Exam

Statistical Physics

Monday April 11, 2016
14:00-17:00

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 of paper for each problem.**
- **Use of a (graphing) calculator is allowed.**
- **This exam consists of 4 problems.**
- **The weight of the problems is: Problem 1 (P1=25 pts); Problem 2 (P2=20 pts); Problem 3 (P3=20 pts); Problem 4 (P4=25 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+P4+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 =5+5+5+5+5=25

A crystal of N atoms has N lattice sites and M interstitial locations. An amount of energy ε is needed to remove an atom from a lattice site and place it in an interstitial. The number n of displaced atoms is large but is also much smaller than N and M.

a) Prove that the total number of microstates Ω corresponding to n atoms in an interstitial is:

$$\Omega(n) = \left(\frac{1}{n!}\right)^2 \frac{N!\,M!}{(N-n)!\,(M-n)!}$$

Suppose for a certain crystal we have $M = N$

b) Use the expression of $\Omega(n)$ to calculate the entropy S of this crystal as a function of the number of displaced atoms n. Use Stirling's approximation to simplify all the factorials in the expression for the entropy.

c) Calculate the total energy $E = n\varepsilon$ of the crystal as a function of the temperature T. Express your answer in terms of k, T, ε and N.

d) Show that at temperature T, the number of displaced atoms n satisfies the following equation.

$$\frac{n}{N-n} = e^{\frac{-\varepsilon}{2kT}}$$

e) In case of low temperatures ($\varepsilon \gg kT$), only a small amount of interstitial sites will be occupied. Obtain an approximate expression for n for low temperatures. Use this expression to calculate the fraction n/N for a crystal at a temperature of 300 K. Assume that the energy ε is 1eV.
Boltzmann's constant: k=8.6·10^{-5} eV/K.

PROBLEM 2

Score: a+b+c+d =5+5+5+5=20

The rotational energy levels of a diatomic molecule are given by:

$$\varepsilon_n = \frac{\hbar^2}{2I} n(n+1) \text{ with } n = 0,1,2,\cdots$$

I is a constant and each energy level ε_n has a $(2n+1)$fold degeneracy.

a) Give the single-molecule partition function Z_1 for the rotational energy levels.
b) Give the probability p_j that the rotational energy level ε_j is occupied.

Consider a gas of N of these diatomic molecules.

c) Show that the contribution of the rotational energy levels of the gas molecules to the heat capacity C_V of the gas in the low temperature limit ($kT \ll \frac{\hbar^2}{2I}$) can be expressed as:

$$C_V = 3Nk\left(\frac{\theta_R}{T}\right)^2 e^{-\frac{\theta_R}{T}}$$

Give an expression for θ_R.

d) Derive an expression for the contribution of the rotational energy levels of the gas molecules to the heat capacity C_V of the gas in the high temperature limit ($kT \gg \frac{\hbar^2}{2I}$).

PROBLEM 3

Score: a+b+c+d =5+5+5+5=20

A *classical ideal* gas of ultra-relativistic particles is confined to a volume V. For an ultra-relativistic particle the energy E and momentum p are related by $E = pc$ with c, the velocity of light.

HINT 1: 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):

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

HINT 2:

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

a) Show that the partition function Z of this gas is given by:

$$Z = \frac{1}{N!}\left(\frac{8\pi V}{\beta^3 c^3 h^3}\right)^N$$

where N is the number of particles.

b) Calculate the energy E and the heat capacity of the gas.
c) Derive the equation of state of the gas.
d) Where do the answers to b) and c) differ from what you expect for a non-relativistic classical ideal gas?

PROBLEM 4

Score: a+b+c+d+e+f+g =4+3+4+4+4+3+3=25

Consider a perfect gas of bosons in an enclosure with volume V that is in contact with both a heat bath and a particle reservoir. A state of the gas is described by the set of occupation numbers $n_1, n_2, \cdots n_i, \cdots$ of the single-boson states with energies $\varepsilon_1 \leq \varepsilon_2 \leq \cdots \leq \varepsilon_i \leq \cdots$, respectively.

