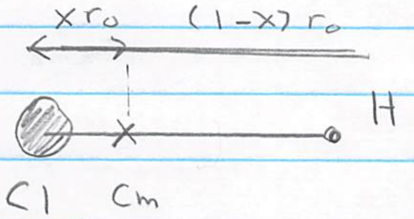
HCl

a) Take $r_0 = 1$ Å

b)



The location of the cm is at $x r_0$

$$I = m_{Cl}(x r_0)^2 + m_H (1-x)^2 r_0^2$$

Now

$$x r_0 = \frac{m_H r_0}{m_H + m_{Cl}} \qquad \text{definition of cm}$$

And $$x = \frac{m_H}{m_H + m_{Cl}} = \frac{m_H}{m_{TOT}} \qquad (1-x) = \frac{m_{Cl}}{m_{TOT}}$$

$$I = m_{TOT} r_0^2 \left[(1-x) x^2 + x(1-x)^2 \right]$$

$$= m_{TOT} r_0^2 \left[x^2 - x^3 + x(1 - 2x + x^2) \right]$$

$$= m_{TOT} r_0^2 \left[(1-x) x \right] = \boxed{\frac{m_H m_{Cl}}{(m_H + m_{Cl})} r_0^2 = \mu r_0^2}$$

So since $m_{Cl} \simeq 35\, m_H$ we expand

$$\frac{I}{r_0^2} = m_H \frac{1}{(1 + m_H/m_{Cl})} \simeq m_H (1 - m_H/m_{Cl} + \ldots)$$

So

$$\boxed{I = m_H r_0^2 \left(1 - m_H/m_{cl} + O\left((m_H/m_{cl})^2\right)\right)}$$

c) So

$$\Delta = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2m_p r_0^2} \simeq \frac{\hbar^2}{2m_e r_0^2 (m_p/m_e)} \simeq \frac{13.6\,eV}{m_p/m_e} \left(\frac{a_0}{r_0}\right)^2$$

We used knowledge of the Bohr atom

$$\frac{\hbar^2}{2ma_0^2} = 13.6eV$$ where $a_0 = 0.53\,\mathring{A}$ is the Bohr radius.

Then $(a/r_0) \simeq 1/2$

$$\boxed{\Delta = \frac{13.6\,eV}{2000}\frac{1}{2^2} = 0.0017\,eV}$$

$$\frac{\Delta}{kT} = 14.7 \quad \text{for} \quad kT = 1/40\,eV$$

So

$$\Delta = \hbar\omega \qquad \omega = \frac{\Delta c}{\hbar c} = \frac{0.0017\,eV \times 3\times10^8\,m/s}{197\,eV \times nm}$$

$$\boxed{\omega = 400\,GHz}$$

b)

We have

$$C_v = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T}\left(\frac{1}{Z}\frac{-\partial Z}{\partial \beta}\right) = -k_B \beta^2 \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\left(\frac{-\partial Z}{\partial \beta}\right)\right)$$

see below

Note $$\boxed{\frac{\partial X}{\partial T} = \frac{\partial X}{\partial \beta}\frac{\partial \beta}{\partial T} = -k\beta^2 \frac{\partial X}{\partial \beta}}$$

$$\frac{\partial}{\partial T}\left(\frac{1}{kT}\right)$$

this is very useful
X is anyting
$\partial X/\partial T = -k\beta^2 \partial X/\partial \beta$

Then differentiating

$$-\frac{\partial}{\partial \beta}\left(\frac{1}{Z}\left(-\frac{\partial Z}{\partial \beta}\right)\right) = \frac{1}{Z}\left(+\frac{\partial^2 Z}{\partial \beta^2}\right) - \frac{1}{Z^2}\left(\frac{-\partial Z}{\partial \beta}\right)\left(\frac{-\partial Z}{\partial \beta}\right)$$

$$= \langle E^2 \rangle - \langle E \rangle^2$$

So

$$\boxed{C_v = -k\beta^2\left[\langle E^2\rangle - \langle E\rangle^2\right]}$$

Finally,

c) Note

$$\boxed{C_v = -k\beta^2 \frac{\partial}{\partial \beta}\frac{1}{Z}\left(\frac{-\partial Z}{\partial \beta}\right) = k\beta^2 \frac{\partial}{\partial \beta}\frac{\partial}{\partial \beta}\ln Z = k\beta^2 \partial_\beta^2 \ln Z}$$

So

$$Z_{TOT} = \frac{1}{N!} Z_1^N \simeq \left(\frac{e Z_1}{N}\right)^N$$

Z_1 is always of this form

$$\boxed{Z_1 = \sum_s \int \frac{d^3r\, d^3p}{h^3}\, e^{-(p^2/2m + \varepsilon^s_{int})/kT}}$$

We used that for one particle

$$E = \frac{\vec{p}^{\,2}}{2m} + \varepsilon_{int}$$

ε_{int} = internal energy levels

$= \dfrac{\hbar^2 \ell(\ell+1)}{2I}$ in this case

$$\boxed{Z_1 = Z_{trans}\, Z_{int}}$$

Where

$$\boxed{Z_{trans} = \int \frac{d^3\vec{r}\, d^3\vec{p}}{h^3}\, e^{-p^2/2mT} = \frac{V}{\lambda^3_{th}} = V n_Q}$$

$$\boxed{Z_{int} = \sum_s e^{-\varepsilon_{int}\beta} = \sum_{\ell, m} e^{-\hbar^2(\ell(\ell+1)/2I)\beta}}$$

$$Z_{int} = \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\hbar^2(\ell(\ell+1)/2I)\beta}$$

$$= \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\beta\varepsilon_\ell} \qquad \varepsilon_\ell \equiv \frac{\ell(\ell+1)\hbar^2}{2I}$$

