

Statistical Mechanics Exam

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Problem 1. Gas of particles @ T whose average energy in a box of volume V is

$$E = bVT^3, \quad (b > 0)$$

(a)

Let's begin with:

$$dE = TdS - PdV$$

which implies that:

$$dS = \frac{1}{T} dE + \frac{P}{T} dV,$$

and from $E = bVT^3$, we have:

$$T = (E/bV)^{1/3},$$

and at constant volume, we have;

$$dS = \frac{1}{T} dE \Rightarrow dS = (bV/E)^{1/3} dE,$$

and if we integrate, we have;

$$S = \int (bV)^{1/3} E^{-1/3} dE = (bV)^{1/3} \frac{E^{2/3}}{(2/3)} + f(V)$$

in which we assume V is constant, and $f(V)$ comes from the fact that we may have an extra

function that only depends on v .

But, we know that $E = bVT^3$, thus, it follows that:

$$S = \frac{3}{2} (bv)^{1/3} (bVT^3)^{2/3} + f(v)$$

$$\Rightarrow S = \frac{3}{2} (bv)^{1/3} (bv)^{2/3} (T^3)^{2/3} + f(v)$$

$$\Rightarrow S = \frac{3}{2} b v T^2 + f(v).$$

In order to find $f(v)$, we're going to use the following Maxwell relation:

$$\left(\frac{\partial S}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_v,$$

$$\text{and } dE = TdS - PdV \Rightarrow P = - \left(\frac{\partial E}{\partial v} \right)_S.$$

On the other hand, we know:

$$S = \frac{3}{2} (bv)^{1/3} E^{2/3} + f(v),$$

and if we assume $f(v) = S_0$, then, we can solve the previous equation for E , this is

$$E = \left(\frac{2}{3} \frac{(S - S_0)}{(bv)^{1/3}} \right)^{3/2}$$

which implies that

$$P = -\left(\frac{\partial E}{\partial V}\right)_S = -\left(\frac{2(S-S_0)}{3}\right)^{3/2} b^{-1/2} \left(-\frac{1}{2} V^{-3/2}\right) \\ = \frac{1}{2} \left(\frac{2(S-S_0)}{3}\right)^{3/2} b^{-1/2} V^{-3/2},$$

but $S-S_0 = \frac{3}{2} b T^2$, thus:

$$P = \frac{1}{2} (b T^2)^{3/2} b^{-1/2} V^{-3/2}$$

$P = \frac{1}{2} b T^3$, and now, we need to verify the previous Maxwell relation, this is;

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{3}{2} b T^2 + f'(V) \quad \text{and}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left[\frac{\partial}{\partial T} \left(\frac{1}{2} b T^3\right)\right]_V = \frac{3}{2} b T^2,$$

$\Rightarrow f'(V) = 0 \Rightarrow f(V)$ is a constant;
and without any loss of generality, we can set that constant equal to zero.

Therefore, we have:

$$S = \frac{3}{2} bVT^2$$

(b) Conserved quantities

→ Since the boxes are thermally isolated, there is no heat exchange. Once the partition is removed, the gases mix, but the total volume remains the same, and moreover, no work is done or on by the system, thus:

→ the total energy is conserved.

→ the total volume is conserved.

→ the number of particles.

(c) change in entropy

We're going from (T_1, V_1, T_2, V_2) ^{initial} → final
thus:

$$S_{\text{initial}} = S_1 + S_2 = \frac{3}{2} bV_1 T_1^2 + \frac{3}{2} bV_2 T_2^2$$

$$\Rightarrow S_{\text{initial}} = \frac{3}{2} bV_1 T_1^2 + \frac{3}{2} bV_2 T_2^2$$

and for the final, we have that $V = V_1 + V_2$, and both reach equilibrium at some temperature T_f , thus:

$$S_{\text{final}} = \frac{3}{2} b V_f T_f^2 = \frac{3}{2} b (V_1 + V_2) T_f^2,$$

