

Solution to Statistical Physics Exam

29th June 2015

Name	Student Number

Problem 1	Problem 2	Problem 3	Problem 4	Total	Percentage	Mark

Useful constants

Gas constant R	$8.31 J / (K \cdot mol)$
Boltzmann constant k_B	$1.38 \cdot 10^{-23} J / K$
Avogadro number N_A	$6.02 \cdot 10^{23} mol^{-1}$
Speed of light c	$300 \cdot 10^6 m / s$

(25P) Problem 1

1. **(2P)** Find the entropy of rolling an octahedral and a dodecahedral “die”, respectively. The entropy S reads

$$S = k_B \sum_{i=1}^n p_i \ln \frac{1}{p_i},$$

where p_i is the probability that the system is in the i -th microstate, and n is the total number of the microstates. For the octahedral “die” one finds $p_i = 1/8$ and $n = 8$, yielding $S = k_B \ln 8$. For the dodecahedral “die” one finds $p_i = 1/12$ and $n = 12$, yielding $S = k_B \ln 12$.

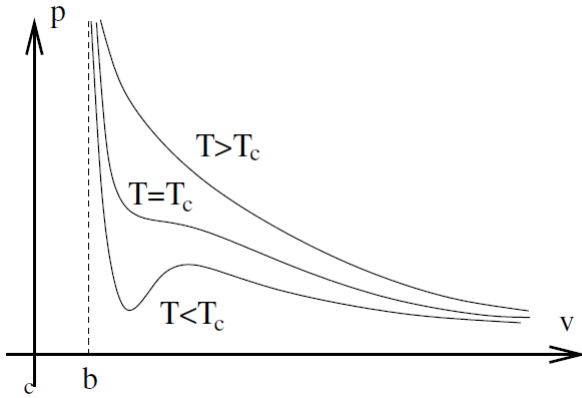
2. **(1P)** How does the phase space density of a microcanonical ensemble in equilibrium change with time? The phase space density of the microcanonical ensemble is constant in equilibrium.
3. **(2P)** Which are the units of the micro-canonical and the grand-canonical partition function, respectively? The partition functions are dimensionless, they are the number of states, in the microcanonical case, those which are compliant with a certain energy, in the grand-canonical case, weighted by the dimensionless Boltzmann factor.
4. **(3P)** Which quantities are constant in a
- micro-canonical ensemble ? N, V, E number of particles, volume, energy
 - canonical ensemble ? N, V, T number of particles, volume, temperature
 - grand-canonical ensemble ? μ, V, T chemical potential, volume, temperature
5. **(1P)** How does the heat capacity of a classical ideal monoatomic gas depend on temperature? $C_v = \frac{3}{2} N k_B$ no temperature dependence.
6. **(1P)** Which thermodynamic potential is constant during a Joule-Thomson process? Enthalpy H
7. **(2P)** Express the heat capacity at constant volume C_V and the heat capacity at constant pressure C_P as a second derivative of an appropriate thermodynamic potential ($N = \text{const}$)
 heat capacity at constant volume $C_V = \left(\frac{\partial Q}{\partial T} \right)_{V,N} = T \left(\frac{dS}{dT} \right)_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_{V,N}$ since $\left(\frac{\partial F}{\partial T} \right)_{V,N} = -S(N, p, T)$

heat capacity at constant pressure $C_p = \left(\frac{\partial Q}{\partial T} \right)_{p,N} = T \left(\frac{dS}{dT} \right)_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{p,N}$ since $\left(\frac{\partial G}{\partial T} \right)_{p,N} = -S(N, p, T)$

1. **(2P)** What is the qualitative difference between the phase diagram of water and that of a “normal substance”, e.g. carbon dioxide? The volume of solid water is larger than that of liquid water at most temperatures. Hence, the melting curve has a negative slope, whereas it has a positive slope for CO₂.
2. **(3P)** Write down the total differential for the Helmholtz Free energy ? The Helmholtz free energy A depends on number of particles N , volume V , and temperature T , hence

$$\begin{aligned} dA &= \frac{\partial A}{\partial N} dN + \frac{\partial A}{\partial V} dV + \frac{\partial A}{\partial T} dT \\ &= \mu dN - P dV - S dT \end{aligned}$$

3. (4P) Which quantities are intensive: volume, temperature, particle number, pressure, entropy?
 Temperature, pressure.
4. (3P) Sketch the isotherms for the van der Waals equation in a P, V (pressure, Volume) diagram for temperature $T > T_c$, $T = T_c$, and $T < T_c$ where T_C is the critical temperature.



