Exam T6

Thermodynamics and Statistical Physics 2019-2020

Tuesday, January 21, 2020, 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=25 pts); Problem 2 (P2=20 pts); Problem 3 (P3=20 pts) and 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 Name S-number		PROBLEM 2 Name S-number		PROBLEM 3 Name S-number		PROBLEM 4 Name S-number	

PROBLEM 1
Score: a+b+c+d+e=5+5+5+5+5=25

An alternative to the van der Waals equation of state for a real gas is the Berthelot equation:

$$P = \frac{RT}{V-b} - \frac{a}{TV^2}$$

in which P, V, T are the pressure, the *molar* volume and the temperature of the gas, respectively. The constant a controls the attractive molecular interactions and the constant b corrects for the volume of the gas molecules.

a) Show that for a gas described by the Berthelot equation (a Berthelot gas) the constants a and b are related to the critical temperature T_c, the critical pressure P_c and the critical volume V_c by

$$a = \frac{27}{64}\frac{R^2 T_c^3}{P_c}; b = \frac{R T_c}{8 P_c} = \frac{V_c}{3}$$

b) Show that the second virial coefficient $B(T)$ of a Berthelot gas is given by:

$$B(T) = \frac{V_c}{3}\left(1 - \frac{27}{8}\left(\frac{T_c}{T}\right)^2\right)$$

c) For a certain Berthelot gas the critical temperature is measured to be 150 K. Calculate the Boyle temperature T_b of this Berthelot gas. Why is this called the Boyle temperature?

d) Rewrite the equation of state of a Berthelot gas in reduced coordinates.

e) For a gas A with $T_c = 130$ K and $P_c = 3.8$ MPa part of the vapor curve is given in the PT diagram below. Use this diagram and the law of corresponding states to construct part of the vapor curve of a gas B with $T_c = 300$ K and $P_c = 7.4$ MPa.
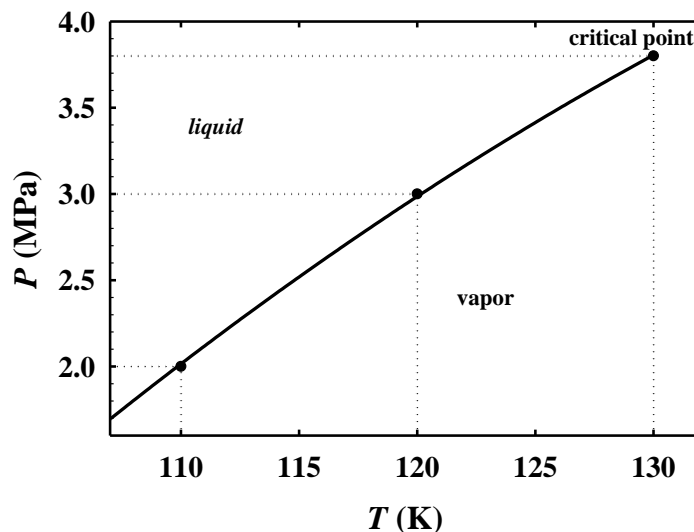
PROBLEM 2
Score: a+b+c+d+e =4+4+4+4+4=20

A Joule expansion is an irreversible expansion of a gas in a vacuum. The figure below shows a schematic of such an expansion. Initially, all gas is contained in a vessel with volume V_1 and then the gas is allowed to expand in an evacuated vessel (with volume V_2) by opening a tap. The combined volume of the two vessels is ($V_{tot} = V_1 + V_2$). We will assume that the system of two vessels is *isolated* from the surroundings.

Before expansion   After expansion

tap

vacuum
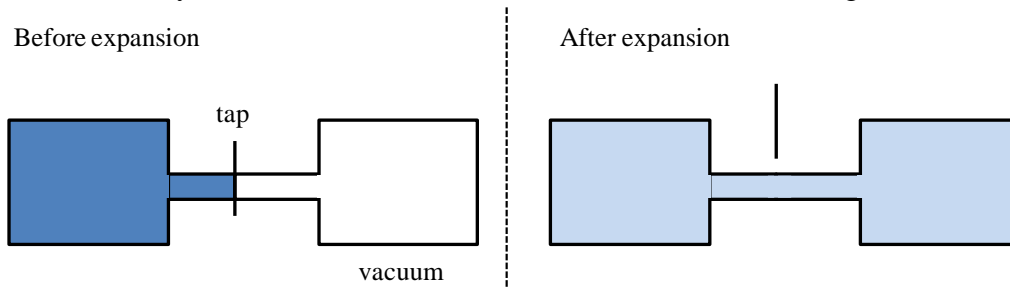
a) Explain why the internal energy U of the gas does not change in this expansion.