and from energy conservation, we can compute T_f , this is:

$$E_{\text{initial}} = E_{\text{final}}$$

$$\Rightarrow b V_1 T_1^3 + b V_2 T_2^3 = b (V_1 + V_2) T_f^3$$

$$\Rightarrow V_1 T_1^3 + V_2 T_2^3 = (V_1 + V_2) T_f^3$$

$$\Rightarrow T_f = \left(\frac{V_1 T_1^3 + V_2 T_2^3}{V_1 + V_2} \right)^{1/3}$$

then, we have:

$$S_{\text{final}} = \frac{3}{2} b (V_1 + V_2) \left(\frac{V_1 T_1^3 + V_2 T_2^3}{V_1 + V_2} \right)^{2/3},$$

and thus, the change in entropy will be given by:

$$\Rightarrow \Delta S = S_{\text{final}} - S_{\text{initial}}$$

thus:

$$\Delta S = \frac{3}{2} b \left[(v_1 + v_2) \left(\frac{v_1 T_1^3 + v_2 T_2^3}{v_1 + v_2} \right)^{2/3} - v_1 T_1^2 - v_2 T_2^2 \right]$$

$$\Rightarrow \Delta S = \frac{3}{2} b \left[(v_1 + v_2)^{1/3} (v_1 T_1^3 + v_2 T_2^3)^{2/3} - v_1 T_1^2 - v_2 T_2^2 \right]$$

④ Let's prove that the change in entropy is never negative:

We want to prove

$\Delta S \geq 0$, which is equivalent to

$(v_1 + v_2) T_f^2 \geq v_1 T_1^2 + v_2 T_2^2$, and if we consider the expression we found for T_f , we have:

$$(v_1 + v_2) \left(\frac{v_1 T_1^3 + v_2 T_2^3}{v_1 + v_2} \right)^{2/3} \geq v_1 T_1^2 + v_2 T_2^2,$$

Now, from here the outline of the proof is as follows; we're going to prove that the function is concave, and from there we're going to use Jensen's inequality

to prove $\Delta S \geq 0$.

① Let's rename; $x = \frac{v_1 T_1^3 + v_2 T_2^3}{v_1 + v_2}$, and let's look at

$$f(x) = x^{2/3},$$

$$\text{then; } f''(x) = -\frac{2}{9} x^{-4/3} \leq 0 \text{ for } \underline{\underline{x > 0}},$$

which implies that $f(x)$ is concave.

② for a concave function, Jensen's inequality tell us that:

$$\frac{\sum w_i f(x_i)}{\sum w_i} \leq f\left(\frac{\sum w_i x_i}{\sum w_i}\right),$$

and if we make $w_1 = v_1$, $w_2 = v_2$, $x_1 = T_1^3$ and $x_2 = T_2^3$, we have;

$$\frac{v_1 (T_1^3)^{2/3} + v_2 (T_2^3)^{2/3}}{v_1 + v_2} \leq \left(\frac{v_1 T_1^3 + v_2 T_2^3}{v_1 + v_2} \right)^{2/3}$$

which is equivalent to

$$\frac{v_1 (T_1^3)^{2/3} + v_2 (T_2^3)^{2/3}}{v_1 + v_2} \leq T_f^2$$

$$\Rightarrow (v_1 + v_2) T_f^2 \geq v_1 T_1^2 + v_2 T_2^2$$

$$\Rightarrow \frac{3}{2} b (v_1 + v_2) T_f^2 \geq \frac{3}{2} b v_1 T_1^2 + \frac{3}{2} b v_2 T_2^2$$

$$\Rightarrow S_{\text{final}} \geq S_{\text{initial}}$$

$$\Rightarrow \Delta S \geq 0, \text{ just as we wanted,}$$

Now, if $T_1 = T_2 = T$ from the expression of ΔS , we have;

$$\Delta S = \frac{3}{2} b \left[(v_1 + v_2)^{1/3} (v_1 + v_2)^{2/3} (T^3)^{1/3} - v_1 T^2 - v_2 T^2 \right]$$

$$\Rightarrow \Delta S = \frac{3}{2} b \left[(v_1 + v_2) T^2 - (v_1 + v_2) T^2 \right] = 0$$

$\therefore \Delta S$ can be zero iff $T_1 = T_2$

Problem 2.

