

# Midterm Exam

## Statistical Physics

Wednesday December 9, 2015

09:00-11:00

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.
- Use of a (graphing) calculator is allowed.
- This exam consists of 3 problems.
- The weight of the problems is Problem 1 (P1=27 pts); Problem 2 (P2=27 pts); Problem 3 (P3=36 pts). Weights of the various subproblems are indicated at the beginning of each problem.
- The grade of the midterm 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:  $a+b+c+d+e+f=5+5+5+4+4+4=27$*

The equation of state of an ideal gas of  $N$  molecules is given by  $PV = NkT$ . The energy of this ideal gas is a function of temperature only and is given by  $E = \frac{3}{2}NkT$ .

Calculate the heat  $Q$  absorbed *by* this gas when:

- the volume of the gas is changed from  $V_i$  to  $V_f$  in a reversible isothermal process.
- the temperature is changed from  $T_i$  to  $T_f$  in a reversible process in which the volume  $V$  is kept constant.
- the temperature is changed from  $T_i$  to  $T_f$  in a reversible process in which the pressure  $P$  is kept constant.

Suppose the ideal gas is initially at temperature  $T_1$  and has a volume  $V_1$ . We will use the notation  $(T_1, V_1)$  for this state of the gas. The gas then undergoes a reversible cyclic process in which it changes to the state  $(T_2, V_2)$  under constant pressure conditions, subsequently it changes to the state  $(T_1, V_2)$  under constant volume conditions and finally it returns to its initial state  $(T_1, V_1)$  under constant temperature conditions.

- Show that the heat  $Q$  absorbed *by* the gas during this cyclic process is given by:

$$Q = Nk(T_2 - T_1) + NkT_1 \ln \frac{V_1}{V_2}$$

- Calculate the work  $W$  done *on* the gas during the process.
- Show that  $W + Q = 0$  and explain why the equality holds.

PROBLEM 2 *Score:  $a+b+c = 9+9+9=27$*

Consider a crystal with  $N$  independent identical atoms. Each atom has a low energy state that is threefold degenerate. Assume that the energy of this low energy state is zero. Each atom has one high energy state with energy  $\varepsilon$ . This high energy state is also threefold degenerate. The number of atoms in the high energy state is  $n$ .

- Explain that the number of microstates  $\Omega$  as a function of the number of atoms  $n$  in the high energy state is given by:

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

- Calculate the energy  $E$  of this system of  $N$  atoms using the micro-canonical ensemble method. Express your answer in terms of  $\varepsilon$ ,  $k$ ,  $T$  and  $N$ .
- Calculate the canonical partition function  $Z$  of this system of  $N$  atoms and calculate the energy of the system *using this partition function*.

PROBLEM 3 Score:  $a+b+c+d = 9+9+9+9=36$

A harmonic oscillator with energy levels given by  $\varepsilon_j = \hbar\omega(j + \frac{1}{2})$  is in equilibrium with a heat bath at temperature  $T$ . The angular frequency of the harmonic oscillator is  $\omega$ .

- a) Proof that the mean energy  $\bar{\varepsilon}$  of this oscillator is given by:  $\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$

Now consider a 1-dimensional linear crystal that consists of  $N$  atoms. The crystal has length  $L$ . Assume that the crystal can be described as a system of  $N$  coupled oscillators and that this system can only vibrate in the longitudinal direction.

- b) Use Debye's theory to show that the number of angular frequencies between  $\omega$  and  $\omega + d\omega$  is given by:

$$f(\omega)d\omega = \frac{L}{\pi v_0} d\omega$$

In this expression  $v_0$  is the velocity of the longitudinal waves.

- c) Explain the meaning of the Debye frequency  $\omega_D$  and show that for this 1-dimensional crystal,

$$\omega_D = N \frac{\pi v_0}{L}$$

- d) Give an expression for the heat capacity  $C_V$  of this 1-dimensional crystal and show that in case  $T \rightarrow 0$  then  $C_V$  decreases like  $T$ .