5. (1P) What is the maximal occupation number of an energy level in an ideal Fermi gas? One for each spin level, or two if spin is not considered.

(25P) Problem 2

Consider a system of N ideal gas particles with mass m at a temperature T . The mean pressure is P . N_g gas particles move freely in a volume $V = L_g^3$. Another N_s ideal gas particles are absorbed on a surface with area L_s^2 , forming a two-dimensional gas and $N = N_g + N_s$. The energy of an absorbed particle is $\varepsilon = \frac{|\mathbf{p}|^2}{2m} - \varepsilon_0$ where \mathbf{p} is the two-dimensional momentum and ε_0 is the binding energy per particle.

1. **(6P)** Calculate the classical partition functions of the free gas Z_g and of the adsorbed gas Z_s . The particles are indistinguishable. **In continuous space**

$$\sum_p \approx \frac{V}{h^3} \int d^3p \quad (1)$$

Such that

$$Z(1) \approx \frac{V}{h^3} \int d^3p \exp[-\beta\varepsilon_p] \quad (2)$$

Plugging in $\beta\varepsilon_p = \frac{p^2}{2mk_B T}$ and integrating over the sphere

$$Z(1) = \frac{V}{h^3} 4\pi \int dp \cdot p^2 \exp\left[-\frac{p^2}{2mk_B T}\right] \quad (3)$$

We now substitute $x^2 = \frac{p^2}{2mk_B T}$ and obtain a standard integral

$$Z(1) = \frac{V}{h^3} 4\pi (2mk_B T)^{\frac{3}{2}} \underbrace{\int_{-\infty}^{\infty} dx \cdot x^2 \exp[-x^2]}_{\frac{1}{4}\sqrt{\pi}} \quad (4)$$

such that

$$Z_g(1, V, T) = \frac{V}{h^3} (2\pi mk_B T)^{\frac{3}{2}} \quad (5)$$

$$Z_g(N_g, V, T) = \frac{V^{N_g}}{N_g! \lambda^{3N_g}} \quad (6)$$

$$Z_s(1, V, T) = \frac{L_s^2}{h^2} (2\pi mk_B T) \cdot \exp\left[\frac{N_s \varepsilon_0}{k_B T}\right] \quad (7)$$

$$Z_s(N_s, V, T) = \frac{L_s^{2N}}{N_s! \lambda^{2N}} \cdot \exp\left[\frac{N_s \varepsilon_0}{k_B T}\right] \quad (8)$$

$$Z_g = \frac{V^{N_g}}{N_g!} \left(\frac{2\pi mk_B T}{h^2}\right)^{\frac{3N_g}{2}}$$

$$Z_s = \frac{L_s^{2N_g}}{N_s!} \left(\frac{2\pi mk_B T}{h^2}\right)^{\frac{2N_g}{2}} \cdot \exp\left[\frac{N_s \varepsilon_0}{k_B T}\right]$$

2. **(4P)** Find an expression for the Gibbs free energies G_g and G_s of the free and the adsorbed gas, respectively, using the partition functions from above.