The grand partition function $\mathcal{Z}$ for this gas of bosons is defined as:

$$\mathcal{Z} = \sum_{n_1, n_2, \cdots} e^{\beta[\mu(n_1+n_2+\cdots)-(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)]}$$

And the probability of finding the gas in the state $n_1, n_2, \cdots n_i, \cdots$ is given by:

$$P(n_1, n_2, \cdots n_i, \cdots) = \frac{e^{\beta[\mu(n_1+n_2+\cdots)-(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)]}}{\mathcal{Z}}$$

a) Show that this grand partition function and probability factorize as:

$$\mathcal{Z} = \prod_{i=1}^{\infty} \mathcal{Z}_i \text{ with } \mathcal{Z}_i = \sum_{n_i} e^{\beta(\mu-\varepsilon_i)n_i}$$

and

$$P(n_1, n_2, \cdots n_i, \cdots) = \prod_{i=1}^{\infty} P_i(n_i) \text{ with } P_i(n_i) = \frac{e^{\beta(\mu-\varepsilon_i)n_i}}{\mathcal{Z}_i}$$

b) Give the interpretation of the function $P_i(n_i)$.

c) Show that for bosons we have:

$$\mathcal{Z}_i = \frac{1}{1 - e^{\beta(\mu-\varepsilon_i)}}$$

d) Prove that the mean occupation number $\overline{n}_i$ of the *i*-th single-boson state can be calculated from:

$$\overline{n}_i = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}_i}{\partial \mu}\right)_{T,V}$$

and use this expression to calculate $\overline{n}_i$.

e) Show that the total number of bosons N in a perfect boson gas is given by,

Problem continues on next page

$$N = \frac{1}{e^{-\beta\mu} - 1} + \left[\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\right] \int_0^\infty \frac{\sqrt{\varepsilon}\,d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$$

Discuss the origin and the meaning of the first term $N_1 = \frac{1}{e^{-\beta\mu}-1}$ in the expression above.

HINT: The density of states for a boson confined to an enclosure with volume V is (expressed as a function of the particle's momentum p):

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

f) The critical temperature T_c for a perfect boson gas occurs when $\mu = 0$. What is the physical interpretation of the critical temperature?

g) Show that the ratio N_1/N can be written as:

$$\frac{N_1}{N} = 1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}}$$

Solutions

PROBLEM 1

a)

The total number of microstates is (the number of ways to take n atoms from N lattice sites) times (the total number of ways to place these n atoms on M interstitial sites). This gives:

$$\Omega(n) = \frac{N!}{n!\,(N-n)!}\frac{M!}{n!\,(M-n)!} = \left(\frac{1}{n!}\right)^2 \frac{N!\,M!}{(N-n)!\,(M-n)!}$$

b)

For this certain crystal ($M = N$) we have:

$$\Omega(n) = \left(\frac{1}{n!}\right)^2 \frac{N!\,N!}{(N-n)!\,(N-n)!}$$

$$S(n) = k\ln\Omega(n) = k\{-2\ln n! + 2\ln N! - 2\ln(N-n)!\} \Rightarrow$$

$$S(n) \approx k\{-2n\ln n + 2n + 2N\ln N - 2N - 2(N-n)\ln(N-n) + 2(N-n)\} \Rightarrow$$

$$S(n) = k\{-2n\ln n + 2N\ln N - 2(N-n)\ln(N-n)\} \Rightarrow$$

$$S(n) = 2k\{N\ln N - n\ln n - (N-n)\ln(N-n)\}$$

c)

The temperature is found from:

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

$$\frac{1}{T} = \frac{2k}{\varepsilon}\frac{\partial}{\partial n}\{N\ln N - n\ln n - (N-n)\ln(N-n)\} \Rightarrow$$

$$\frac{1}{T} = \frac{2k}{\varepsilon}\{-1 - \ln n + \ln(N-n) + 1\} \Rightarrow$$

$$\frac{1}{T} = \frac{2k}{\varepsilon}\{-\ln n + \ln(N-n)\} \Rightarrow$$

$$\frac{1}{T} = \frac{2k}{\varepsilon}\left\{\ln\left(\frac{(N-n)}{n}\right)\right\}$$