## Solutions

### PROBLEM 1

In this problem we use the first law:  $dE = \bar{d}Q + \bar{d}W = \bar{d}Q - PdV$

a)

As the energy  $E$  is a function of  $T$  only, we have for an isothermal process:  $dE = 0$  and thus,

$$\bar{d}Q = PdV \Rightarrow Q = \int_{V_i}^{V_f} PdV = NkT \int_{V_i}^{V_f} \frac{dV}{V} = NkT \ln \frac{V_f}{V_i}$$

b)

If  $V$  is constant then  $dV = 0$  and,

$$\bar{d}Q = dE = \frac{3}{2}NkdT \Rightarrow Q = \frac{3}{2}Nk \int_{T_i}^{T_f} dT = \frac{3}{2}Nk(T_f - T_i)$$

c)

In this case  $\bar{d}Q = dE + PdV = \frac{3}{2}NkdT + PdV$  and we use the equation of state (with  $P$  constant) to find  $PdV = NkdT$  and,

$$\bar{d}Q = \frac{3}{2}NkdT + NkdT = \frac{5}{2}NkdT \Rightarrow Q = \frac{5}{2}Nk \int_{T_i}^{T_f} dT = \frac{5}{2}Nk(T_f - T_i)$$

d)

During step 1 (constant pressure, see c)):  $Q_1 = \frac{5}{2}Nk(T_2 - T_1)$

During step 2 (constant volume, see b)):  $Q_2 = \frac{3}{2}Nk(T_1 - T_2)$

During step 3 (constant temperature, see a)):  $Q_3 = NkT_1 \ln \frac{V_1}{V_2}$

And in total:

$$Q = Q_1 + Q_2 + Q_3 = Nk(T_2 - T_1) + NkT_1 \ln \frac{V_1}{V_2}$$

e)

During step 1:  $\bar{d}W = -PdV$

$$W_1 = -P \int_{V_1}^{V_2} dV = P(V_1 - V_2)$$

During step 2:  $W_2 = 0$  because  $V$  is constant and thus  $dV = 0$ .

During step 3:  $\bar{d}W = -PdV$

$$W_3 = - \int_{V_2}^{V_1} PdV = - \int_{V_2}^{V_1} \frac{NkT_1}{V} dV = NkT_1 \ln \frac{V_2}{V_1}$$

Total work done on the gas is:

$$W = W_1 + W_2 + W_3 = P(V_1 - V_2) + NkT_1 \ln \frac{V_2}{V_1}$$

Because of the equation of state we have,

$$PV_1 = NkT_1 \text{ and } PV_2 = NkT_2$$

Substituting this in the equation above we find:

$$W = Nk(T_1 - T_2) + NkT_1 \ln \frac{V_2}{V_1}$$

f)

$$W + Q = Nk(T_1 - T_2) + NkT_1 \ln \frac{V_2}{V_1} + Nk(T_2 - T_1) + NkT_1 \ln \frac{V_1}{V_2} = 0$$

This equality is valid because the energy is a function of state and thus during a cyclic process,

$$\Delta E = 0 = W + Q$$

## PROBLEM 2

a)

There are  $\frac{N!}{(N-n)!}$  ways to pick  $n$  atoms out of  $N$ . The factor  $\frac{1}{n!}$  accounts for the fact that the atoms are indistinguishable. Because the low energy state is threefold degenerate for each atom in this state there are 3 possibilities. There are  $N - n$  atoms in this low energy state, this gives a factor  $3^{N-n}$ . The high energy state is also threefold degenerate, thus for each atom in this state there are three possibilities. There are  $n$  atoms in the high energy state, this gives a factor  $3^n$ . Combining all these factors:

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

b)

The entropy  $S$  is given by,

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

Using Stirling's approximation this can be written as:

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

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,

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

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

And

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

c)

The single atom partition function is:

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

The  $N$  atoms are independent thus the partition function for the  $N$  atoms is:

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

$$E = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln(Z_1)^N}{\partial \beta} = -N \frac{\partial \ln Z_1}{\partial \beta} = \frac{3N\varepsilon e^{-\beta\varepsilon}}{3 + 3e^{-\beta\varepsilon}} = \frac{N\varepsilon}{1 + e^{\frac{\varepsilon}{kT}}}$$



### PROBLEM 3

a)

The partition function for the oscillator is given by:

$$Z = \sum_{j=1}^{\infty} e^{-\beta \varepsilon_j} = \sum_{j=1}^{\infty} e^{-\beta \hbar \omega (j + \frac{1}{2})} = e^{-\frac{x}{2}} \sum_{j=1}^{\infty} e^{-jx} = \frac{e^{-\frac{x}{2}}}{1 - e^{-x}}$$

With  $x = \beta \hbar \omega$ .

$$\bar{\varepsilon} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial x} \frac{\partial x}{\partial \beta} = -\hbar \omega \frac{\partial}{\partial x} \left( -\frac{x}{2} - \ln(1 - e^{-x}) \right) = \frac{1}{2} \hbar \omega + \frac{\hbar \omega e^{-x}}{1 - e^{-x}}$$