$$G = A + PV = -k_B T \ln Z + Nk_B T$$

where we have used the ideal gas law $PV = Nk_B T$. Hence

$$\begin{aligned}
G_g &= -k_B T \ln \left[\frac{V^{N_g}}{N_g!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N_g}{2}} \right] + N_g k_B T \\
&= -k_B T \left[\ln \frac{V^{N_g}}{N_g!} + \frac{3N_g}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] + N_g k_B T \\
&= -k_B T \left[\ln V^{N_g} - \ln N_g! + \frac{3N_g}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] + N_g k_B T \\
&\approx -k_B T \left[\ln V^{N_g} - N_g \ln N_g - N_g + \frac{3N_g}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] + N_g k_B T \\
&= -N_g k_B T \left[\ln V - \ln N_g + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] \\
&= N_g k_B T \left[\ln \frac{N_g}{V} - \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] \\
\\
G_s &= -k_B T \ln \left[\frac{L_s^{2N_s}}{N_s!} \left(\frac{2\pi m k_B T}{h^2} \right)^{N_s} \cdot \exp \left[\frac{N_s \varepsilon_0}{k_B T} \right] \right] + N_s k_B T \\
&= -k_B T \left[\ln \frac{L_s^{2N_s}}{N_s!} + N_s \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{N_s \varepsilon_0}{k_B T} \right] + N_s k_B T \\
&= -k_B T \left[\ln L_s^{2N_s} - \ln N_s! + N_s \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{N_s \varepsilon_0}{k_B T} \right] + N_s k_B T \\
&\approx -k_B T \left[\ln L_s^{2N_s} - N_s \ln N_s - N_s + N_s \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{N_s \varepsilon_0}{k_B T} \right] + N_s k_B T \\
&= -N_s k_B T \left[\ln L_s^2 - \ln N_s + \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} \right] \\
&= N_s k_B T \left[\ln \frac{N_s}{L_s^2} - \ln \left(\frac{2\pi m k_B T}{h^2} \right) - \frac{\varepsilon_0}{k_B T} \right]
\end{aligned}$$

3. **(4P)** Find the chemical potentials μ_g and μ_s of the free and the absorbed gas, respectively. The chemical potential is the Gibbs free energy per particle $\mu = \frac{G}{N}$ or also $\mu = \left(\frac{\partial G}{\partial N} \right)_{p,T}$. Hence,

$$\mu_g = -k_B T \left[\ln \frac{V}{N_g} + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

and

$$\mu_s = -k_B T \left[\ln \frac{L_s^2}{N_s} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} \right]$$

4. **(4P)** At temperature T , the free gas particles and the absorbed gas particles are in equilibrium. Calculate the mean number of gas particles absorbed per unit area in terms of of the given conditions (temperature pressure, ...) In equilibrium, the two chemical potentials are equal

$$\begin{aligned}
\mu_g &= \mu_s \\
-k_B T \left[\ln \frac{V}{N_g} + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] &= -k_B T \left[\ln \frac{L_s^2}{N_s} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} \right] \\
\ln \frac{V}{N_g} + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) &= \ln \frac{L_s^2}{N_s} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} \tag{9}
\end{aligned}$$

We are interested in the number of particles per area, i.e. solving for $\frac{N}{L_s^2}$:

$$\begin{aligned}
-\ln \frac{L_s^2}{N_s} &= \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} - \ln \frac{V}{N_g} - \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \\
&= -\frac{1}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} - \ln \frac{V}{N_g} \\
\ln \frac{N_s}{L_s^2} &= \ln \frac{N_g}{V} + \ln \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{1}{2}} + \frac{\varepsilon_0}{k_B T} \\
\frac{N_s}{L_s^2} &= \frac{N_g}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{1}{2}} \cdot \exp \left[\frac{\varepsilon_0}{k_B T} \right] \tag{10}
\end{aligned}$$

5. **(2P)** Keeping temperature T and total number of particles N the same, now the volume in which the free gas particles can move is increased. What consequences does this have for the equilibrium between the free gas particles and the gas particles absorbed on the surface, i.e. are more or less particles absorbed compared to the case with smaller volume? Justify your answer. According to eq. 10 the number of absorbed particles per area (L_s^2) decreases. One can think of there is more space for particles to move freely, and hence the probability to “find” space in the larger volume is larger.
6. **(3P)** What do partition function, Gibbs free energy, and chemical potential for gas particles absorbed on a one-dimensional “surface” look like?

$$\begin{aligned}
Z_l &= \frac{L_s^{2N}}{N_l!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{1N}{2}} \cdot \exp \left[\frac{N_l \varepsilon_0}{k_B T} \right] \\
G_l &= N_l k_B T \left[\ln \frac{N_l}{L_l} - \frac{1}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) - \frac{\varepsilon_0}{k_B T} \right] \\
\mu_l &= -k_B T \left[\ln \frac{L_l^1}{N_l} + \frac{1}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} \right]
\end{aligned}$$

