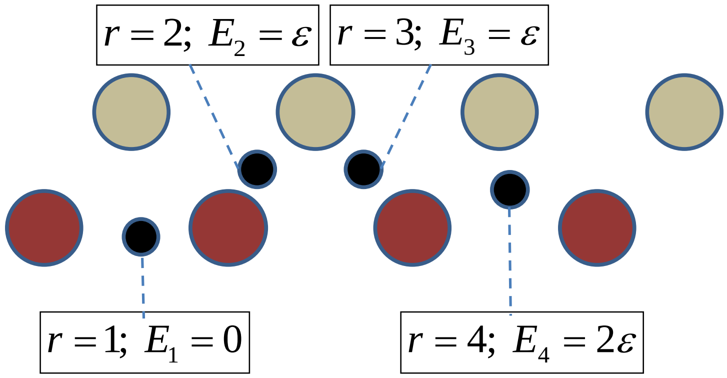
$$E_A = \frac{1}{2} M_A\left(v_x^2 + v_y^2\right) + a_0 x^2$$

$$E_B = \frac{1}{2} M_B\left(v_x^2 + v_y^2\right) + b_0 y^2 + b_1 y^4$$

with M_A, M_B the masses of type A and B atoms, respectively, $\vec{v} = (v_x, v_y)$ their velocity, $\vec{x} = (x, y)$ their position (relative to their equilibrium position), a_0, b_0 and b_1 are positive constants describing the strength of the bonds between the atoms.

a) *Use the Boltzmann distribution* to show that the contribution to the mean energy of an atom of mass M (either M_A or M_B) due to its x-component of the velocity is given by: $\langle \frac{1}{2} M v_x^2 \rangle = \frac{1}{2} kT$.
b) State the equipartition theorem.
c) *Use the Boltzmann distribution* to show that the contribution of the power 4 term to the mean energy of an atom of type B is given by: $\langle b_1 y^4 \rangle = \frac{1}{4} kT$.
d) Give an expression for the mean total energy $\langle E \rangle$ of *the crystal*.
e) Give an expression for the heat capacity C_V of *the crystal*.

PROBLEM 2 *Score: a+b+c+d+e =7+7+6+6+4=30*



A diatomic crystal in equilibrium with a heat bath at temperature T contains N defects that are similar but are distinguishable by their location in the crystal. The defects consist of atoms of a third type that can be at one of four positions (see figure above). These four positions represent four possible states of the defect, $r = 1, 2, 3, 4$. The energies of these states are: $E_1 = 0$, $E_2 = E_3 = \varepsilon$ and $E_4 = 2\varepsilon$.

a) Show that the partition function of a single defect is given by:

$$Z_1 = (1 + e^{-\beta\varepsilon})^2$$

b) Give the partition function of the N defects.
c) Calculate the internal energy U and the Helmholtz free energy F of the N defects.
d) Calculate the defects contribution to the entropy S of the crystal.
e) Consider the high temperature limit $T \to \infty$. For each state $r = 1, 2, 3, 4$ find the probability p_r in this limit. Use this result to calculate the mean energy of a defect when $T \to \infty$.

PROBLEM 3 *Score: a+b+c+d+e=7+5+7+5+6=30*

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

> HINT: The density of states 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 atom partition function Z_1 is given by,

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

b) Suppose we have a classical ideal gas of N of these atoms enclosed in a volume V. What are the assumptions that justify writing the N-atom partition function as:

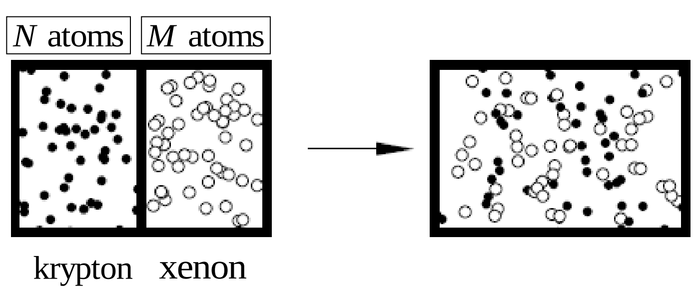
$$Z_N = \frac{1}{N!}(Z_1)^N$$

c) Calculate the internal energy U for this classical ideal gas of N atoms.

d) Assuming that N is a very large number, show that the entropy S of this classical ideal gas of N atoms is given by:

$$S = Nk\left[\frac{5}{2} - \ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}\right)\right]$$

e) Consider a volume V that is subdivided by a partition into two equal sized compartments. Compartment 1 contains N atoms of krypton (mass m_K and compartment 2 contains M atoms of xenon (mass m_X). Calculate the difference in entropy between this situation and the situation that is established after removal of the partition and the atoms have been allowed to completely mix.



