

# Solutions exam 2

## Problem 1

- (a) Which of those quantities defines a thermodynamic potential. Why? (2 points)
- (i)  $T, p, N$  Gibbs free energy  $G$
  - (ii)  $T, p, \mu$  no thermodynamic potential, since  $T, p, \mu$  are not independent of each other
  - (iii)  $S, p, N$  Enthalpy  $H$
- (b) Suppose we have a box with two chambers. In each of the two chambers we have the same ideal gas. Which conditions need to be fulfilled by
- (i) Thermal equilibrium? Heat exchange or  $T_1 = T_2$
  - (ii) Chemical equilibrium? Particle exchange or  $\mu_1 = \mu_2$
  - (iii) Mechanical equilibrium? Volume exchange or  $P_1 = P_2$

(3 points)

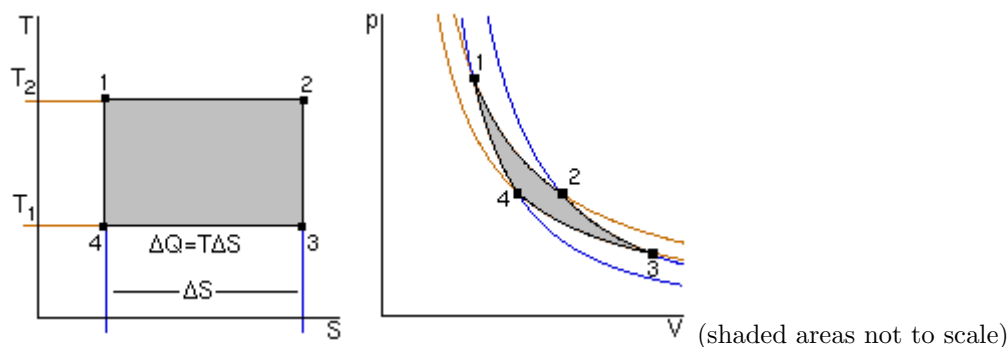
- (c) What is extremized in the microcanonical, the canonical, and the grand canonical ensemble? Is it a maximum or a minimum? (3 points) microcanonical: entropy is maximal or partition function maximal canonical: Helmholtz free energy is minimal, or entropy is maximal s.t. boundary conditions, or partition function maximal grand-canonical: Grand-potential is minimal, or entropy is maximal s.t. boundary conditions, or partition function maximal
- (d) Define the Bose-Einstein condensation. What are the volume and chemical potential in the condensed phase? Explain why. (4 points)

Below a critical temperature  $T_c$  a phase transition sets in, i.e. particles go from the gas phase in the condensate. At low temperature most particles occupy the lowest energy level (at  $T = 0$  all particles, see problem f) with

$$\frac{\langle N_0 \rangle}{N} = 1 - \left( \frac{T}{T_c} \right)^{3/2} \quad (1)$$

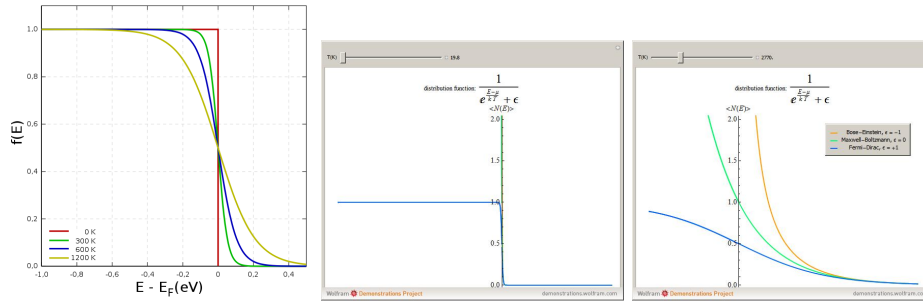
The volume of the condensate is  $V_{cond} \approx 0$  and the chemical potential is  $\mu = 0$ .