The Hamiltonian is given by

$$H = \sum_i \epsilon_i n_i$$

And we have a system of two non-interacting particles, and even more, the system is held at temperature T , and the energy levels are given by

$$\epsilon_0 = 0, \epsilon_1 = \epsilon_0, \epsilon_2 = 2\epsilon_0$$

- ① If we treat the particles classically, and consider them distinguishable the state of the system is given by the energy levels of the two particles (i, j) , where $i, j \in \{0, 1, 2\}$. And even more, the total energy is given by

$$E_{i,j} = \epsilon_i + \epsilon_j$$

Since we have two particles and 3 energy levels, the number of possible states is given by:

$$3^2 = 9$$

Since the two particles are non-interacting, we can factorize the partition function of the whole system as

$$Z = (Z_1)^n, \text{ where}$$

n is the number of particles, in this case $n=2$. And Z_1 is the single partition function, which

is given by:

$$Z_1 = \sum_i \exp(-\beta \epsilon_i) \quad ; \quad \beta = 1/k_B T$$

thus;

$$Z_1 = \exp(0) + \exp(-\beta \epsilon_0) + \exp(-2\beta \epsilon_0)$$

$$\Rightarrow Z_1 = 1 + \exp(-\beta \epsilon_0) + \exp(-2\beta \epsilon_0)$$

And from here, the whole partition function is given by:

$$Z = (1 + e^{-\beta \epsilon_0} + e^{-2\beta \epsilon_0})^2$$

Now, one way to compute the probability of the particles being in different levels could be to "brute force" that calculation, but another way is to compute the probabilities for the particles being in the same energy levels and then consider this

$$P(\text{different}) = 1 - P(\text{same}).$$

I'll follow this procedure:

- the states of the particles when on the same level are: $(0,0)$, $(1,1)$, $(2,2)$
- the respective energies are given by:
 $0, 2\epsilon_0, 4\epsilon_0$.

And from this, we have;

$$P(\text{same}) = \frac{1}{z} [\exp(-0) + \exp(-2\beta\epsilon_0) + \exp(-4\beta\epsilon_0)]$$

$$\Rightarrow P(\text{same}) = \frac{1}{z} [1 + e^{-2\beta\epsilon_0} + e^{-4\beta\epsilon_0}]$$

$$\Rightarrow P(\text{different}) = 1 - \frac{1}{z} (1 + e^{-2\beta\epsilon_0} + e^{-4\beta\epsilon_0}),$$

$\approx \text{diff}$

but, we know that:

$$z = (1 + e^{-\beta\epsilon_0} + e^{-2\beta\epsilon_0})^2, \text{ thus:}$$

$$P(\text{diff}) = \frac{(1 + e^{-\beta\epsilon_0} + e^{-2\beta\epsilon_0})^2 - (1 + e^{-2\beta\epsilon_0} + e^{-4\beta\epsilon_0})}{(1 + e^{-\beta\epsilon_0} + e^{-2\beta\epsilon_0})^2}$$

and if we expand the square, we have:

$$(1 + e^{-\beta\epsilon_0} + e^{-2\beta\epsilon_0})^2 = 1 + e^{-2\beta\epsilon_0} + e^{-4\beta\epsilon_0} + \underbrace{2e^{-\beta\epsilon_0} + 2e^{-2\beta\epsilon_0} + 2e^{-3\beta\epsilon_0}}_{\text{these terms cancel,}}$$

Then, we have:

$$P(\text{diff}) = \frac{2e^{-\beta\epsilon_0} + 2e^{-2\beta\epsilon_0} + 2e^{-3\beta\epsilon_0}}{(1 + e^{-\beta\epsilon_0} + e^{-2\beta\epsilon_0})^2}$$

classically.