Solutions

PROBLEM 1

a)

For the energy of an atom (either type A or B) we can write:

$$E = \frac{1}{2}Mv_x^2 + \acute{E}$$

Then using the Boltzmann distribution we find,

$$\langle\frac{1}{2}Mv_x^2\rangle = \frac{\int_{-\infty}^{\infty}\frac{1}{2}Mv_x^2 e^{-\beta E}dxdydv_xdv_y}{\int_{-\infty}^{\infty} e^{-\beta E}\,dxdydv_xdv_y} \Rightarrow$$

$$\langle\frac{1}{2}Mv_x^2\rangle = \frac{\int_{-\infty}^{\infty}\frac{1}{2}Mv_x^2 e^{-\frac{1}{2}\beta Mv_x^2}dv_x \int_{-\infty}^{\infty} e^{-\beta\acute{E}}\,dxdydv_y}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta Mv_x^2}dv_x \int_{-\infty}^{\infty} e^{-\beta\acute{E}}\,dxdydv_y} \Rightarrow$$

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

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

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

And

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

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

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:

$$\langle b_1 y^4 \rangle = \frac{\int_{-\infty}^{\infty} b_1 y^4 e^{-\beta b_1 y^4} dy}{\int_{-\infty}^{\infty} e^{-\beta b_1 y^4} dy} = -\frac{\partial \ln I}{\partial \beta}$$

With

$$I = \int_{-\infty}^{\infty} e^{-\beta b_1 y^4} dy$$

WELL, that was how I planned the exercise. However, I forgot about the y^2 term that should have been omitted from the expression for the total energy of atoms of type B. Since it is in there, we have

$$\langle b_1 y^4 \rangle = \frac{\int_{-\infty}^{\infty} b_1 y^4 e^{-\beta (b_0 y^2 + b_1 y^4)} dy}{\int_{-\infty}^{\infty} e^{-\beta (b_0 y^2 + b_1 y^4)} dy}$$

This integral can not be solved easily and does not lead to a $1/4\ kT$ term.

What we decided for the grading. If you did not see the problem with the y^2 term and just made the same mistake as I did, you get all the points. If you correctly wrote the expression above but ran in to trouble, you get all the points. If you mentioned the problem and stated something like that the problem was wrong and that this does not lead to a $1/4\ kT$ term, you get 2 bonus points.

Here, the solution proceeds but with the assumption that $b_0 = 0$.

Idem, but now with substitution $z^4 = \beta y^4$ then $z = \beta^{\frac{1}{4}} y$ and $dy = \frac{dz}{\beta^{\frac{1}{4}}}$ and the integral becomes

$$I = \frac{1}{\beta^{\frac{1}{4}}} \int_{-\infty}^{\infty} e^{-b_1 z^4} dz$$

And

$$\langle E \rangle = -\frac{\partial \ln I}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\ln \frac{1}{\beta^{\frac{1}{4}}} + \ln\left\{\int_{-\infty}^{\infty} e^{-b_1 z^4} dz\right\}\right] = -\left[\beta^{\frac{1}{4}}\left(-\frac{1}{4}\frac{1}{\beta^{\frac{5}{4}}}\right) + 0\right] \Rightarrow$$

$$\langle E \rangle = \frac{1}{4\beta} = \frac{1}{4} kT$$

d)
For a single atom of type A we have,

$$\langle E_A \rangle = \langle \frac{1}{2} M_A \left(v_x^2 + v_y^2 \right) + a_0 x^2 \rangle = 3 \times \frac{1}{2} kT = \frac{3}{2} kT$$

For a single atom of type B we have,

$$\langle E_B \rangle = \langle \frac{1}{2} M_B \left(v_x^2 + v_y^2 \right) + b_0 y^2 + b_1 y^4 \rangle = 3 \times \frac{1}{2} kT + 1 \times \frac{1}{4} kT = \frac{7}{4} kT$$

The crystal consists of $\frac{1}{2} N^2$ type A atoms and $\frac{1}{2} N^2$ type B atoms, so we find

$$\langle E_{crystal} \rangle = \frac{1}{2} N^2 \times \frac{3}{2} kT + \frac{1}{2} N^2 \times \frac{7}{4} kT = \frac{13 N^2}{8} kT$$

Where we used the results a) and c) and used equipartition of energy,

e) $C_V = \frac{\partial \langle E_{crystal} \rangle}{\partial T} = \frac{13 N^2}{8} k$

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

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

$$\langle b_1 y^4 \rangle = \frac{\int_{-\infty}^{\infty} b_1 y^4 e^{-\beta b_1 y^4} dy}{\int_{-\infty}^{\infty} e^{-\beta b_1 y^4} dy} = b_1 \frac{\left(\frac{1}{2} \frac{\Gamma\left(\frac{5}{4}\right)}{c^{\frac{5}{4}}} \right)}{\left(\frac{2\Gamma\left(\frac{5}{4}\right)}{c^{\frac{1}{4}}} \right)} = \frac{1}{4} b_1 \frac{1}{c} = \frac{1}{4} b_1 \frac{1}{\beta b_1} = \frac{1}{4} kT$$

