

Exam

Statistical Physics

Thursday January 22, 2015

8:30-11:30

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 4 problems.
- The weight of the problems is Problem 1 (P1=20 pts); Problem 2 (P2=25 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: $a+b+c+d = 4+6+5+5=20$

A spin system consists of N spins that have a non-degenerate ground state and an m -fold degenerate excited state with energy $\Delta\varepsilon$. The spins are interacting so weakly that they can be considered as independent. The number of spins in an excited state is denoted by n .

- a) Show (make plausible) that the number of microstates $\Omega(n)$ corresponding to the macrostate in which n spins are excited is given by:

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

- b) Use the expression of a) to show that the number of excited spins n as a function of the temperature T is given by,

$$n = \frac{mN}{m + e^{\frac{\Delta\varepsilon}{kT}}}$$

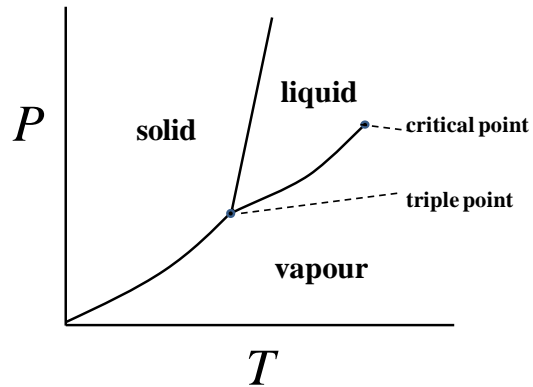
- c) Now consider the system of N spins to be in contact with a heat bath at temperature T and use the canonical approach to calculate the number of spins n in the excited state as a function of the temperature T .
- d) Calculate the heat capacity C_V of the system as a function of temperature.

In this problem you may assume that n and N are large numbers and the use of Stirling's approximation is justified.

PROBLEM 2

Score: $a+b+c+d+e=4+6+4+5+6=25$

The figure on the right gives a typical pressure (P) – temperature (T) phase diagram of a one-component system with only one triple point.



The Clausius-Clapeyron equation is:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

- Describe in words when this equation can be applied and explain all the symbols in the equation.
- Derive the Clausius-Clapeyron equation starting from the premises that the Gibbs free energy per molecule (g) in phase 1 and phase 2 is equal in the situation when equilibrium between these phases exists. Thus, $g_1(T, P) = g_2(T, P)$.
- Describe in words what happens at the critical point.
- Use the Clausius-Clapeyron equation to explain that the substance in the phase diagram expands upon melting.

Consider the vapour curve in the phase diagram. Assume that 1) the latent heat L (in Joule per mole) for vaporization is independent of temperature, 2) the vapour obeys the ideal gas law and 3) the volume of the liquid is small compared to the volume of the vapour.

- Show that under these assumptions the vapour pressure is given by:

$$P_{vap} = C e^{-\frac{L}{RT}}$$

where, C is a constant.

PROBLEM 3

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

A gas of photons is confined to a cavity with volume V . The cavity is kept at a temperature T and the gas and the cavity are in thermal equilibrium. The single particle (photon) energy levels are ε_i , $i = 1, 2, \dots$ and the occupation numbers of these energy levels are n_i , $i = 1, 2, \dots$. The partition function Z_{ph} for this gas can be expressed as:

$$Z_{ph} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\dots)}$$

- a) Show that the mean number of photons \bar{n}_i in the state with energy ε_i can be found from this partition function by,

$$\bar{n}_i = -\frac{1}{\beta} \left(\frac{\partial \ln Z_{ph}}{\partial \varepsilon_i} \right)_T$$

with $\beta = \frac{1}{kT}$

- b) Show that the mean number of photons in the state with energy ε_i is:

$$\bar{n}_i = \frac{1}{e^{\beta\varepsilon_i} - 1}$$

- c) Derive Planck's radiation law which gives the distribution of the energy density $u(\omega, T)$ as a function of the photon frequency ω for radiation in thermal equilibrium (e.g. photons in our cavity),

$$u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

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):

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

- d) Give an equation for the value of the frequency ($\omega = \omega_{max}$) for which the energy density distribution obtains its maximum. You do not have to solve this equation.