② Now, for two indistinguishable fermions, due to the Pauli exclusion principle, we know that, the two particles can not occupy the same energy level. Now, with two particles and three levels, the only possibilities are the states where the two particles occupy different levels, this is:

$$\{0,1\}, \{0,2\} \text{ and } \{1,2\}.$$

On the other hand, the energies of these states are;

$$\{0,1\}: \epsilon_0 + \epsilon_1 = \epsilon_0$$

$$\{0,2\}: \epsilon_0 + \epsilon_2 = 2\epsilon_0$$

$$\{1,2\} = \epsilon_1 + \epsilon_2 = 3\epsilon_0$$

Moving on, the partition function of this system is given by

$$Z = e^{-\beta\epsilon_0} + e^{-2\beta\epsilon_0} + e^{-3\beta\epsilon_0}.$$

Moreover since all allowed states for these two particles in three distinct levels must have the particles in different levels, then the probability that the particles are in different levels is 1, this is:

$$P(\text{different}) = 1.$$

③ Now, we have bosons and these particles do not have the previous restriction, this is any number of particles can occupy the same energy level. In this case we need to use the occupation number (n_0, n_1, n_2) such that:

$$n_0 + n_1 + n_2 = 2.$$

Now, the possible states are given by:

- $(2, 0, 0)$ with energy 0
- $(0, 2, 0)$ with energy $2\epsilon_0$
- $(0, 0, 2)$ with energy $4\epsilon_0$
- $(1, 1, 0)$ with energy ϵ_0
- $(1, 0, 1)$ with energy $2\epsilon_0$
- $(0, 1, 1)$ with energy $3\epsilon_0$

And from here, it follows that the partition function is given by:

$$Z = 1 + e^{-\beta\epsilon_0} + 2e^{-2\beta\epsilon_0} + e^{-3\beta\epsilon_0} + e^{-4\beta\epsilon_0}.$$

On the other hand, the states where the particles are in different levels are $(1, 1, 0)$, $(1, 0, 1)$ and $(0, 1, 1)$, and from this it follows that:

$$P(\text{diff}) = \frac{e^{-\beta \epsilon_0} + e^{-2\beta \epsilon_0} + e^{-3\beta \epsilon_0}}{1 + e^{-\beta \epsilon_0} + 2e^{-2\beta \epsilon_0} + e^{-3\beta \epsilon_0} + e^{-4\beta \epsilon_0}}$$

④ Now, let's check the limit $\epsilon_0 \gg k_B T$, which corresponds to $T \rightarrow 0$, which implies that

$$e^{-\beta E} = e^{-E/k_B T} \rightarrow 0 \text{ for } E > 0,$$

thus:

→ classical:

$$P(\text{diff}) = \frac{2e^{-\beta \epsilon_0} + 2e^{-2\beta \epsilon_0} + 2e^{-3\beta \epsilon_0}}{(1 + e^{-\beta \epsilon_0} + e^{-2\beta \epsilon_0})^2} \quad P(\text{diff}) \rightarrow \frac{2(0+0+0)}{(1+0+0)^2} = \frac{0}{1^2} = 0,$$

this is at low temperatures, classical particles will occupy the lowest energy state, $(0,0)$, and they will be in the same level.

→ Fermions:

$P(\text{diff}) \rightarrow 1$, they are always in different levels

→ Bosons:

$$P(\text{diff}) = \frac{e^{-\beta \epsilon_0} + e^{-4\beta \epsilon_0} + e^{-9\beta \epsilon_0}}{1 + e^{-\beta \epsilon_0} + 2e^{-2\beta \epsilon_0} + e^{-3\beta \epsilon_0} + e^{-4\beta \epsilon_0}} \quad P(\text{diff}) \rightarrow \frac{0+0+0}{1+0+0+0+0} = \frac{0}{1} = 0$$

which again, at low temperatures, we know that bosons condensate to the lowest energy state $(2,0,0)$, and they are in the same energy level.