The Joule coefficient describes the change in temperature T of the gas when the volume V of the gas is changed at constant internal energy U:

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$$

b) Show that μ_J can be written as (hint: use the reciprocity and the reciprocal theorem):

$$\mu_J = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$$

   with C_V the heat capacity at constant volume of the gas

c) Show that μ_J can be expressed as (hint: use the first law and a Maxwell relation):

$$\mu_J = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]$$

with P the pressure of the gas.
The equation of state of a certain gas is given by (with V the molar volume):

$$P = \frac{RT}{V-b} - \frac{a}{V^3}$$

d) Calculate μ_J for this gas.
e) Calculate the difference $\Delta T = T_2 - T_1$ in temperature before (T_1) and after (T_2) the expansion of the gas. Express your answer in terms of C_V, V_1, V_{tot} and a. In case a is a positive constant, is the temperature difference positive or negative? Explain your answer also in terms of the intermolecular interactions.

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PROBLEM 3 *Score: a+b+c+d+e =4+4+4+4+4=20*

Consider a system of three identical non-interacting particles. Each particle can be in one of three single particle states: φ_1, φ_2 and φ_3 with energies 0, ε and ε, respectively. *Note: identical implies that if the particles have spin this is also pointing in the same direction!*

Use the notation (n_1, n_2, n_3) for three particle states with n_i $(i = 1,2,3)$ the occupation number of single-particle state φ_i $(i = 1,2,3)$, respectively. For example: $(1,1,1)$ means that one particle is in state φ_1, one particle is in state φ_2 and one particle is in state φ_3.

List all three-particle states with their energy and degeneracy in case the three particles are:

a) Distinguishable classical particles
b) Indistinguishable fermions
c) Indistinguishable bosons
d) Give the partition functions for situations a), b) and c).
e) Calculate the mean energy as a function of temperature for situations a), b) and c). Compare the mean energies for situations a), b) and c) in the limit $T \to \infty$. Is this what you expected? Why?

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

A gas of *non-interacting* bosons each with mass m and spin $S = 1$ is enclosed in a volume V and is in contact with both a heat bath at temperature T and a particle reservoir characterized by the chemical potential μ. 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:
$$\mathcal{Z}_i = \frac{1}{1 - e^{\beta(\mu-\varepsilon_i)}}$$

d) Prove that the mean occupation number $\langle n_i \rangle$ of the i-th single-boson state can be calculated from:
$$\langle n_i \rangle = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}_i}{\partial \mu}\right)_{T,V}$$

and use this expression to calculate $\langle n_i \rangle$.

e) Show that the total number of bosons N of the gas is given by,

$$N = \frac{1}{e^{-\beta\mu} - 1} + \left[\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\right] \int_0^\infty \frac{\sqrt{\varepsilon}d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$$

Discuss the origin and the meaning of the first term $N_0 = \frac{1}{e^{-\beta\mu}-1}$ in the expression above.

HINT: The density of states for a boson with spin $S = 0$ confined to an enclosure with volume V is (expressed as a function of the particle's momentum p):

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

f) Calculate the condensation temperature T_c of the boson gas in terms of $\frac{N}{V}$ and m and fundamental constants.

g) Show that the ratio N_0/N can be written as:

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

Solutions

PROBLEM 1

a)
The critical point is found when the isotherm of the gas has an infliction point, thus as,

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

This gives (together with the Berthelot equation of state) three equations with three unknowns namely:

$$P = \frac{RT}{V-b} - \frac{a}{TV^2} \qquad eq(1)$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{TV^3}$$

Thus $\left(\frac{\partial P}{\partial V}\right)_T = 0$ leads to

$$\left(\frac{-RT}{(V-b)^2} + \frac{2a}{TV^3}\right) = 0 \Rightarrow \frac{2RT^2}{(V-b)^2} = \frac{4a}{V^3} \qquad eq(2)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \left(\frac{2RT}{(V-b)^3} - \frac{6a}{TV^4}\right)$$

And $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$ leads to

$$\left(\frac{2RT}{(V-b)^3} - \frac{6a}{TV^4}\right) = 0 \Rightarrow \frac{2RT^2}{(V-b)^2} = \frac{6a(V-b)}{V^4} \qquad eq(3)$$