And putting back  $x = \beta \hbar \omega$  we find:

$$\bar{\varepsilon} = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}$$

b)

Use the Debye approach and consider elastic waves through the crystal. From the solution of the 1D-wave equation:  $\varphi = A \sin k_x x$  and taking this function to vanish at  $x = 0$  and at  $x = L$  results in,

$$k_x = \frac{n_x \pi}{L} \quad \text{with } n_x \text{ a non-zero positive integer.}$$

The total number of states with  $|\vec{k}| < k$  is then given by the length of the line representing positive integers (thus length  $k$ ) divided by the unit length of one state, in  $k$ -space.

$$\Gamma(k) = \frac{k}{\frac{\pi}{L}} = \frac{kL}{\pi}$$

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

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

From the wave equation we also have  $\omega = kv_0$ , substituting this in the equation above leads to,

$$f(\omega)d\omega = \frac{L}{\pi v_0} d\omega$$

There is only independent wave mode for this 1-dimensional crystal (given in the exercise) namely, longitudinal (in a 3-dimensional crystal there are generally 3 modes, because then transversal waves can exist in both directions perpendicular to the direction of wave propagation, this would give a factor 3 in the equation above).

c)

The total number of frequencies (modes) should be  $N$  as there are  $N$  atoms. This is forced in the theory by introducing the Debye frequency which is the maximum frequency that cuts off higher modes,

$$\int_0^{\omega_D} f(\omega)d\omega = N = \int_0^{\omega_D} \frac{L}{\pi v_0} d\omega = \frac{L\omega_D}{\pi v_0}$$

It follows that:

$$\omega_D = N \frac{\pi v_0}{L}$$

Using the Debye frequency we can rewrite,

$$f(\omega)d\omega = \frac{L}{\pi v_0} d\omega = \frac{N d\omega}{\omega_D}$$

d)

First we derive an expression for the energy of the crystal,

$$\begin{aligned} E &= \int_0^{\omega_D} f(\omega) \bar{\varepsilon}(\omega) d\omega = \int_0^{\omega_D} \left( \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right) \frac{N d\omega}{\omega_D} \\ &= \frac{N}{\omega_D} \int_0^{\omega_D} \left( \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right) d\omega = \frac{1}{2} N \hbar \omega_D + \frac{N}{\omega_D} \int_0^{\omega_D} \left( \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right) d\omega \end{aligned}$$

The heat capacity follows from,

$$\begin{aligned}
C_V &= \left( \frac{\partial E}{\partial T} \right)_V = \left( \frac{\partial E}{\partial \beta} \right)_V \left( \frac{\partial \beta}{\partial T} \right)_V = -\frac{1}{kT^2} \left( \frac{\partial E}{\partial \beta} \right)_V \\
&= -\frac{1}{kT^2} \frac{\partial}{\partial \beta} \left( \frac{1}{2} N \hbar \omega_D + \frac{N}{\omega_D} \int_0^{\omega_D} \left( \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right) d\omega \right) = \\
&= -\frac{1}{kT^2} \frac{N}{\omega_D} \left( \int_0^{\omega_D} \frac{\partial}{\partial \beta} \left( \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right) d\omega \right) \\
&= -\frac{1}{kT^2} \frac{N}{\omega_D} \left( \int_0^{\omega_D} \frac{\hbar^2 \omega^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} d\omega \right) \\
&= \frac{\hbar^2}{k^2 T^2} \left( \frac{kT}{\hbar} \right)^3 \frac{Nk}{x_D} \left( \frac{\hbar}{kT} \right) \left( \int_0^{x_D} \frac{x^2 e^x}{(e^x - 1)^2} dx \right) = \frac{Nk}{x_D} \left( \int_0^{x_D} \frac{x^2 e^x}{(e^x - 1)^2} dx \right)
\end{aligned}$$

With

$$x_D = \frac{\hbar \omega_D}{kT} = \frac{\theta_D}{T}$$

When  $T \rightarrow 0$  then  $x_D = \frac{\theta_D}{T} \rightarrow \infty$  and,

$$C_V = Nk \left( \frac{T}{\theta_D} \right) \left( \int_0^{\infty} \frac{x^2 e^x}{(e^x - 1)^2} dx \right)$$

The definite integral is a number and independent of the temperature thus, when  $T \rightarrow 0$  then  $C_V$  decreases like  $T$ .