⑤ Finally, the limit $\epsilon_0 \ll k_B T$, which corresponds to high temperature:

$$T \rightarrow \infty \Rightarrow e^{\epsilon_0/k_B T} \rightarrow 1, \text{ thus:}$$

→ Classical

$$P(\text{diff}) = \frac{2e^{\beta\epsilon_0} + 2e^{-2\beta\epsilon_0} + 2e^{-3\beta\epsilon_0}}{(1 + e^{\beta\epsilon_0} + e^{-2\beta\epsilon_0})^2} \quad P(\text{diff}) = \frac{2+2+2}{(1+1+1)^2} = \frac{6}{3^2} = \frac{6}{9} = \frac{2}{3}$$

$$\Rightarrow P(\text{diff}) = \frac{2}{3}.$$

At high T , all 9 classical states are equally likely, and 6 of these states have particles in different levels.

→ Fermions:

$P(\text{diff}) \rightarrow 1$, they are always in different levels

→ Bosons:

$$P(\text{diff}) = \frac{e^{-\beta\epsilon_0} + e^{-2\beta\epsilon_0} + e^{-3\beta\epsilon_0}}{1 + e^{-\beta\epsilon_0} + 2e^{-2\beta\epsilon_0} + e^{-3\beta\epsilon_0} + e^{-4\beta\epsilon_0}} \quad P(\text{diff}) = \frac{1+1+1}{1+1+2+1+1} = \frac{3}{6} = \frac{1}{2}$$

and at high T_0 , all bosonic states become equally likely, and 3 of these states have particles in different levels.

Problem 3.

① We have particles with spin $= 3/2$, thus the possible configurations for one are: $\{-3/2, -1/2, 1/2, 3/2\}$

And then, the possible microstates are given by combinations of

$$\begin{array}{cccc} -3/2 & \rightarrow & \{-3/2, -1/2, 1/2, 3/2\} \\ -1/2 & \downarrow & " & " \\ 1/2 & \downarrow & " & " \\ 3/2 & \downarrow & " & " \end{array} \left. \vphantom{\begin{array}{cccc} -3/2 & \rightarrow & \{-3/2, -1/2, 1/2, 3/2\} \\ -1/2 & \downarrow & " & " \\ 1/2 & \downarrow & " & " \\ 3/2 & \downarrow & " & " \end{array}} \right\} 4 \times 4 = 16$$

\therefore 16 microstates or 2^4

And for macrostates, we can use combinatorics:

$$C(n, k) = \frac{n!}{k! (n-k)!} \quad \left(\begin{array}{l} \text{number of ways} \\ \text{we can arrange} \end{array} \right)$$

$$C(4, 2) = \frac{4!}{2! 2!} = \frac{4 \cdot 3 \cdot \cancel{2} \cdot \cancel{1}}{2! \cdot \cancel{2} \cdot \cancel{1}} = \frac{12}{2} = 6$$

\therefore # macrostates = 6

② In the absence of an external magnetic field, the energy of all microstates is the same, and one of basic postulates of statistical mechanics is that the probability of each microstate is the same, however, the most likely macrostate is the one with the biggest number of associated microstates.
 → The microstate with total spin of zero is the most likely, since there are four ways to obtain this macrostate, this is, it has four microstates associated, those are;

$$\{-3/2, 3/2\}, \{-1/2, 1/2\}$$

$$\{3/2, -3/2\}, \{1/2, -1/2\}$$

③ → $H = -\vec{\mu} \cdot \vec{B} \Rightarrow H = -\gamma \vec{S} \cdot \vec{B}$

Since the system is in contact with a large reservoir @ temperature T , it follows that we can use the canonical ensemble;