7. **(2P)** The N_l particles absorbed on the one-dimensional surface are now in equilibrium with the free gas particles. (There are no particles on a two-dimensional surface and $N = N_g + N_l$). How does the number of particles per unit length in this equilibrium compare to the number of particles per unit area (from the equilibrium above) under the same (temperature, pressure, mass...) conditions?

$$\mu_g = \mu_l$$

$$\begin{aligned}
\ln \frac{V}{N_g} + \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) &= \ln \frac{L_l^1}{N_l} + \frac{1}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} \\
\ln \frac{N_l}{L_l^1} &= \frac{1}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} - \ln \frac{V}{N_g} - \frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) \\
&= \ln \frac{N_g}{V} - \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{\varepsilon_0}{k_B T} \\
\frac{N_l}{L_l^1} &= \frac{N_g}{V} \left(\frac{h^2}{2\pi m k_B T} \right) \cdot \exp \left[\frac{\varepsilon_0}{k_B T} \right]
\end{aligned}$$

Hence

$$\frac{N_l}{L_l^1} = \left(\frac{h^2}{2\pi m k_B T} \right)^{\frac{1}{2}} = \sqrt{\lambda}$$

(25P) Problem 3

Consider an ideal Fermi gas of N particles in a volume V and in a magnetic field H at temperature $T = 0$. The energy of a particle is

$$\varepsilon = \frac{p^2}{2m} \pm \mu_B H \quad (11)$$

where μ_B is Bohr's magneton.

1. **(6P)** Give an expression for the chemical potential μ_0 in terms of the number of particles N for vanishing magnetic field. For zero temperature, the Fermi-Dirac distribution is a step function. To get the number of particles N , we integrate up to the Fermi momentum p_F

$$\begin{aligned} N &= 2 \cdot \frac{V}{h^3} \int_0^{p_F} d^3 p \\ &= 2 \cdot \frac{V}{h^3} 4\pi \int_0^{p_F} p^2 dp \\ &= 2 \cdot \frac{4\pi V}{3h^3} p_F^3 \end{aligned}$$

At $T = 0$ and for vanishing magnetic field, the chemical potential equals the Fermi energy $\mu_0 = \varepsilon_F = \frac{p_F^2}{2m}$. Hence,

$$p_F = \left(\frac{N}{2 \cdot 4\pi V} 3h^3 \right)^{\frac{1}{3}}$$

and

$$\mu_0 = \frac{\left(\frac{N}{8\pi V} 3h^3 \right)^{\frac{2}{3}}}{2m} \quad (12)$$

$$= \frac{\hbar^3 \left(3\pi^2 \frac{N}{V} \right)^{\frac{2}{3}}}{2m} \quad (13)$$

2. **(4P)** Write down the Fermi momenta of the spins oriented parallel and anti-parallel, respectively, to the external magnetic field $H \neq 0$ For finite magnetic field

$$\varepsilon_F = \frac{p_F^2}{2m} \pm \mu_B H \quad (14)$$

and with $\mu_0 = \varepsilon_F$

$$\begin{aligned} p_{F+} &= [2m(\mu_0 - \mu_B H)]^{\frac{1}{2}} \\ p_{F-} &= [2m(\mu_0 + \mu_B H)]^{\frac{1}{2}} \end{aligned}$$

3. **(8P)** Find the total energy of spins oriented parallel E_- and anti-parallel E_+ , respectively. The total energy of the spins oriented anti-parallel to the external magnetic field is

$$\begin{aligned} E_+ &= \frac{V}{h^3} \int_0^{p_{F+}} \left(\frac{p^2}{2m} + \mu_B H \right) dp \\ &= \frac{4\pi V}{h^3} \int_0^{p_{F+}} \left(\frac{p^2}{2m} + \mu_B H \right) p^2 dp \\ &= \frac{4\pi V}{h^3} \int_0^{p_{F+}} \left(\frac{p^4}{2m} + \mu_B H p^2 \right) dp \\ &= \frac{4\pi V}{h^3} \left(\frac{p_{F+}^5}{10m} + \frac{\mu_B H p_{F+}^3}{3} \right) \end{aligned}$$

and the total energy of the spins oriented parallel to the external magnetic field is

$$E_- = \frac{4\pi V}{h^3} \left(\frac{p_{F-}^5}{10m} - \frac{\mu_B H p_{F-}^3}{3} \right)$$