- (e) Plot qualitatively the Carnot-cycle in a  $T-S$  and a  $p-V$  diagram. Show where the heat is going in and out of the system. (4 points)



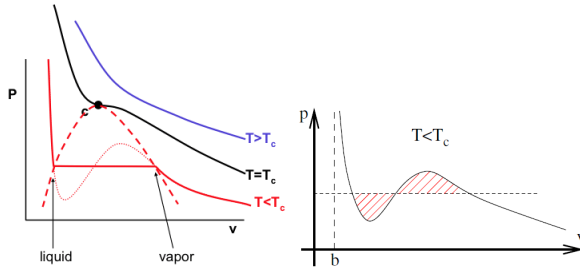
Heat goes into the system at step 1→2 (isothermal expansion) and out at step 3→4 (isothermal compression). Steps 2→3 and 4→1 are adiabatic ( $dQ = 0$ ) expansion and adiabatic ( $dQ = 0$ ) compression, respectively

- (f) Plot qualitatively the Fermi-Dirac and Bose-Einstein as a function of  $\beta(E - \mu)$  for  $T \gg 0K$  and  $T \approx 0K$ . (4 points)



left: Fermi distribution at different temperatures, middle Fermi, Bose and Boltzmann distribution at  $T=0K$ , right: Fermi, Bose and Boltzmann distribution at higher temperature.

(g) What is the Maxwell construction for the van der Waals gas? Why is it used? (5 points)



Below a critical temperature  $T_c$  a gas can condense to a liquid. The equation for the van der Waals gas (that includes interaction such that in principle the phase transition to liquid phase is possible) is cubic in the volume and hence has three solutions, possible volumes for a given pressure. One of those can be dismissed because of the positive slope of the vdW curve, corresponding to unphysical behaviour. The other two solutions correspond to liquid phase (lower volume) and gas phase (higher volume). The Maxwell construction finds the corresponding pressure from the horizontal line that equates the areas between the line and the vdW isotherm (below and above). This is the pressure at which, for the given temperature, liquid and gas phase coexist

## Problem 2 - Gas with two energy states

A classical gas in a volume  $V$  is composed of  $N$  non-interacting and indistinguishable particles. The single particle Hamiltonian is  $H = p^2/2m + \epsilon$ , with  $m$  the mass of the particle and  $p$  the absolute value of the momentum. Moreover, for each particle, we find two internal energy levels: a ground state with energy  $\epsilon = 0$  and degeneracy  $g_1$ , and an excited state with energy  $\epsilon = \epsilon_1$  and degeneracy  $g_2$ .

(a) Determine the canonical and grand canonical partition function for  $N$  particles. Show that the Helmholtz free energy has the form

$$A = -k_B T \left[ \ln \left( \frac{V^N}{h^{3N} N!} \right) + \frac{3N}{2} \ln \left( \frac{2\pi m}{\beta} \right) + N \ln(g_1) - N\beta \epsilon \ln(g_2) \right]$$

(10 points)

**Solution:**

When computing the canonical partition function, we have to consider the continuous part of the Hamiltonian  $p^2/2m$ , plus the contribution coming from the internal degrees of freedom. The partition function for the  $N$  particles is then the product of  $N$  single particle partition functions

$$\begin{aligned} Z_N(T, V, N) &= \frac{V^N}{h^{3N} N!} \left( \int_{-\infty}^{\infty} e^{-\beta \frac{p^2}{2m}} dp \right)^{3N} (g_1 + g_2 e^{-\beta \epsilon})^N \\ &= \frac{V^N}{h^{3N} N!} \left( \frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} (g_1 + g_2 e^{-\beta \epsilon})^N \end{aligned}$$

Using  $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$ . The factorial  $N!$  accounts for the classical indistinguishability of the particles. From the partition function we compute the free energy

$$A = -k_B T \ln Z_N = -k_B T \left[ \ln \left( \frac{V^N}{h^{3N} N!} \right) + \frac{3N}{2} \ln \left( \frac{2\pi m}{\beta} \right) + N \ln(g_1) - N\beta \epsilon \ln(g_2) \right]$$