$$Z = \sum_i \exp(-\beta E_i)$$

then, the single partition function is given by

$$\Rightarrow Z = \sum_i \exp(-\beta \gamma S_i B)$$

$$\Rightarrow Z_1 = \exp[-\beta \gamma (-3/2) B] + \exp[-\beta \gamma (-1/2) B] \\ + \exp[-\beta \gamma (1/2) B] + \exp[-\beta \gamma (3/2) B]$$

$$Z = \exp\left[\frac{3}{2} \beta \gamma B\right] + \exp\left[\frac{1}{2} \beta \gamma B\right] \\ + \exp\left[-\frac{1}{2} \beta \gamma B\right] + \exp\left[-\frac{3}{2} \beta \gamma B\right]$$

$$\Rightarrow Z = 2 \cosh\left(\frac{3}{2} \beta \gamma B\right) + 2 \cosh\left(\frac{1}{2} \beta \gamma B\right)$$

$$\Rightarrow \frac{Z}{2} = \cosh\left(\frac{3}{2} \beta \gamma B\right) + \cosh\left(\frac{1}{2} \beta \gamma B\right)$$

and the whole partition function is

$$Z = Z_1^2$$

On the other hand, the average total magnetic moment is given by

$$m = \langle \mu \rangle = -\left(\frac{\partial F}{\partial B}\right)_T$$

where F is the free energy, which is given by

$$F = -k_B T \ln Z$$

$$\Rightarrow F = -k_B T \ln (Z^2)$$

$$F = -2 k_B T \ln Z$$

therefore, we have:

$$F = -2 k_B T \ln \left(Z \left(\cosh\left(\frac{3}{2} \beta \gamma B\right) + \cosh\left(\frac{1}{2} \beta \gamma B\right) \right) \right)$$

And, it follows that

$$m = \frac{2 k_B T}{2 \left[\cosh\left(\frac{3}{2} \beta \gamma B\right) + \cosh\left(\frac{1}{2} \beta \gamma B\right) \right]} \times Z \left\{ \frac{3}{2} \beta \gamma \sinh\left(\frac{3}{2} \beta \gamma B\right) + \frac{1}{2} \beta \gamma \sinh\left(\frac{1}{2} \beta \gamma B\right) \right\}$$

$$\therefore m = \frac{\gamma}{\left[\cosh\left(\frac{3}{2} \beta \gamma B\right) + \cosh\left(\frac{1}{2} \beta \gamma B\right) \right]} \left\{ 3 \sinh\left(\frac{3}{2} \beta \gamma B\right) + \sinh\left(\frac{1}{2} \beta \gamma B\right) \right\}$$

④ Now, using a Taylor expansion, we have:

$$\cosh x \approx 1 + \frac{x^2}{2}$$

$$\Rightarrow \cosh\left(\frac{3}{2} \beta \gamma B\right) \approx 1 + \left(\frac{3}{2} \beta \gamma B\right)^2 / 2$$

$$\cosh\left(\frac{1}{2} \beta \gamma B\right) \approx 1 + \left(\frac{1}{2} \beta \gamma B\right)^2 / 2$$

$$+ \frac{1}{2} \left(2 + \frac{9}{4} \beta^2 \gamma^2 B^2 + \frac{1}{4} \beta^2 \gamma^2 B^2 \right) = 2 + \frac{10}{4} \beta^2 \gamma^2 B^2 = 2 + \frac{5}{2} \beta^2 \gamma^2 B^2$$

on the other hand:

$$\sinh x \approx x \Rightarrow$$

$$\beta = 1/k_B T$$

$$\sinh\left(\frac{3}{2}\beta\gamma B\right) \approx \frac{3}{2}\beta\gamma B$$

$$\sinh\left(\frac{1}{2}\beta\gamma B\right) \approx \frac{1}{2}\beta\gamma B$$

$$+ \frac{\approx 4/2 \beta\gamma B}{}$$

$$\Rightarrow m \approx \frac{\gamma}{2 + \frac{5}{2}\beta^2\gamma^2 B^2} \times \frac{4}{2}\beta\gamma B$$