4. **Bonus Task (3P)** Show that for weak external magnetic fields, $\mu_0 \gg \mu_B H$, the average energy per particle

$$\frac{E}{N} \approx \frac{3}{5} \mu_0 \left[1 - \frac{5}{2} \left(\frac{\mu_B H}{\mu_0} \right)^2 \right] \quad (15)$$

The average energy per particle is

$$\begin{aligned} \frac{E}{N} &= \frac{E_+ + E_-}{N} \\ &= \frac{1}{N} \left[\frac{4\pi V}{h^3} \left(\frac{p_{F+}^5}{10m} + \frac{p_{F+}^3 \mu_B H}{3} \right) + \frac{4\pi V}{h^3} \left(\frac{p_{F-}^5}{10m} - \frac{p_{F-}^3 \mu_B H}{3} \right) \right] \\ &= \frac{4\pi V}{N h^3} \left(\frac{p_{F+}^5 + p_{F-}^5}{10m} + \frac{\mu_B H (p_{F+}^3 - p_{F-}^3)}{3} \right) \end{aligned}$$

Using eq.12

$$\frac{4\pi V}{N h^3} = \frac{1}{2 \cdot (2m\mu_0)^{\frac{3}{2}}}$$

we have

$$\frac{E}{N} = \frac{3}{2 \cdot (2m\mu_0)^{\frac{3}{2}}} \left(\frac{p_{F+}^5 + p_{F-}^5}{10m} + \frac{\mu_B H (p_{F+}^3 - p_{F-}^3)}{3} \right)$$

we can write

$$\begin{aligned} \frac{p_{F+}^5 + p_{F-}^5}{10m} &= \frac{[2m(\mu_0 - \mu_B H)]^{\frac{5}{2}} + [2m(\mu_0 + \mu_B H)]^{\frac{5}{2}}}{10m} \\ &= \frac{2m \frac{(2m)^{\frac{3}{2}}}{10m} (\mu_0 - \mu_B H)^{\frac{5}{2}} + (2m)^{\frac{3}{2}} (\mu_0 + \mu_B H)^{\frac{5}{2}}}{10m} \\ &= \frac{(2m)^{\frac{3}{2}} \left[(\mu_0 - \mu_B H)^{\frac{5}{2}} + (\mu_0 + \mu_B H)^{\frac{5}{2}} \right]}{5} \end{aligned}$$

and

$$(p_{F+}^3 - p_{F-}^3) \frac{\mu_B H}{3} = \frac{\mu_B H}{3} \left([2m(\mu_0 - \mu_B H)]^{\frac{3}{2}} - [2m(\mu_0 + \mu_B H)]^{\frac{3}{2}} \right)$$

For $\mu_0 \gg \mu_B H$ we can expand

$$\begin{aligned} \left[(\mu_0 - \mu_B H)^{\frac{5}{2}} + (\mu_0 + \mu_B H)^{\frac{5}{2}} \right] &\approx \left[\left(\mu_0^{\frac{5}{2}} - \frac{5}{2} \mu_0^{\frac{3}{2}} \mu_B H \dots \right) + \left(\mu_0^{\frac{5}{2}} + \frac{5}{2} \mu_0^{\frac{3}{2}} \mu_B H \dots \right) \right] \\ &\approx 2\mu_0^{\frac{5}{2}} \end{aligned} \quad (16)$$

and

$$\begin{aligned} \left[(\mu_0 - \mu_B H)^{\frac{3}{2}} - (\mu_0 + \mu_B H)^{\frac{3}{2}} \right] &= \left[\left(\mu_0^{\frac{3}{2}} - \frac{3}{2} \mu_0^{\frac{1}{2}} \mu_B H \dots \right) - \left(\mu_0^{\frac{3}{2}} + \frac{3}{2} \mu_0^{\frac{1}{2}} \mu_B H \dots \right) \right] \\ &\approx -3\mu_0^{\frac{1}{2}} \mu_B H \end{aligned} \quad (17)$$