PROBLEM 4

Score: $a+b+c+d+e=5+5+5+5+5=25$

Consider a completely degenerate perfect gas of N fermions confined to a volume V at zero absolute temperature.

a) Show that the maximum energy ε_F of a fermion in this gas is,

$$\varepsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{\frac{2}{3}}$$

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):

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

b) Show that the total energy E of this gas is:

$$E = \frac{3}{5} N \varepsilon_F$$

c) Use the fundamental thermodynamic relation in the form:

$$dS = \frac{dE}{T} + \frac{P}{T} dV$$

to show that,

$$T \left(\frac{\partial P}{\partial T} \right)_V = P + \left(\frac{\partial E}{\partial V} \right)_T$$

HINT: Consider T and V as the independent variables and use the fact that S is an exact differential.

d) Show that the pressure P of the total degenerate fermion gas is,

$$P = \frac{h^2}{5m} \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} \left(\frac{N}{V} \right)^{\frac{5}{3}}$$

e) At zero absolute temperature the pressure of an ideal classical gas is zero. From the result of d) we conclude that for a ideal gas of fermions this is not the case. Qualitatively describe what causes this pressure at absolute zero temperature for an ideal gas of fermions.

Solutions

PROBLEM 1

a)

The factor $\frac{N!}{n!(N-n)!}$ gives the number of possible ways that n spins can be picked out of N spins. The factor m^n account for the fact that the excited state is m -fold degenerate thus for each excited spin there are m possibilities.

b)

First calculate the entropy for the situation with n spins in the excited state, using Stirling's approximation,

$$\begin{aligned} S(n) &= k \ln \Omega(n) = k \ln \left(\frac{m^n N!}{n!(N-n)!} \right) = k \{n \ln m + \ln N! - \ln n! - \ln(N-n)!\} \\ &= k \{n \ln m + N \ln N - N - n \ln n + n - (N-n) \ln(N-n) + (N-n)\} \\ &= k \{n \ln m + N \ln N - n \ln n - (N-n) \ln(N-n)\} \end{aligned}$$

And with $E = n\Delta\varepsilon$ we find from the microcanonical definition of temperature,

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

This can be solved for n ,

$$n = \frac{mN}{m + e^{\frac{\Delta\varepsilon}{kT}}}$$

c)

The partition function Z_1 for one spin is:

$$Z_1 = 1 + me^{-\beta\Delta\varepsilon} = 1 + me^{-\frac{\Delta\varepsilon}{kT}}$$

The probability p_e that a spin is in the excited state is:

$$p_e = \frac{me^{-\frac{\Delta\varepsilon}{kT}}}{Z_1} = \frac{me^{-\frac{\Delta\varepsilon}{kT}}}{1 + me^{-\frac{\Delta\varepsilon}{kT}}}$$

But we also have, $p_e = \frac{n}{N}$ thus,

$$\frac{n}{N} = \frac{me^{-\frac{\Delta\varepsilon}{kT}}}{1 + me^{-\frac{\Delta\varepsilon}{kT}}} \Rightarrow n = \frac{mN}{m + e^{\frac{\Delta\varepsilon}{kT}}}$$

d)

The energy E of the system is $E = n\Delta\varepsilon$.