- (b) Compute the energy  $E$  of the total system as a function of the temperature  $T$ . (5 points)

**Solution:**

$$E = - \left( \frac{\partial \ln Z_N}{\partial \beta} \right)_{V,N} = \frac{3}{2} N k_B T + N \frac{g_2 \epsilon e^{-\epsilon/k_B T}}{g_1 + g_2 e^{-\epsilon/k_B T}}$$

- (c) Compute specific heat  $C_V$  as a function of  $T$ . (5 points)

**Solution:**

An the specific heat

$$C_V = \left( \frac{\partial E}{\partial T} \right)_{V,N} = \frac{3}{2} N k_B + \frac{d}{dT} \left( \frac{N g_2 \epsilon e^{-\epsilon/k_B T}}{g_1 + g_2 e^{-\epsilon/k_B T}} \right) = \frac{3}{2} N k_B + \frac{N g_1 g_2 \epsilon^2 e^{\epsilon/k_B T}}{k_B T^2 (g_2 + g_1 e^{\epsilon/k_B T})^2}$$

- (d) Analyze the limit of low temperatures of the specific heat and explain this result. (5 points)

**Solution:**

For low temperatures, we find

$$\frac{N g_1 g_2 \epsilon^2 e^{\epsilon/k_B T}}{k_B T^2 (g_2 + g_1 e^{\epsilon/k_B T})^2} \approx \frac{g_1 g_2 \epsilon^2}{k_B T^2 g_1^2 e^{2\epsilon/k_B T}} \rightarrow 0$$

That is the expected result because in such limit only the ground state (the one with energy 0) is populated.

### Problem 3 - Relativistic fermi gas

In high energy physics it is convenient to take into account relativistic effects. We now want to calculate the energy and pressure of the non-interacting relativistic fermi gas. In this situation, the energy of one particle is given by  $\epsilon_p^2 = p^2 c^2 + m^2 c^4$ . Assume that we are dealing with spin-1/2 particles, further let be  $\rho(\epsilon)$  the density of states and  $\Omega(\epsilon)$  the number of states with energy smaller than  $\epsilon$ .

- (a) The grand-canonical partition sum for fermions reads as

$$\Xi = \prod_p \left( 1 + e^{-\beta(\epsilon_p - \mu)} \right)$$

Assuming we have a large system and small differences between the energy levels, we can transform the sum over all states, that appears in the corresponding grand canonical potential, into an integral:

$$\sum_p \rightarrow \int_0^\infty d\epsilon \rho(\epsilon)$$

Perform this transformation and show that the grand canonical potential for a general system of fermions can then be expressed as

$$\Phi(T, V, \mu) = -k_B T \int_0^\infty d\epsilon \frac{\Omega(\epsilon)}{1 + e^{\beta(\epsilon - \mu)}}.$$

Explain all vanishing terms that appear during your calculation. (9 points)

**Solution:**

The expression for the grand-canonical potential reads as

$$\begin{aligned}
\Phi(T, V, \mu) &= -k_B T \ln \Xi = -k_B T \sum_p \ln \left( 1 + e^{-\beta(\epsilon_p - \mu)} \right) \\
&= -k_B T \int_0^\infty d\epsilon \rho(\epsilon) \ln \left( 1 + e^{-\beta(\epsilon - \mu)} \right) \\
&= -k_B T \Omega(\epsilon) \ln \left( 1 + e^{-\beta(\epsilon - \mu)} \right) \Big|_0^\infty + k_B T \int_0^\infty d\epsilon \Omega(\epsilon) \frac{-\beta e^{-\beta(\epsilon - \mu)}}{1 + e^{-\beta(\epsilon - \mu)}} \\
&= - \int_0^\infty d\epsilon \frac{\Omega(\epsilon)}{1 + e^{\beta(\epsilon - \mu)}}.
\end{aligned}$$

Here we performed a partial integration. The boundary term vanishes since for  $\epsilon = 0$  we get  $\Omega = 0$  from a).