$$= \frac{\gamma}{\frac{1}{2}(4 + 5\beta^2\gamma^2 B^2)} \times \frac{4}{2}\beta\gamma B$$

$$\Rightarrow m = \frac{4\beta\gamma^2 B}{4 + 5\beta^2\gamma^2 B^2} = \frac{\beta\gamma^2 B}{1 + \frac{5}{4}\beta^2\gamma^2 B^2}$$

and neglecting the term with B^2 , we have

$$\boxed{m \approx \beta\gamma^2 B}$$

⑤ Now, for a very large B and fixed T , we have:

$$\sinh(x) \approx e^x/2$$

$$\cosh(x) \approx e^x/2,$$

and if we make

$$u = \frac{1}{2}\beta\gamma B, \text{ we have,}$$

$$\sinh(3u) \approx e^{3u}/2$$

$$\cosh(u) \approx e^u/2, \text{ therefore, we have:}$$

$$m \approx \gamma \frac{\frac{1}{2}(3e^{3u} + e^u)}{\frac{1}{2}(e^{3u} + e^u)}$$

$$= \gamma \frac{3e^{3u} + e^u}{e^{3u} + e^u}$$

and if we divide by e^{3u} , we have:

$$m \approx \gamma \frac{3 + e^{-2u}}{1 + e^{-2u}}$$

and if we take the limit $u \rightarrow \infty$, we have:

$$m \approx 3\gamma$$

this is, a high values of u or equivalently B the magnetic moment saturates.

⑥ Sketch

→ At $\beta = 0$, we have:

$$\sinh(0) = 0 \text{ and } \cosh(0) = 1,$$

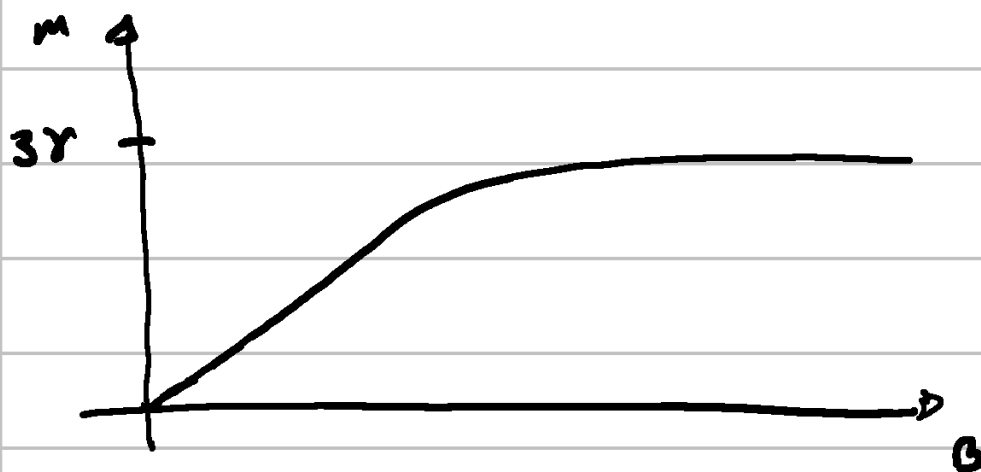
which implies that:

$$m \approx \gamma \frac{(0) + (0)}{(0) + (0)}$$

$$\boxed{m=0}$$

→ At small β , we got that β is linear

→ At very big β , the curve reaches a saturation value of 3γ , thus;



⑦ transition;

I think the transition from low-field or linear behavior to high-field saturation behavior, occurs when the magnetic field is comparable to the thermal energy scale, thus I would expect a transition on the scale of some order of $k_B T$, this is:
transition occurs when

$$\gamma B \approx k_B T$$

Problem 4

Let's derive an expression for the change in entropy. The whole process consists of:

- Evaporation of liquid nitrogen
- heating of nitrogen to gas
- mixing of nitrogen gas with oxygen gas.