Combining 2 and 3 leads to

$$\frac{4a}{V^3} = \frac{6a(V-b)}{V^4} \Rightarrow 4V = 6(V-b) \Rightarrow V_c = 3b$$

Substituting this in equation 2 gives,

$$\frac{2RT^2}{(3b-b)^2} = \frac{4a}{(3b)^3} = 0 \Rightarrow \frac{2RT^2}{4b^2} = \frac{4a}{27b^3} \Rightarrow T_c = \frac{2}{3}\sqrt{\frac{2}{3}\frac{a}{bR}}$$

and $T_c = \frac{2}{3}\sqrt{\frac{2}{3}\frac{a}{bR}}$ and $V_c = 3b$ in equation 1 gives,

$$P_c = \frac{R\frac{2}{3}\sqrt{\frac{2}{3}\frac{a}{bR}}}{3b-b} - \frac{a}{\frac{2}{3}\sqrt{\frac{2}{3}\frac{a}{bR}}(3b)^2} = \frac{1}{3b}\sqrt{\frac{2}{3}\frac{aR}{b}} - \frac{3a}{18b^2}\sqrt{\frac{3}{2}\frac{bR}{a}}$$

$$= \frac{1}{3b}\sqrt{\frac{2}{3}\frac{aR}{b}} - \frac{9}{36b}\sqrt{\frac{2}{3}\frac{aR}{b}} = \frac{1}{12b}\sqrt{\frac{2}{3}\frac{aR}{b}}$$

And thus,

$$T_c^2 = \left(\frac{2}{3}\right)^3 \frac{a}{bR} \text{ and } P_c^2 = \left(\frac{1}{2\times3}\right)^3 \frac{aR}{b^3} \Rightarrow$$

$$\frac{T_c^2}{P_c^2} = \frac{\left(\frac{2}{3}\right)^3 \frac{a}{bR}}{\left(\frac{1}{2\times3}\right)^3 \frac{aR}{b^3}} = (2)^6 \frac{b^2}{R^2} \Rightarrow b = \frac{R\,T_c}{8\,P_c}$$

And,

$$a = \frac{bRT_c^2}{\left(\frac{2}{3}\right)^3} = \frac{RT_c^2}{\left(\frac{2}{3}\right)^3}\frac{R\,T_c}{8\,P_c} = \frac{27}{64}\frac{R^2 T_c^3}{P_c}$$

b)
Rewrite the Berthelot equation as:

$$\frac{PV}{RT} = \frac{1}{\left(1 - \frac{b}{V}\right)} - \frac{a}{RT^2 V}$$

and expand the first term on the right hand side in powers of $\frac{1}{V}$:

$$\frac{PV}{RT} = \left(1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \cdots\right) - \frac{a}{RT^2 V} \Rightarrow$$

$$\frac{PV}{RT} = 1 + \left(b - \frac{a}{RT^2}\right)\frac{1}{V} + \cdots$$

Thus,

$$B(T) = b - \frac{a}{RT^2} = \frac{V_c}{3} - \frac{27}{64}\frac{R^2T_c^3}{P_c}\frac{1}{RT^2}$$

Using

$$b = \frac{R}{8}\frac{T_c}{P_c} \Rightarrow P_c = \frac{R}{8}\frac{T_c}{b} = \frac{3R}{8}\frac{T_c}{V_c}$$

We find

$$B(T) = \frac{V_c}{3} - \frac{27}{64}\frac{R^2T_c^3}{\left(\frac{3R}{8}\frac{T_c}{V_c}\right)}\frac{1}{RT^2} = \frac{V_c}{3}\left(1 - \frac{27}{8}\left(\frac{T_c}{T}\right)^2\right)$$

c) The temperature at which the second virial coefficient is zero is called the Boyle temperature.

$$B(T) = 0 \Rightarrow 1 - \frac{27}{8}\left(\frac{T_c}{T}\right)^2 = 0 \Rightarrow T_b = \sqrt{\frac{27}{8}}T_c = 1.84 \times 150 = 276 \text{ K}$$

At this temperature Boyle's law ($PV = constant$) approximately holds for a real gas.

d)
We introduce reduced coordinates:

$$\tilde{P} = \frac{P}{P_c}; \ \tilde{T} = \frac{T}{T_c}; \ \tilde{V} = \frac{V}{V_c}$$