- (b) Calculate the number of states in 3 dimensions

$$\Omega(\epsilon) = \frac{2V}{h^3} \int_{\epsilon_p < \epsilon} d^3 p$$

with the fermion energy  $\epsilon_p$  being smaller than  $\epsilon$ . (5 points)

**Solution:**

As usual:

$$\begin{aligned}
\Omega(E) &= \frac{2V}{h^3} \int_{\epsilon_p < E} d^3 p = \frac{8\pi V}{h^3} \int_{p^2 c^2 < E^2 - m^2 c^4} p^2 dp = \frac{8\pi V}{3h^3} p^3 \Big|_{p=\sqrt{E^2/c^2 - m^2 c^2}} \\
&= \frac{8\pi V}{3h^3} \left( \frac{E^2}{c^2} - m^2 c^2 \right)^{3/2}
\end{aligned}$$

- (c) Go to the limit of highly relativistic particles ( $\epsilon \gg mc^2$ ). Show that the density of states is then given by  $\rho(\epsilon) = 3\Omega(\epsilon)/\epsilon$ . (4 points)

**Solution:**

In the highly relativistic limit we have  $E^2/c^2 - m^2 c^2 \approx E^2/c^2$ . We then just calculate the derivative:

$$\rho(E) = \frac{d\Omega(E)}{dE} = \frac{8\pi V}{3h^3} \frac{d}{dE} \frac{E^3}{c^3} = \frac{8\pi V E^2}{h^3 c^3} = \frac{3\Omega(E)}{E}.$$

- (d) Use your result from a) and the expression for the number of fermions per state  $\langle n(\epsilon) \rangle = dN/d\Omega$  to show that  $\Phi = -E/3$ , where  $E = \int dN \epsilon(N)$  is the total energy of the system (the integral over all single fermion energies). (5 points)

**Solution:**

From the lecture we know that

$$\langle n(\epsilon) \rangle = \frac{1}{1 + e^{\beta(\epsilon - \mu)}}$$

It thus follows with part b) that

$$\Phi(T, V, \mu) = -\frac{1}{3} \int_0^\infty d\epsilon \epsilon \rho(\epsilon) \langle n(\epsilon) \rangle = -\frac{1}{3} \int_0^\infty d\epsilon \epsilon \frac{d\Omega(\epsilon)}{d\epsilon} \frac{dN}{d\Omega} = -\frac{1}{3} \int_0^\infty dN \epsilon(N) = -\frac{1}{3} E.$$

- (e) Use the thermodynamic definition of the grand-canonical potential to obtain an expression for the pressure  $p(E, V)$ . (2 points)

**Solution:**

We know that  $\Phi = E - TS - \mu N = TS - pV + \mu N - TS - \mu N = -pV$ , hence  $p = E/3V$ .

## Problem 4 - Gas with hard core interaction

A gas obeys the equation of state

$$P(V - Nb) = Nk_B T \exp\left(-\frac{\alpha}{V - Nb}\right),$$

where  $\alpha$  and  $b$  are the parameters of system and  $N$  is kept fixed in the following.

- (a) Find the Maxwell relation involving  $(\partial S/\partial V)_T$ . (3 points)

**Solution:**

Using Helmholtz free energy we have

$$dA = d(E - TS) = -SdT - PdV \quad \Rightarrow \quad (\partial S/\partial V)_T = (\partial P/\partial T)_V$$

- (b) Use a differential for  $S$  to calculate  $dE(T, V)$ . Show that for the upper equation of state  $E$  is a function of  $T$  only. (9 points)

**Solution:**

We have

$$\begin{aligned} dE = TdS - PdV &= T \left( \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV \right) - PdV \\ &= T \left( \frac{\partial S}{\partial T} \right)_V dT + \left[ T \left( \frac{\partial S}{\partial V} \right)_T - P \right] dV \\ &= T \left( \frac{\partial S}{\partial T} \right)_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \end{aligned}$$