The heat capacity C_V is,

$$C_V = \left(\frac{dE}{dT}\right)_V = \frac{d}{dT} \frac{mN\Delta\varepsilon}{m + e^{\frac{\Delta\varepsilon}{kT}}} = \frac{mN \frac{\Delta\varepsilon}{kT^2} e^{\frac{\Delta\varepsilon}{kT}}}{\left(m + e^{\frac{\Delta\varepsilon}{kT}}\right)^2} = Nk \left(\frac{\Delta\varepsilon}{kT}\right)^2 \frac{me^{-\frac{\Delta\varepsilon}{kT}}}{\left(1 + me^{-\frac{\Delta\varepsilon}{kT}}\right)^2}$$

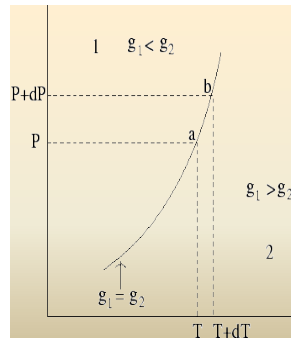
PROBLEM 2

a)

This equation can be applied in the situation of a phase transition between, say, phase 1 and phase 2 of a one-component system. ΔS and ΔV are the change in entropy and volume when a certain amount (1 molecule, 1 gram, 1 mole etc.) of the substance is transformed from phase 1 to phase 2. The equation then relates these changes to the slope of the equilibrium curve in the PT -diagram.

b)

Take two points a and b at the equilibrium curve separated by dT and dP (see figure). Then at point a : $g_1^a = g_2^a$ and at point b : $g_1^b = g_2^b$ which leads to $dg_1 = dg_2$ when moving from point a to point b .



Gibbs free energy is given by,

$$G = E + PV - TS \Rightarrow dG = dE + PdV + VdP - TdS - SdT$$

And using the fundamental thermodynamic relation for a system with variable particle number:

$$dE = TdS - PdV + \mu dN$$

We find,

$$dG = -SdT + VdP + \mu dN$$

Which holds for each phase and using ($\mu = g$) this results in ($i = 1,2$):

$$dG_i = -S_i dT + V_i dP + g_i dN$$

We also have $G_i = N_i g_i \Rightarrow dG_i = N_i dg_i + g_i dN_i$

Combining both expressions for dG_i we derive: $N_i dg_i = -S_i dT + V_i dP$ or $dg_i = -s_i dT + v_i dP$ where s_i and v_i are the entropy and volume per molecule.

Thus,

$$dg_1 = -s_1 dT + v_1 dP = dg_2 = -s_2 dT + v_2 dP \Rightarrow \frac{dP}{dT} = \frac{\Delta s}{\Delta v}$$

which is the Clausius-Clapeyron equation with ΔS and ΔV expressed on a per molecule basis.

c)

If we proceed along the vapour curve to higher temperatures the latent heat of vaporization decreases and becomes zero at the critical point, also the volume change of the phase transition becomes zero at this point. At temperatures and pressure higher than the temperature and pressure of the critical point there is no difference between the liquid and the gas phase.

d)

The Clausius-Clapeyron equation gives the slope of the melting curve. From the figure we see that this slope is positive, In the transformation from solid to liquid the entropy increases ($\Delta S = S_{liquid} - S_{solid} > 0$). For a positive slope we should have $\Delta V = V_{liquid} - V_{solid} > 0$, and thus the volume of the substance increases upon melting.

e)

The entropy change per mole is $\Delta S = \frac{L}{T}$.

The volume change is $\Delta V = V_{vapour} - V_{liquid} \approx V_{vapour}$.

The ideal gas law for one mole of vapour is : $PV_{vapour} = RT$.

Then from the Clausius-Clapeyron equation we find,

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T} \frac{1}{V_{vapour}} = \frac{LP}{RT^2} \Rightarrow$$

$$\frac{dP}{P} = \frac{LdT}{RT^2} \Rightarrow d \ln P = d \frac{-L}{RT} \Rightarrow \ln P = \frac{-L}{RT} + C \Rightarrow P = C e^{-\frac{L}{RT}}$$

PROBLEM 3

a)