And rewrite the Berthelot equations as,

$$\tilde{P}P_c = \frac{R\tilde{T}T_c}{\tilde{V}V_c - b} - \frac{a}{\tilde{T}T_c(\tilde{V}V_c)^2} \Rightarrow \tilde{P}\frac{1}{12b}\sqrt{\frac{2}{3}\frac{aR}{b}} = \frac{R\tilde{T}\frac{2}{3}\sqrt{\frac{2}{3}\frac{a}{bR}}}{3\tilde{V}b - b} - \frac{a}{\tilde{T}\frac{2}{3}\sqrt{\frac{2}{3}\frac{a}{bR}}9b^2\tilde{V}^2} \Rightarrow$$

$$\tilde{P}\sqrt{\frac{2}{3}\frac{aR}{b}} = \frac{R\tilde{T}8\sqrt{\frac{2}{3}\frac{a}{bR}}}{3\tilde{V} - 1} - \frac{12a}{6\tilde{T}\sqrt{\frac{2}{3}\frac{a}{bR}}b\tilde{V}^2} \Rightarrow \tilde{P} = \frac{8\tilde{T}}{3\tilde{V} - 1} - \frac{12\sqrt{\frac{3ab}{2R}}}{6\tilde{T}\sqrt{\frac{2}{3}\frac{ab}{R}}\tilde{V}^2} \Rightarrow$$

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$$\tilde{P} = \frac{8\tilde{T}}{3\tilde{V}-1} - \frac{12\frac{3}{2}}{6\tilde{T}\tilde{V}^2} = \frac{8\tilde{T}}{3\tilde{V}-1} - \frac{3}{\tilde{T}\tilde{V}^2}$$

e)

We use the law of corresponding states that implies that in reduced parameters the PT diagrams of both gasses lie on top of each other.
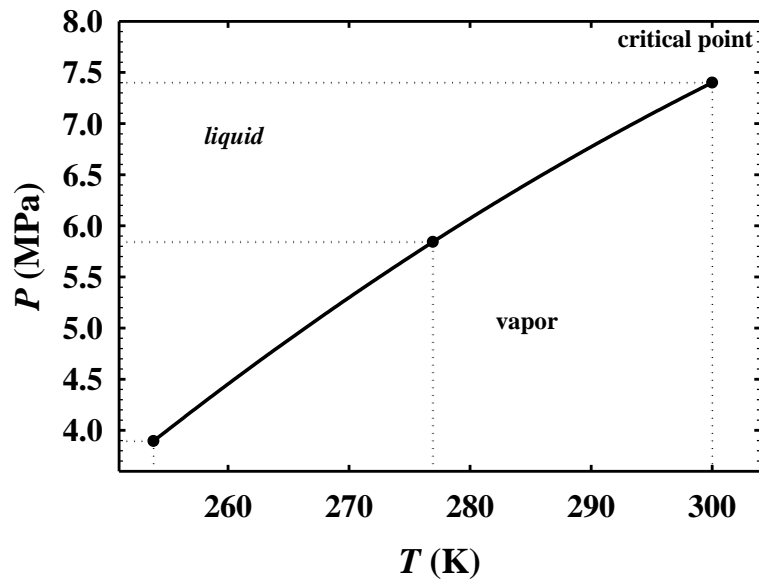
This means that we have:

$$\widetilde{T^A} = \widetilde{T^B} \Rightarrow \frac{T^A}{T_c^A} = \frac{T^B}{T_c^B} \text{ and } \widetilde{P^A} = \widetilde{P^B} \Rightarrow \frac{P^A}{P_c^A} = \frac{P^B}{P_c^B}$$

So, we can convert the data from the diagram for gas A to data for the diagram for gas B.

$$T^B = \frac{T_c^B}{T_c^A}T^A = 2.31 \times T^A \text{ and } P^B = \frac{P_c^B}{P_c^A}P^A = 1.95 \times P^A$$

This results in the following diagram.

PROBLEM 2

a) No work is done so $dW = 0$; system is isolated so, $dQ = 0$.
Thus, $dU = dW + dQ = 0$

b)

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$$

Reciprocity and reciprocal theorem:

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{-1}{\left(\frac{\partial V}{\partial U}\right)_T \left(\frac{\partial U}{\partial T}\right)_V} = -\frac{1}{\left(\frac{\partial U}{\partial T}\right)_V}\left(\frac{\partial U}{\partial V}\right)_T$$

And with $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ we find,

$$\mu_J = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$$

c)
From the first law: $dU = TdS - PdV$ we derive,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Maxwell relation can be used from the formula sheet or can be derived from the fact that F is exact:

Thus, $dF = -SdT - PdV = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \Rightarrow$

$$-S = \left(\frac{\partial F}{\partial T}\right)_V \Rightarrow -\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial^2 F}{\partial V \partial T}\right)_{V,T} = \left(\frac{\partial^2 F}{\partial T \partial V}\right)_{T,V} = -\left(\frac{\partial P}{\partial T}\right)_V$$

Substitution gives:

$$\mu_J = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]$$

d)

$$P = \frac{RT}{V - b} - \frac{a}{V^3}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

Thus,

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$$\mu_J = -\frac{1}{C_V}\left[\frac{TR}{V-b} - \frac{RT}{V-b} + \frac{a}{V^3}\right] = -\frac{a}{V^3 C_V}$$

e)

$$\Delta T = \int_{V_1}^{V_{tot}} \left(\frac{\partial T}{\partial V}\right)_U dV = \int_{V_1}^{V_{tot}} \mu_J dV = -\int_{V_1}^{V_{tot}} \frac{a}{V^3 C_V} dV = -\frac{a}{2C_V}\left(\frac{1}{V_1^2} - \frac{1}{V_{tot}^2}\right)$$

This is a negative quantity because $V_{tot} > V_1 \Rightarrow \left(\frac{1}{V_1^2} - \frac{1}{V_{tot}^2}\right) > 0$, thus the gas cools on expansion. In terms of the intermolecular forces this can be explained by the fact that these forces are attractive (in case a is positive) and thus the potential energy due to the attraction of the molecules becomes less negative when these molecules are farther apart (as is the case after the expansion). As the potential energy U_{pot} part of the total internal energy U increases, the kinetic energy part U_{kin} has to decrease as $dU = 0 = dU_{pot} + dU_{kin}$. Decreasing kinetic energy results in decreasing temperature.

Note: the volume in the equation of state and in the expression for the Joule coefficient are molar volumes. So, to use the Joule coefficient in e) you actually have to replace the molar volume V by the real volume nV in which n is the number of moles. The conclusions will not change.

PROBLEM 3

a)   (1,1,1) with energy 2ε, and degeneracy: 6
        (2,1,0) with energy ε, and degeneracy: 3
        (1,2,0) with energy 2ε, and degeneracy: 3
        (1,0,2) with energy 2ε and degeneracy: 3
        (2,0,1) with energy ε and degeneracy:3
        (0,2,1) with energy 3ε and degeneracy:3
        (0,1,2) with energy 3ε, and degeneracy: 3
        (3,0,0) with energy 0, and degeneracy: 1
        (0,3,0) with energy 3ε, and degeneracy: 1
        (0,0,3) with energy 3ε, and degeneracy: 1

Remark, because the particles are distinguishable interchanging the particles gives a different state if the particles are in different single-energy states.

b)   (1,1,1) with energy 2ε, and degeneracy: 1

c) The same as in a) except now all degeneracies are 1

        (1,1,1) with energy 2ε, and degeneracy: 1
        (2,1,0) with energy ε, and degeneracy: 1
        (1,2,0) with energy 2ε, and degeneracy: 1
        (1,0,2) with energy 2ε and degeneracy: 1
        (2,0,1) with ε and degeneracy:1
        (0,2,1) with 3ε and degeneracy:1
        (0,1,2) with energy 3ε, and degeneracy: 1
        (3,0,0) with energy 0, and degeneracy: 1
        (0,3,0) with energy 3ε, and degeneracy: 1
        (0,0,3) with energy 3ε, and degeneracy: 1

d)
Situation a) $Z = 1 + 6e^{-\beta\varepsilon} + 12e^{-2\beta\varepsilon} + 8e^{-3\beta\varepsilon}$
Situation b) $Z = e^{-2\beta\varepsilon}$
Situation c) $Z = 1 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + 4e^{-3\beta\varepsilon}$

e)
Situation a)

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \varepsilon \frac{6e^{-\beta\varepsilon} + 24e^{-2\beta\varepsilon} + 24e^{-3\beta\varepsilon}}{1 + 6e^{-\beta\varepsilon} + 12e^{-2\beta\varepsilon} + 8e^{-3\beta\varepsilon}}$$

Situation b)

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \varepsilon \frac{2e^{-2\beta\varepsilon}}{e^{-2\beta\varepsilon}} = 2\varepsilon$$

Situation c)

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \varepsilon \frac{2e^{-\beta\varepsilon} + 6e^{-2\beta\varepsilon} + 12e^{-3\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + 4e^{-3\beta\varepsilon}}$$