Using equation of state we have:

$$\left( \frac{dP}{dT} \right)_V = \frac{Nk_B}{(V - Nb)} \exp\left(-\frac{\alpha}{V - Nb}\right) = \frac{P}{T}$$

Then for  $dE$  we can write

$$dE = T \left( \frac{\partial S}{\partial T} \right)_V dT + \left[ T \frac{P}{T} - P \right] dV = T \left( \frac{\partial S}{\partial T} \right)_V dT$$

Then we can see that  $E$  is just a function of  $T$ , i.e  $E = E(T)$

- (c) Using  $C_P = \left( \frac{\partial H}{\partial T} \right)_P$  and the definition of the enthalpy show that:

$$\gamma = C_P/C_V = 1 + \frac{Nk_B}{C_V} \frac{(V - Nb)}{(V - Nb) - \alpha} \exp\left(-\frac{\alpha}{V - Nb}\right).$$

(9 points)

**Solution:**

Using enthalpy definition  $H = E + PV$  we have

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P = \left( \frac{\partial(E + PV)}{\partial T} \right)_P = \left( \frac{\partial E}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P.$$

Also because  $E = E(T)$  for heat capacity  $C_V$  at constant volume we have

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \left( \frac{\partial E}{\partial T} \right)_P.$$

Then for  $C_P$  we can write

$$C_P = C_V + P \left( \frac{\partial V}{\partial T} \right)_P.$$

For finding  $\left(\frac{\partial V}{\partial T}\right)_P$  it is easiest to calculate  $\left(\frac{\partial T}{\partial V}\right)_P = 1/\left(\frac{\partial V}{\partial T}\right)_P$ . Then for this reason we rewrite equation of state for  $T$

$$T = \frac{P(V - Nb)}{Nk_B} \exp\left(\frac{\alpha}{V - Nb}\right)$$

Then we have

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_P &= \frac{P}{Nk_B} \exp\left(\frac{\alpha}{V - Nb}\right) - \frac{P(V - Nb)}{Nk_B} \frac{\alpha}{(V - Nb)^2} \exp\left(\frac{\alpha}{V - Nb}\right) \\ &= \left[\frac{1}{Nk_B} - \frac{\alpha}{Nk_B(V - Nb)}\right] P \exp\left(\frac{\alpha}{V - Nb}\right). \end{aligned}$$

With substituting  $P$  as a state function in above relation we have

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_P &= \frac{V - Nb - \alpha}{Nk_B(V - Nb)} \left[\frac{Nk_B T}{V - Nb} \exp\left(-\frac{\alpha}{V - Nb}\right)\right] \exp\left(\frac{\alpha}{V - Nb}\right) \\ &= T \left[\frac{V - Nb - \alpha}{(V - Nb)^2}\right] \end{aligned}$$

Then

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_P} = \frac{(V - Nb)^2}{T(V - Nb - \alpha)}$$

Then for  $C_P$  and substituting  $P$  as a state function we can write

$$\begin{aligned} C_P &= C_V + P \left(\frac{\partial V}{\partial T}\right)_P = C_V + \frac{P(V - Nb)^2}{T(V - Nb - \alpha)} \\ &= C_V + \frac{(V - Nb)^2 Nk_B T}{T(V - Nb - \alpha)(V - Nb)} \exp\left(-\frac{\alpha}{V - Nb}\right) \\ &= C_V + Nk_B \frac{(V - Nb)}{V - Nb - \alpha} \exp\left(-\frac{\alpha}{V - Nb}\right) \end{aligned}$$

Then for  $\gamma$  we have

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{Nk_B(V - Nb)}{C_V(V - Nb - \alpha)} \exp\left(-\frac{\alpha}{V - Nb}\right)$$

- (d) In which limit does  $\gamma$  go to the value obtained from an ideal gas? (4 points)

**Solution:**

In the limit of  $\alpha \rightarrow 0$  we have  $\gamma = 1 + \frac{Nk_B}{C_V}$ . That is the same as the ideal gas relation for  $\gamma$ .