The partition function is (with $\beta = \frac{1}{kT}$):

$$Z_{ph} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\dots)}$$

Differentiating $\ln Z_{ph}$ with respect to ε_i gives:

$$\begin{aligned} \frac{\partial \ln Z_{ph}}{\partial \varepsilon_i} &= \frac{-\beta}{Z_{ph}} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots n_i e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\dots)} \Rightarrow \\ \frac{\partial \ln Z_{ph}}{\partial \varepsilon_i} &= -\beta \frac{\sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots n_i e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\dots)}}{\sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\dots)}} \\ &= -\beta \frac{\sum_{n_i=0}^{\infty} n_i e^{-\beta n_i \varepsilon_i} \sum_{n_1, n_2, \dots, n_{i-1}, n_{i+1}, \dots=0}^{\infty} \dots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\dots)}}{\sum_{n_i=0}^{\infty} e^{-\beta n_i \varepsilon_i} \sum_{n_1, n_2, \dots, n_{i-1}, n_{i+1}, \dots=0}^{\infty} \dots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\dots)}} \\ &= \beta \frac{\sum_{n_i=0}^{\infty} n_i e^{-\beta n_i \varepsilon_i}}{\sum_{n_i=0}^{\infty} e^{-\beta n_i \varepsilon_i}} = \bar{n}_i \Rightarrow \\ \bar{n}_i &= -\frac{1}{\beta} \left(\frac{\partial \ln Z_{ph}}{\partial \varepsilon_i} \right)_T \end{aligned}$$

b)

The partition function can be further evaluated as

$$Z_{ph} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\dots)} = \prod_{i=1}^{\infty} \sum_{n_i=0}^{\infty} e^{-\beta(n_i\varepsilon_i)} = \prod_{i=1}^{\infty} \frac{1}{1 - e^{-\beta\varepsilon_i}}$$

Taking the logarithm :

$$\ln Z_{ph} = - \sum_{i=1}^{\infty} \ln(1 - e^{-\beta\varepsilon_i})$$

The mean number of photons then follows from:

$$\bar{n}_i = -\frac{1}{\beta} \left(\frac{\partial \ln Z_{ph}}{\partial \varepsilon_i} \right)_T = -\frac{1}{\beta} \left(\frac{e^{-\beta \varepsilon_i}}{1 - e^{-\beta \varepsilon_i}} \right) (-\beta) = \frac{1}{e^{\beta \varepsilon_i} - 1}$$

c)

For photons $\varepsilon = \hbar\omega$ and $p = \frac{\varepsilon}{c}$. Using these equation together with the hint we find for the density of states for the photons in terms of frequency ω (remember to multiply with a factor 2 for the two possible polarization states of the photon):

$$f(\omega)d\omega = 2 \frac{V}{h^3} 4\pi p^2 dp = \frac{V}{h^3} 4\pi \left(\frac{\hbar\omega}{c} \right)^2 \frac{\hbar d\omega}{c} = \frac{V}{\pi^2 c^3} \omega^2 d\omega$$

The number of photons dN and the energy dE in the range ω to $\omega + d\omega$ are given by,

$$dN = \frac{V}{\pi^2 c^3} \omega^2 \frac{1}{e^{\beta \hbar \omega} - 1} d\omega$$

And

$$dE = \hbar\omega dN = \frac{V}{\pi^2 c^3} \frac{\hbar \omega^3}{e^{\beta \hbar \omega} - 1} d\omega$$

And for the energy density we find,

$$u(\omega, T) d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta \hbar \omega} - 1} d\omega$$

d)

The maximum occurs when,

$$\frac{\partial u(\omega, T)}{\partial \omega} = 0 \Rightarrow \frac{3\omega^2}{e^{\beta \hbar \omega} - 1} - \frac{\beta \hbar \omega^3 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} = 0 \Rightarrow 3\omega^2 (e^{\beta \hbar \omega} - 1) - \beta \hbar \omega^3 e^{\beta \hbar \omega} = 0 \Rightarrow$$

$$(3 - \beta \hbar \omega) e^{\beta \hbar \omega} = 3$$

This leads to $\omega_{max} = a \hbar k T$, in which a is a constant ($a \approx 2.8$). This means the maximum shifts to higher frequencies if the temperature increases.