Such that plugging this in

$$\begin{aligned}
\frac{E}{N} &\approx \frac{3}{2 \cdot (2m\mu_0)^{\frac{3}{2}}} \left(\frac{(2m)^{\frac{3}{2}} 2\mu_0^{\frac{5}{2}}}{5} + \frac{\mu_B H}{3} (2m)^{\frac{3}{2}} (-3\mu_0^{\frac{1}{2}} \mu_B H) \right) \\
&= \frac{3}{2 \cdot (\mu_0)^{\frac{3}{2}}} \left(\frac{2\mu_0^{\frac{5}{2}}}{5} + \frac{\mu_B H}{3} (-3\mu_0^{\frac{1}{2}} \mu_B H) \right) \\
&= \frac{3}{2} \left(\frac{2\mu_0}{5} - \frac{\mu_B H}{\mu_0} (\mu_B H) \right) \\
&= \frac{3}{5} \left(\mu_0 - \frac{5}{2} \frac{(\mu_B H)^2}{(\mu_0)} \right) \\
&= \frac{3}{5} \mu_0 \left(1 - \frac{5}{2} \frac{(\mu_B H)^2}{(\mu_0)^2} \right)
\end{aligned} \tag{18}$$

5. **Bonus Task (4P)** Calculate the susceptibility $\chi = \frac{\partial M}{\partial H}$ for weak external magnetic fields, where M is the average magnetisation per volume.

$$\begin{aligned}
M &= \frac{\mu_B (N_- - N_+)}{V} \\
&= \frac{\mu_B \left(\frac{4\pi V}{3h^3} \mathcal{P}_{F-}^3 - \frac{4\pi V}{3h^3} \mathcal{P}_{F+}^3 \right)}{V} \\
&= \frac{\mu_B \frac{4\pi V}{3h^3} \left([2m(\mu_0 + \mu_B H)]^{\frac{3}{2}} - [2m(\mu_0 - \mu_B H)]^{\frac{3}{2}} \right)}{V}
\end{aligned}$$

and again with eq. 12

$$\frac{4\pi V}{3h^3 N} = \frac{1}{2 \cdot (2m\mu_0)^{\frac{3}{2}}}$$

thus

$$\begin{aligned}
M &= \frac{\mu_B \frac{N}{2 \cdot (2m\mu_0)^{\frac{3}{2}}} \left([2m(\mu_0 + \mu_B H)]^{\frac{3}{2}} - [2m(\mu_0 - \mu_B H)]^{\frac{3}{2}} \right)}{V} \\
&= \mu_B \frac{N}{2V(\mu_0)^{\frac{3}{2}}} \left([(\mu_0 + \mu_B H)]^{\frac{3}{2}} - [(\mu_0 - \mu_B H)]^{\frac{3}{2}} \right)
\end{aligned}$$

In the limit of low magnetic field and $\mu_B H \ll \mu \approx \varepsilon_F$ we expand again

$$\begin{aligned}
\left[(\mu_0 + \mu_B H)^{\frac{3}{2}} - (\mu_0 - \mu_B H)^{\frac{3}{2}} \right] &= \left[\left(\mu_0^{\frac{3}{2}} + \frac{3}{2} \mu_0^{\frac{1}{2}} \mu_B H + \dots \right) - \left(\mu_0^{\frac{3}{2}} - \frac{3}{2} \mu_0^{\frac{1}{2}} \mu_B H \dots \right) \right] \\
&\approx 3\mu_0^{\frac{1}{2}} \mu_B H
\end{aligned}$$

$$\begin{aligned}
M &= \mu_B \frac{N}{2V(\mu_0)^{\frac{3}{2}}} \left(3\mu_0^{\frac{1}{2}} \mu_B H \right) \\
&= \mu_B \frac{3N}{2V(\mu_0)} (\mu_B H) \\
&= \frac{3N}{2V\mu_0} \mu_B^2 H
\end{aligned} \tag{19}$$