Using $n = \frac{E}{\varepsilon}$ we find

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

d) This follows immediately from the results under c),

$$\frac{-\varepsilon}{2kT} = \ln\left(\frac{n}{N-n}\right) \Rightarrow$$

$$\frac{n}{N-n} = e^{\frac{-\varepsilon}{2kT}}$$

e)
We have, $n \ll N$ and thus,

$$\frac{n}{N-n} \approx \frac{n}{N} \Rightarrow n = Ne^{\frac{-\varepsilon}{2kT}}$$

$$n = Ne^{\frac{-\varepsilon}{2kT}} \Rightarrow \frac{n}{N} = e^{\frac{-\varepsilon}{2kT}} \approx e^{-19.4} \approx 3.8 \cdot 10^{-9}$$

PROBLEM 2

a) Single particle partition function

$$Z_1 = \sum_{n=0}^{\infty} (2n+1) e^{-\frac{\beta\hbar^2}{2I} n(n+1)}$$

b) Conform Mandl 2.23

$$p_j = \frac{g(\varepsilon_j) e^{-\beta\varepsilon_j}}{Z_1} = \frac{(2j+1) e^{-\frac{\beta\hbar^2}{2I} j(j+1)}}{Z_1}$$

c)

In this limit terms with higher n become less and less important.

$$Z_1 = 1 + 3e^{-\frac{\beta\hbar^2}{I}} + \cdots$$

The mean energy of one molecule is given by,

$$\bar{\varepsilon} = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{3\frac{\hbar^2}{I} e^{-\frac{\beta\hbar^2}{I}}}{1 + 3e^{-\frac{\beta\hbar^2}{I}}} \approx 3\frac{\hbar^2}{I} e^{-\frac{\beta\hbar^2}{I}}$$

And the heat capacity (for *N* gas molecules):

$$C_V = \frac{\partial N\bar{\varepsilon}}{\partial T} = -3N\left(\frac{\hbar^2}{I}\right)^2 e^{-\frac{\beta\hbar^2}{I}} \frac{\partial\beta}{\partial T} = 3Nk\left(\frac{1}{kT}\right)^2 \left(\frac{\hbar^2}{I}\right)^2 e^{-\frac{\beta\hbar^2}{I}} \Rightarrow$$

$$C_V = 3Nk\left(\frac{\theta_R}{T}\right)^2 e^{-\frac{\theta_R}{T}}$$

With $\theta_R = \frac{\hbar^2}{Ik}$

d)

$$Z_1 = \sum_{n=0}^{\infty} (2n+1) e^{-\frac{\beta\hbar^2}{2I} n(n+1)} \approx \int_0^{\infty} (2y+1) e^{-\frac{\beta\hbar^2}{2I} y(y+1)} dy$$

Because the energy levels are now very closely spaced (small compared to kT).

Use the substitution: $z = y(y+1)$ which gives $dz = (2y+1)dy$ and the integral transforms to:

$$Z_1 = \int_0^{\infty} e^{-\frac{\beta\hbar^2 z}{2I}} dz = \frac{2I}{\beta\hbar^2}$$

This results in the mean energy per molecule,

$$\bar{\varepsilon} = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{\beta\hbar^2}{2I}\frac{2I}{\beta^2\hbar^2} = \frac{1}{\beta} = kT$$

And in the heat capacity,

$$C_V = \frac{\partial N\bar{\varepsilon}}{\partial T} = Nk$$

PROBLEM 3

a)
The single particle partition function is given by:

$$Z_1 = \int_0^\infty f(p) e^{-\beta E} dp = \int_0^\infty \frac{V}{h^3} 4\pi p^2 e^{-\beta pc} dp = \frac{4\pi V}{\beta^3 c^3 h^3} \int_0^\infty x^2 e^{-x} dx = \frac{8\pi V}{\beta^3 c^3 h^3}$$

Where we used HINT 2: $\int_0^\infty x^2 e^{-x} dx = 2$

The partition function Z for the N classical particles is (see chapter 7 Mandl):

$$Z = \frac{1}{N!}(Z_1)^N = \frac{1}{N!}\left(\frac{8\pi V}{\beta^3 c^3 h^3}\right)^N$$

b)
The energy of the gas is:

$$E = -\frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial}{\partial \beta}\left[\ln\left(\frac{8\pi V}{c^3 h^3}\right) - 3\ln\beta\right] + \frac{\partial}{\partial \beta}[\ln(N!)] = \frac{3N}{\beta} = 3NkT$$

c)
The equation of state is found through Helmholtz free energy $F = E - TS = -\frac{\ln Z}{\beta}$