PROBLEM 4

a)

Using the hint: the density of states in terms of energy is, using $\varepsilon = \frac{p^2}{2m}$, and multiplying by a factor of two to account for the two spin states:

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

For a completely degenerate gas all energy levels up to a maximum level ε_F are filled with 1 fermion each. Consequently, the total number of fermions N is given by,

$$N = \int_0^{\varepsilon_F} f(\varepsilon)d\varepsilon = \frac{4\pi V}{h^3} (2m)^{\frac{3}{2}} \int_0^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon = \frac{4\pi V}{h^3} (2m)^{\frac{3}{2}} \left(\frac{2}{3} \varepsilon_F^{\frac{3}{2}} \right)$$

Solving for ε_F ,

$$\varepsilon_F = \frac{h^2}{2m} \left(\frac{3 N}{8\pi V} \right)^{\frac{2}{3}}$$

b)

$$E = \int_0^{\varepsilon_F} \varepsilon f(\varepsilon)d\varepsilon = \frac{4\pi V}{h^3} (2m)^{\frac{3}{2}} \int_0^{\varepsilon_F} \varepsilon^{\frac{3}{2}} d\varepsilon = \frac{4\pi V}{h^3} (2m)^{\frac{3}{2}} \left(\frac{2}{5} \varepsilon_F^{\frac{5}{2}} \right) = \frac{3}{5} N \varepsilon_F$$

c)

Use the hint to expand dE in terms of dT and dV .

$$dS = \frac{1}{T} \left(\left(\frac{\partial E}{\partial V} \right)_T dV + \left(\frac{\partial E}{\partial T} \right)_V dT \right) + \frac{P}{T} dV = \frac{1}{T} \left(\left(\frac{\partial E}{\partial V} \right)_T + \frac{P}{T} \right) dV + \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_V dT$$

As S is an exact differential we have:

$$\frac{\partial}{\partial T} \left\{ \frac{1}{T} \left(\left(\frac{\partial E}{\partial V} \right)_T + \frac{P}{T} \right) \right\}_V = \frac{\partial}{\partial V} \left\{ \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_V \right\}_T \Rightarrow$$

$$-\frac{1}{T^2} \left(\frac{\partial E}{\partial V} \right)_T + \frac{1}{T} \left(\frac{\partial^2 E}{\partial T \partial V} \right)_{T,V} - \frac{P}{T^2} + \frac{1}{T} \left(\frac{\partial P}{\partial T} \right)_V = \frac{1}{T} \left(\frac{\partial^2 E}{\partial V \partial T} \right)_{V,T}$$

The mixed second order derivatives cancel en we find (multiplying with T^2):

$$-\left(\frac{\partial E}{\partial V}\right)_T - P + T \left(\frac{\partial P}{\partial T}\right)_V = 0 \Rightarrow T \left(\frac{\partial P}{\partial T}\right)_V = P + \left(\frac{\partial E}{\partial V}\right)_T$$

d)

Use the equation derived under c) with $T = 0$.

Then

$$\begin{aligned} P &= -\left(\frac{\partial E}{\partial V}\right)_T = -\frac{3}{5}N \frac{\partial \varepsilon_F}{\partial V} = -\frac{3}{5}N \frac{h^2}{2m} \left(\frac{3N}{8\pi}\right)^{\frac{2}{3}} \frac{\partial V^{-\frac{2}{3}}}{\partial V} = \frac{2}{5}N \frac{h^2}{2m} \left(\frac{3N}{8\pi}\right)^{\frac{2}{3}} \frac{1}{V^{\frac{5}{3}}} \\ &= \frac{h^2}{5m} \left(\frac{3}{8\pi}\right)^{\frac{2}{3}} \left(\frac{N}{V}\right)^{\frac{5}{3}} \end{aligned}$$

e)

The pressure remains non zero at absolute zero temperature. Adding particles or reducing the volume forces the particles into higher-energy quantum states. This requires a compression force which shows as a resisting pressure. This zero-temperature pressure essentially originates from the uncertainty relation: $\Delta p \Delta x \geq \hbar$. When the system is compressed and the distance between the electrons decreases, the momenta of electrons increase giving rise to the zero-temperature pressure.