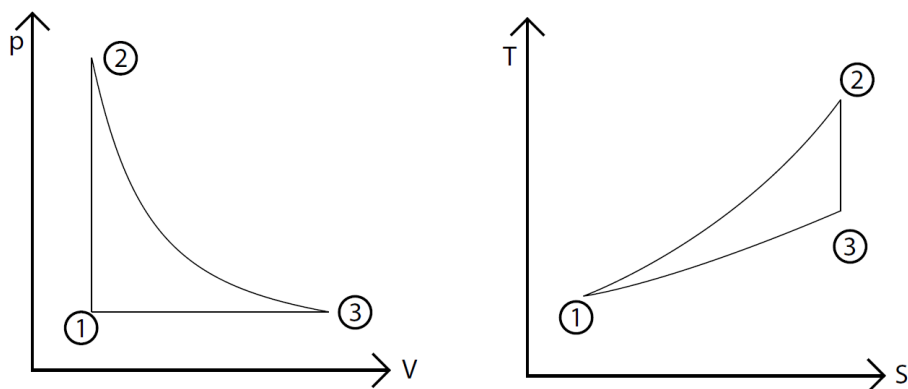


Figure 1: Pressure-Volume (left) and temperature-entropy (right) diagram of a three-step cyclic process.

(25P) Problem 4

A.) Figure 1 shows a three-steps cyclic process as Pressures-volume (P, V) and temperature-entropy (T, S) diagram, respectively. Consider 1 mol of an ideal gas which has initially volume V_1 , pressure P_1 , and temperature T_1 , undergoing such a cyclic process.

- (3P) Describe the steps $1 \rightarrow 2$; $2 \rightarrow 3$; and $3 \rightarrow 1$ sketched in the two diagrams: Which thermodynamic quantity changes, which is kept constant? $1 \rightarrow 2$ isochoric heating to T_2 ; $2 \rightarrow 3$ isentropic (adiabatic) expansion to V_3 ; and $3 \rightarrow 1$ isobaric cooling to T_1
- (12P) For each step calculate the performed work W and the heat transfer Q in terms of pressure P_1 and volumes V_1, V_3 .

$1 \rightarrow 2$:

$$W_{12} = \int_{V_1}^{V_2} P_1 dV = 0$$

since $V_2 = V_1$

$$\begin{aligned} Q_{12} &= C_V (T_2 - T_1) \\ &= C_V \frac{V_1}{R} (P_2 - P_1) \\ &= C_V \frac{V_1 P_1}{R} \left(\frac{P_2}{P_1} - 1 \right) \\ &= C_V \frac{V_1 P_1}{R} \left(\frac{P_2}{P_3} - 1 \right) \\ &= C_V \frac{V_1 P_1}{R} \left(\left(\frac{V_3}{V_2} \right)^\gamma - 1 \right) \\ &= C_V \frac{V_1 P_1}{R} \left(\left(\frac{V_3}{V_1} \right)^\gamma - 1 \right) \end{aligned}$$

where we have used the ideal gas law $PV = RT$ and the adiabatic relation $V_1^\gamma P_1 = V_2^\gamma P_2$ and $V_1 = V_2$ together with $P_1 = P_3$.

$2 \rightarrow 3$:

$$Q_{23} = 0$$

since $S_3 = S_2$ (adiabatic process). Hence $\Delta U = W$ and

$$W_{23} = U_3 - U_2$$

From the definition of the heat capacity at constant volume we rewrite

$$\begin{aligned} U_3 - U_2 &= C_V (T_3 - T_2) \\ &= \frac{C_V}{R} (P_1 V_3 - P_2 V_1) \end{aligned}$$

where we have used the ideal gas law again as $P_3 V_3 = RT_3 = P_1 V_3$ and $P_2 V_2 = RT_2 = P_2 V_1$. Using the adiabatic relations we then arrive at

$$\begin{aligned} W_{23} &= \frac{C_V P_1}{R} \left(V_3 - \frac{P_2}{P_1} V_1 \right) \\ &= \frac{C_V P_1}{R} \left(V_3 - \left(\frac{P_2}{P_3} \right) V_1 \right) \\ &= \frac{C_V P_1}{R} \left(V_3 - \left(\frac{V_3}{V_2} \right)^\gamma V_1 \right) \\ &= \frac{C_V P_1}{R} \left(V_3 - V_1 \left(\frac{V_3}{V_1} \right)^\gamma \right) \end{aligned}$$