We have: $dF = dE - TdS - SdT = TdS - PdV - TdS - SdT = -PdV - SdT$

Which implies: $P = -\left(\frac{\partial F}{\partial V}\right)_T$

Thus:

$$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{1}{\beta}\frac{\partial}{\partial V} N\left(\ln\left(\frac{8\pi}{\beta^3 c^3 h^3}\right) + \ln V - \frac{\ln N!}{N}\right) = \frac{N}{\beta V} = \frac{NkT}{V}$$

The heat capacity is found from:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk$$

d)

For the 'normal' classical ideal gas we have $E = \frac{3}{2}NkT$; the equation of state is the same and the heat capacity is $C_V = \frac{3}{2}Nk$.

PROBLEM 4

a)

$$\mathcal{Z} = \sum_{n_1,n_2,\cdots} e^{\beta[\mu(n_1+n_2+\cdots)-(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)]} = \sum_{n_1,n_2,\cdots} e^{\beta(\mu-\varepsilon_1)n_1+\beta(\mu-\varepsilon_2)n_2+\cdots} \Rightarrow$$

$$\mathcal{Z} = \sum_{n_1,n_2,\cdots} e^{\beta(\mu-\varepsilon_1)n_1} e^{\beta(\mu-\varepsilon_2)n_2} \times \cdots = \sum_{n_1} e^{\beta(\mu-\varepsilon_1)n_1} \sum_{n_2} e^{\beta(\mu-\varepsilon_2)n_2} \times \cdots \Rightarrow$$

The equality above holds because for each n_i the factor $e^{\beta(\mu-\varepsilon_i)n_i}$ is a constant for all the sums over n_j, with $j \neq i$.

$$\mathcal{Z} = \prod_{i=1}^{\infty} \sum_{n_i} e^{\beta(\mu-\varepsilon_i)n_i} = \prod_{i=1}^{\infty} \mathcal{Z}_i$$

Start with

$$P(n_1, n_2, \cdots n_i, \cdots) = \frac{e^{\beta[\mu(n_1+n_2+\cdots)-(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)]}}{\mathcal{Z}} \Rightarrow$$

$$P(n_1, n_2, \cdots n_i, \cdots) = \frac{e^{\beta(\mu-\varepsilon_1)n_1+\beta(\mu-\varepsilon_2)n_2+\cdots}}{\mathcal{Z}} \Rightarrow$$

$$P(n_1, n_2, \cdots n_i, \cdots) = \frac{e^{\beta(\mu-\varepsilon_1)n_1} e^{\beta(\mu-\varepsilon_2)n_2} \times \cdots}{\mathcal{Z}} \Rightarrow$$

$$P(n_1, n_2, \cdots n_i, \cdots) = \frac{\prod_{i=1}^{\infty} e^{\beta(\mu-\varepsilon_i)n_i}}{\prod_{i=1}^{\infty} \mathcal{Z}_i} \Rightarrow$$

$$P(n_1, n_2, \cdots n_i, \cdots) = \prod_{i=1}^{\infty} P_i(n_i) \text{ with } P_i(n_i) = \frac{e^{\beta(\mu-\varepsilon_i)n_i}}{\mathcal{Z}_i}$$

This means that the probability to find n_i bosons in the i-th single energy state is independent of the occupancies of all other single energy states.

b)

The function $P_i(n_i)$ is the probability of finding n_i bosons in the i-th single boson state.