In the limit $T \to \infty$

Situation a)

$$\langle E \rangle \to \varepsilon \frac{6 + 24 + 24}{1 + 6 + 12 + 8} = \frac{54}{27}\varepsilon = 2\varepsilon$$

Situation b)

$$\langle E \rangle \to 2\varepsilon$$

Situation c)

$$\langle E \rangle \to \varepsilon \frac{2 + 6 + 12}{1 + 2 + 3 + 4} = \frac{20}{10}\varepsilon = 2\varepsilon$$

At high temperatures the system becomes classical and all states are equally probable and thus have on average 1 particle (because there are 3 states and three particles) and thus the mean energy becomes $(0 + \varepsilon + \varepsilon) = 2\varepsilon$.

PROBLEM 4

a)

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

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

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 $j \neq i$.

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

Start with

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

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

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

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

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

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,

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

d)
The mean occupation number is defined as:

$$\langle n_i \rangle = \sum_{n_i} n_i \, P_i(n_i)$$

Performing the differentiation:

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

$$\frac{1}{\beta}\left(\frac{\partial \ln Z_i}{\partial \mu}\right)_{T,V} = \sum_{n_i} n_i \frac{e^{\beta(\mu-\varepsilon_i)n_i}}{Z_i} = \sum_{n_i} n_i P_i(n_i) = \langle n_i \rangle$$

We now can calculate $\langle n_i \rangle$ as:

$$\langle n_i \rangle = \frac{1}{\beta}\left(\frac{\partial \ln Z_i}{\partial \mu}\right)_{T,V} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln\left(\frac{1}{1-e^{\beta(\mu-\varepsilon_i)}}\right) = \frac{e^{\beta(\mu-\varepsilon_i)}}{1-e^{\beta(\mu-\varepsilon_i)}} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1}$$

e)

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

In this $g(\varepsilon)d\varepsilon$ is the density of states and $n(\varepsilon)$ is the mean occupation number.

The density of states follows from the hint (using a factor $2S+1 = 3$ for the fact we have spin 1 bosons instead of the spin 0 bosons in 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

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

(where we inserted the factor 3 for the spin states) to find,

$$g(\varepsilon)d\varepsilon = 3\frac{V}{h^3}4\pi2m\varepsilon\frac{(2m)^{\frac{1}{2}}}{2\sqrt{\varepsilon}}d\varepsilon = \frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\sqrt{\varepsilon}d\varepsilon$$

The mean occupation number is (from d):

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

$$N = \int_0^\infty \frac{\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)}-1}d\varepsilon = \left[\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)}-1}d\varepsilon$$

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: $N_0 = \frac{1}{e^{-\beta\mu}-1}$, thus,

$$N = N_0 + \left[\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)}-1}d\varepsilon$$

f)
At the condensation temperature T_c we have essentially $N_0 = 0$ and $\mu = 0$ and thus (using $z = \beta_c\varepsilon = \frac{\varepsilon}{kT_c}$, in the integral)

$$N = \left[\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\beta_c\varepsilon}-1}d\varepsilon = \left[\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\left(\frac{1}{\beta_c}\right)^{\frac{3}{2}}\int_0^\infty \frac{\sqrt{z}}{e^z-1}dz \Rightarrow$$

$$N = \left[\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\left(\frac{1}{\beta_c}\right)^{\frac{3}{2}}2.612\frac{\sqrt{\pi}}{2} \Rightarrow (kT_c)^{\frac{3}{2}} = \frac{N}{\left[\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\left(2.612\frac{\sqrt{\pi}}{2}\right)} \Rightarrow$$

$$T_c = \left(\frac{N}{V}\right)^{\frac{2}{3}}\left(\frac{1}{3\times2.612}\right)^{\frac{2}{3}}\frac{h^2}{2\pi mk}$$

g)
Below the condensation temperature the chemical potential is essentially zero and we have for $T < T_c$;

$$N = N_0 + \left[\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\beta\varepsilon}-1}d\varepsilon = N_0 + \left[\frac{6\pi V}{h^3}(2m)^{\frac{3}{2}}\right]\left(\frac{1}{\beta}\right)^{\frac{3}{2}}2.612\frac{\sqrt{\pi}}{2} \Rightarrow$$

$$N = N_0 + N\left(\frac{\beta_c}{\beta}\right)^{\frac{3}{2}} \Rightarrow \frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}}$$