3 \rightarrow 1:

$$W_{31} = \int_{V_3}^{V_1} P_1 dV = P_1 (V_1 - V_3)$$

From the first law we know

$$Q_{31} = W_{31} + U_1 - U_3$$

plugging in the expression for work and rearranging

$$\begin{aligned} (U_1 + P_1 V_1) - (U_3 + P_1 V_3) &= (H_1 - H_3) \\ &= C_P (T_1 - T_3) \\ &= \gamma C_V (T_1 - T_3) \end{aligned}$$

where we have used the definition of the enthalpy, and the heat capacity at constant pressure such that we finally obtain

$$Q_{31} = -\frac{\gamma C_V P_1}{R} (V_3 - V_1) < 0$$

B.) **Bonus Task** For a low-density gas the virial expansion can be terminated at first order in the density and the equation of state is:

$$P = \frac{N k_B T}{V} \left[1 + \frac{N}{V} B_2(T) \right] \quad (20)$$

where P : pressure, V : volume, N : number of particles, T : temperature and k_B : Boltzmann's constant. $B_2(T)$ is the second virial coefficient. The heat capacity will have corrections to its ideal gas value. We can write it in the form

$$C_{V,N} = \frac{3}{2} N k_B - \frac{N^2 k_B}{V} f(T) \quad (21)$$

1. **(3P)** Find the entropy and internal energy as partial derivatives of the Helmholtz free energy, A (*Hint*: use the relation between pressure P and Helmholtz free energy at constant temperature). Regarding to Helmholtz free energy for canonical ensemble we have

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \quad (22)$$

$$P = \frac{Nk_B T}{V} + \frac{N^2 k_B T}{V^2} B_2(T) = P_{ideal} + \delta P \quad (23)$$

Using equ.22 the free energy is

$$A = A_{ideal} + k_B T B_2(T) \frac{N^2}{V} \quad (24)$$

Then

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = S_{ideal} + \delta S, \quad \delta S = -k_B \frac{N^2}{V} [B_2(T) + T B_2'(T)] \quad (25)$$

Since we know both entropy and Helmholtz free energy, we find the internal energy as

$$U = A + TS = U_{ideal} + k_B T B_2(T) \frac{N^2}{V} - k_B T \frac{N^2}{V} [B_2(T) + T B_2'(T)] = U_{ideal} + \delta U \quad (26)$$

$$\delta U = -k_B T^2 B_2'(T) \frac{N^2}{V} \quad (27)$$

2. **(4P)** Find the form that $f(T)$ must have in order for the two equations to be thermodynamically consistent. As a result of subtask 1,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V^{ideal} + \delta C_V \implies \delta C_V = -k_B T \frac{N^2}{V} [2B_2'(T) + T B_2''(T)] \quad (28)$$

We find in this way,

$$f(T) = 2T B_2'(T) + T^2 B_2''(T) \quad (29)$$

3. **(3P)** Find the heat capacity at constant pressure and constant number of particles $C_{P,N}$. Let us express the equation of state as $V(P, T)$. Since the density is assumed to be small in the correction one can use equation for the ideal gas to find the the volume. We have,

$$V = \frac{Nk_B T}{P} + N B_2(T) \quad (30)$$

Consequently, the entropy can be expressed as

$$S = S_{ideal} + \delta S_1 \quad (31)$$

with replacing equ.30 in δS in equ.25 we have

$$\delta S_1 = -k_B N \frac{B_2 + T B_2'}{\frac{k_B T}{P} + B_2} \quad (32)$$

now

$$C_P = C_P^{ideal} + T \left(\frac{\partial \delta S_1}{\partial T}\right)_P \quad (33)$$

$$= -k_B N \frac{(B_2 + TB_2)' \left(\frac{k_B T}{P} + B_2 \right) - \left(\frac{k_B}{P} + B_2' \right) (B_2 + TB_2')}{\left(\frac{k_B T}{P} + B_2 \right)^2} \quad (34)$$

$$= C_P^{ideal} - k_B \frac{N^2}{V} [T(2B_2' + TB_2'') - (B_2 + TB_2')] \quad (35)$$

$$= C_P^{ideal} + \delta C_V + k_B \frac{N^2}{V} (B_2 + TB_2') \quad (36)$$

As a result,

$$C_P - C_V = (C_P - C_V)^{ideal} + k_B \frac{N^2}{V} (B_2 + TB_2') \quad (37)$$