PROBLEM 2

a) Partition function of a single defect is:

$$Z_1 = \sum_{r=0}^{4} e^{-\beta E_r} = e^{-\beta\times 0} + e^{-\beta\times\varepsilon} + e^{-\beta\times\varepsilon} + e^{-\beta\times 2\varepsilon} = 1 + 2e^{-\beta\varepsilon} + \left(e^{-\beta\varepsilon}\right)^2 \Rightarrow$$

$$Z_1 = (1 + e^{-\beta\varepsilon})^2$$

b)
Because the defects are distinguishable we have,

$$Z_N = {Z_1}^N = (1 + e^{-\beta\varepsilon})^{2N}$$

c)
The internal energy of the defects is given by,

$$U = \langle E \rangle = -\frac{\partial \ln Z_N}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\left(\ln(1 + e^{-\beta\varepsilon})^{2N}\right)\right] = -2N\frac{\partial}{\partial \beta}\left[\ln\left(1 + e^{-\beta\varepsilon}\right)\right] \Rightarrow$$

$$U = \frac{-2N}{1 + e^{-\beta\varepsilon}}\left(-\varepsilon e^{-\beta\varepsilon}\right) = \frac{2N\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}$$

The Helmholtz free energy is $F = -kT \ln Z_N$.

$$F = -kT \ln Z_N = -kT\left[\ln(1 + e^{-\beta\varepsilon})^{2N}\right] = -2NkT \ln(1 + e^{-\beta\varepsilon}).$$

d)
Use the definition of F namely, $F = U - TS$ to find S:

$$S = \frac{U - F}{T} = \frac{1}{T}\left(\frac{2N\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}\right) + 2Nk \ln(1 + e^{-\beta\varepsilon})$$

$$S = 2Nk\left[\left(\frac{\varepsilon\beta e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}\right) + \ln(1 + e^{-\beta\varepsilon})\right]$$

e)
In case $T \to \infty$ we have for $r = 1, 2, 3, 4.$,

$$p_r = \frac{e^{-\beta E_r}}{Z_1} \approx \frac{1}{Z_1}$$

and

$$Z_1 = (1 + e^{-\beta\varepsilon})^2 \approx (1+1)^2 = 4$$

Thus, $p_r = \frac{1}{4}$ and

$$\langle\varepsilon\rangle = \sum_{r=0}^{4} p_r E_r = \frac{1}{4}(0 + \varepsilon + \varepsilon + 2\varepsilon) = \varepsilon$$

PROBLEM 3

a)

Single atom partition function:

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

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

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

The integral was solved using the formula sheet.

b)

The particles are indistinguishable (2 pts) and situations that have two or more particles occupying the same energy level do not occur (3 pts).

c)

Use the N-atom partition function:

$$Z_N = \frac{1}{N!}(Z_1)^N = \frac{1}{N!}\left(V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right)^N = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}N} = \frac{V^N}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}N}$$

to find

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = -\frac{\partial}{\partial \beta}\left(\ln\left[\frac{V^N}{N!}\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}N}\right] + \ln \beta^{-\frac{3}{2}N}\right) = \frac{3}{2}N\frac{\partial}{\partial\beta}(\ln\beta) = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT$$

d)

We first write:

$$\ln Z_N = \ln\left[\frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}N}\right] = N\ln V - \ln N! + \frac{3}{2}N\ln\frac{2\pi mkT}{h^2}$$

Then use Stirling's approximation $\ln N! \approx N\ln N - N$ to find

$$\ln Z_N \approx N \ln V - \mathrm{N}\ln N + N + \frac{3}{2} N \ln \frac{2\pi mkT}{h^2} = N\left[1 - \ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}\right)\right]$$

And

$$F = -kT \ln Z_N = -NkT\left[1 - \ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}\right)\right]$$

We calculate S using:

$$S = \frac{U-F}{T} = \frac{\frac{3}{2}NkT + NkT\left[1 - \ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}\right)\right]}{T} = Nk\left[\frac{5}{2} - \ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}\right)\right]$$

e)

$$\Delta S = S_{after} - S_{before}$$

$$S_{before} = Nk\left[\frac{5}{2} - \ln\left(\frac{N}{\left(\frac{1}{2}V\right)}\left(\frac{h^2}{2\pi m_K kT}\right)^{\frac{3}{2}}\right)\right] + Mk\left[\frac{5}{2} - \ln\left(\frac{M}{\left(\frac{1}{2}V\right)}\left(\frac{h^2}{2\pi m_X kT}\right)^{\frac{3}{2}}\right)\right]$$

$$S_{after} = Nk\left[\frac{5}{2} - \ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi m_K kT}\right)^{\frac{3}{2}}\right)\right] + Mk\left[\frac{5}{2} - \ln\left(\frac{M}{V}\left(\frac{h^2}{2\pi m_X kT}\right)^{\frac{3}{2}}\right)\right]$$

$$\Delta S = -Nk \ln\frac{N}{V} - Mk \ln\frac{M}{V} + Nk \ln\frac{2N}{V} + Mk \ln\frac{2M}{V} = (N+M)k \ln 2$$