And, we can calculate the total change in entropy as the change in entropy of the nitrogen and oxygen from their initial to final states as follows.

→ Nitrogen. ΔS_N

Initially, we have 1 mole of liquid nitrogen at its boiling point T_{bN} . Finally, we have 1 mole of nitrogen gas fully mixed with oxygen at temperature T_a and partial pressure P_N .

And if we consider a reversible path, we have;

① Evaporation;

$$\Delta S_{\text{vap}} = \frac{L}{T_{bN}} \quad \leftarrow \text{latent heat}$$

- ② Heating nitrogen gas from T_{bN} to T_a at constant pressure P_a ; assuming the molar heat capacity of the nitrogen is constant, $C_{p,N}$, we have:

$$\Delta S_{\text{heat},N} = \int_{T_{bN}}^{T_a} \frac{C_{p,N}}{T} dT = C_{p,N} \ln \left(\frac{T_a}{T_{bN}} \right)$$

$$\Rightarrow \Delta S_{\text{heat},N} = C_{p,N} \ln \left(\frac{T_a}{T_{bN}} \right)$$

- ③ Isothermal mixing:

the entropy change for this isothermal process is equivalent to an expansion from pressure P_a to P_N , where P_N is a partial pressure:

$$\Delta S_{\text{mixing},N} = n_N R \ln \left(\frac{P_a}{P_N} \right), \text{ but } n_N = 1$$

but $P_N = P_a X_N$, where X_N is the molar fraction of nitrogen, thus:

$$\Delta S_{\text{mixing},N} = -R \ln (X_N)$$

↖ I will find an expression for this at the end.

thus, we have;

$$\Delta S_N = \frac{L}{T_{b,N}} + C_{p,N} \ln\left(\frac{T_g}{T_{b,N}}\right) - R \ln(X_N)$$

On the other hand, for the change in entropy of the oxygen, we have:

→ At first, we have n_{O_2} moles of oxygen at T_a , atmospheric pressure P_a , in a tank of volume V . And at the end, we have n_{O_2} moles of oxygen in the mixture at T_a , occupying the same volume, but at a partial pressure P_{O_2} . And following the same procedure as before, this is, by assuming an isothermal process from pressure $P_a \rightarrow P_{O_2}$, we have:

$$\Delta S_{O_2} = -n_{O_2} R \ln\left(\frac{P_{O_2}}{P_a}\right) = -n_{O_2} R \ln(X_{O_2})$$

where again, I used $P_{O_2} = P_a X_{O_2}$, where P_{O_2} is the molar fraction of oxygen.

Now, in order to determine these X_{O_2} , X_N , I will assume that the gases obey the ideal gas law, thus;

$$n_{O_2} = \frac{P_a V}{RT_a} \quad \text{and} \quad x_N = \frac{n_N}{n_N + n_{O_2}} \quad (n_N = 1)$$

$$\Rightarrow x_N = \frac{1}{1 + \frac{P_a V}{RT_a}} \Rightarrow x_N = \frac{RT_a}{RT_a + P_a V}$$

and;

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_N} = \frac{\frac{P_a V}{RT_a}}{1 + \frac{P_a V}{RT_a}} = \frac{P_a V}{RT_a + P_a V}$$

$$\Rightarrow x_{O_2} = \frac{P_a V}{RT_a + P_a V} ;$$

And finally, the total change in entropy is:

$$\Delta S_{\text{total}} = \frac{L}{T_{bN}} + C_{p,N} \ln\left(\frac{T_a}{T_{bN}}\right) - R \ln\left(\frac{RT_a}{RT_a + P_a V}\right) - \frac{P_a V}{T_a} \ln\left(\frac{P_a V}{RT_a + P_a V}\right)$$