c)
There can be any number of bosons in each single boson state ($n_i = 0,1,2,3,\cdots$) thus,

$$\mathcal{Z}_i = \sum_{n_i=0,}^{\infty} e^{\beta(\mu-\varepsilon_i)n_i} = \sum_{n_i=0,}^{\infty} \left(e^{\beta(\mu-\varepsilon_i)}\right)^{n_i} = \frac{1}{1-e^{\beta(\mu-\varepsilon_i)}}$$

d)
The mean occupation number is defined as:

$$\overline{n}_i = \sum_{n_i} n_i\, P_i(n_i)$$

Performing the differentiation:

$$\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}_i}{\partial \mu}\right)_{T,V} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln\left(\sum_{n_i} e^{\beta(\mu-\varepsilon_i)n_i}\right) = \frac{\sum_{n_i} n_i e^{\beta(\mu-\varepsilon_i)n_i}}{\sum_{n_i} e^{\beta(\mu-\varepsilon_i)n_i}} = \sum_{n_i} n_i \frac{e^{\beta(\mu-\varepsilon_i)n_i}}{\mathcal{Z}_i} \Rightarrow$$

$$\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}_i}{\partial \mu}\right)_{T,V} = \sum_{n_i} n_i \frac{e^{\beta(\mu-\varepsilon_i)n_i}}{\mathcal{Z}_i} = \sum_{n_i} n_i P_i(n_i) = \overline{n}_i$$

We now can calculate $\overline{n}_i$ as:

$$\overline{n}_i = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}_i}{\partial \mu}\right)_{T,V} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln\left(\frac{1}{1-e^{\beta(\mu-\varepsilon_i)}}\right) = \frac{e^{\beta(\mu-\varepsilon_i)}}{1-e^{\beta(\mu-\varepsilon_i)}} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1}$$

e)

$$N = \int_0^{\infty} f(\varepsilon)n(\varepsilon)d\varepsilon$$

In this $f(\varepsilon)d\varepsilon$ is the density of states and $n(\varepsilon)$ is the mean occupation number.
The density of states follows from the hint and converting momentum to energy (using $= \frac{p^2}{2m}$) as the variable,

Substitute

$$p^2 = 2m\varepsilon \text{ and } 2pdp = 2(2m\varepsilon)^{\frac{1}{2}}dp = 2md\varepsilon \Rightarrow dp = \frac{(2m)^{\frac{1}{2}}}{2\sqrt{\varepsilon}}d\varepsilon$$

in

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

to find,

$$f(\varepsilon)d\varepsilon = \frac{V}{h^3}4\pi 2m\varepsilon\frac{(2m)^{\frac{1}{2}}}{2\sqrt{\varepsilon}}d\varepsilon = \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\sqrt{\varepsilon}d\varepsilon$$

The mean occupation number is (from d):

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

$$N = \int_0^\infty \frac{\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)} - 1}d\varepsilon = \left[\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)} - 1}d\varepsilon$$

However, the ground state $\varepsilon = 0$ has zero weight in this integral because of the $\sqrt{\varepsilon}$ dependency and is completely neglected. This situation can be mended by considering the ground state separately, the occupation number of the ground state is: $N_1 = \frac{1}{e^{-\beta\mu}-1}$, thus,

$$N = N_1 + \left[\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)} - 1}d\varepsilon$$

f)

At temperatures above the critical temperature T_c the fraction of particles in the ground state is practically zero; as the temperature decreases below T_c the fraction of particles in the ground state increases. These particles have zero energy and zero momentum.

g)

At the critical temperature we have essentially $N_1 = 0$ and $\mu = 0$ and thus (using $z = \beta_c\varepsilon$, in the integral)

$$N = \left[\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\beta_c\varepsilon} - 1}d\varepsilon = \left[\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\left(\frac{1}{\beta_c}\right)^{\frac{3}{2}}\int_0^\infty \frac{\sqrt{z}}{e^z - 1}dz \Rightarrow$$

$$N = \left[\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\left(\frac{1}{\beta_c}\right)^{\frac{3}{2}} 2.612\frac{\sqrt{\pi}}{2} \Rightarrow T_c^{\frac{3}{2}} = \frac{N}{\left[\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\left(2.612\frac{\sqrt{\pi}}{2}\right)k^{\frac{3}{2}}}$$

Below the critical temperature the chemical potential is essentially zero and we have for $T < T_C$;

$$N = N_1 + \left[\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\beta\varepsilon} - 1}d\varepsilon = N_1 + \left[\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\left(\frac{1}{\beta}\right)^{\frac{3}{2}} 2.612\frac{\sqrt{\pi}}{2} \Rightarrow$$

$$N = N_1 + N\left(\frac{\beta_c}{\beta}\right)^{\frac{3}{2}} \Rightarrow \frac{N_1}{N} = 1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}}$$