So

$$\log Z_{TOT} = N \Big[\underbrace{\log \left(\frac{e Z_{trans}}{N} \right)}_{\text{this is a mono-atomic ideal gas} \equiv MAIG} + \log Z_{int} \Big]$$

Now

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_{TOT}$$

$$= N \left[\langle \varepsilon \rangle_{MAIG} + \langle \varepsilon_{rot} \rangle \right]$$

$$\boxed{\langle E \rangle = N \left[\frac{3}{2} k_B T + \langle \varepsilon_{rot} \rangle \right]}$$

Where $\langle \varepsilon_{rot} \rangle = \frac{1}{Z} \sum_{\ell} (2\ell+1)\, e^{-\hbar^2 \ell(\ell+1)/2I)\beta} \left(\frac{\hbar^2 \ell(\ell+1)}{2I} \right)$

Differentiating again

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = N \left[\frac{3}{2} k_B T + \frac{\partial}{\partial T} \langle \varepsilon_{rot} \rangle \right]$$

Finally since

$$\frac{\partial}{\partial T} = -k_B \beta^2 \frac{\partial}{\partial \beta}$$

We get defining $\varepsilon_l \equiv l(l+1)\hbar^2/2I$

$$\frac{\partial \mathcal{E}_{rot}}{\partial T} = -k\beta^2 \frac{\partial}{\partial \beta}\left[\underbrace{\frac{1}{Z}\sum_l (2l+1)\, e^{-\beta \varepsilon_l}\, \varepsilon_l}_{= \frac{1}{Z_{rot}} \frac{-\partial Z_{rot}}{\partial \beta}}\right]$$

So

$$\frac{\partial \mathcal{E}_{rot}}{\partial T} = k\beta^2 \left[\frac{1}{Z}\sum_l (2l+1)\, e^{-\beta\varepsilon_l}\, \varepsilon_l^2 - \left(\frac{-1}{Z}\frac{\partial Z}{\partial \beta}\right)\left(\frac{-1}{Z}\frac{\partial Z}{\partial \beta}\right)\right]$$

$$\boxed{\frac{\partial \mathcal{E}_{rot}}{\partial T} = k\beta^2 \left[\langle \varepsilon_{rot}^2 \rangle - \langle \varepsilon_{rot} \rangle^2\right]}$$

Where

$$\beta^2 \langle \varepsilon_{rot}^2 \rangle \equiv \frac{1}{Z}\sum_{l=0}^{\infty} e^{-\beta\varepsilon_l} (\beta\varepsilon_l)^2 (2l+1)$$

$$\beta \langle \varepsilon \rangle \equiv \frac{1}{Z}\sum_{l=0}^{\infty} e^{-\beta\varepsilon_l}\, \beta\varepsilon_l$$

So Finally

$$\boxed{C_V = Nk_B\left[\frac{3}{2}k_B T + \beta^2\left(\langle \varepsilon_{rot}^2\rangle - \langle \varepsilon_{rot}\rangle^2\right)\right]}$$

A graph is shown in the problem statement.

d) Looking at the graph, We see a 10% deviation from one when

$$k_B T/\Delta \sim 1$$

Or

$$k_B T \sim \Delta$$

$$T \sim \frac{0.0017\,eV}{\frac{0.025\,eV}{300°K}}$$

$$\boxed{T \sim 20.4\,°K}$$

Paramagnets

a) Then

$$Z = Z_1^N \qquad Z_1 = \sum_s e^{-\beta \varepsilon_s}$$

So

$$= e^{\beta \mu_B B} + e^{-\beta \mu_B B}$$

$$F = -k_B T \ln Z \qquad = 2\cosh(\beta \mu_B B)$$

$$= -kTN \ln Z_1$$

$$\boxed{F = -kTN \ln(2\cosh(\beta \mu_B B))}$$

So

$$S = -\left(\frac{\partial F}{\partial T}\right)_B = Nk \ln(2\cosh(\mu_B B \beta))$$

$$+ kTN \frac{2\sinh(\beta \mu_B B)}{2\cosh(\beta \mu_B B)} \left(\frac{-1}{kT^2} \mu_B B\right)$$

So

$$\boxed{S = Nk \left[\ln(2\cos(\mu_B B \beta)) - \tanh(\beta \mu_B B)\, \beta \mu_B B \right]}$$

Then $F = U - TS$ or $U = F + TS$ or

$$U = -NkT \cdot \tanh(\beta \mu_B B)\, \beta \mu_B B = \boxed{-N\mu_B B \tanh(\beta \mu_B B)}$$

So

$$C = \left(\frac{\partial U}{\partial T}\right)_B = -N\mu_B B \frac{\partial}{\partial T} \tanh(\beta\mu_B B)$$

$$\frac{d}{dx}\frac{\sinh x}{\cosh x} = \frac{\cosh x}{\cosh x} - \frac{\sinh^2 x}{\cosh^2 x} = 1 - \tanh^2 x = \operatorname{sech}^2 x$$

So

$$C = -N\mu_B B \operatorname{sech}^2(\beta\mu_B B)(-\beta^2 k_B \mu_B B)$$

$$\boxed{C = N k_B (\beta\mu_B B)^2 \operatorname{sech}^2(\beta\mu_B B)}$$

$\boxed{\text{b)}}$ Then

$$n = \frac{N\downarrow}{N} = \frac{e^{\beta\mu_B B}}{Z_1} = \text{this is the probability of being spin} \downarrow$$

$$n = \frac{e^{\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} = \boxed{\frac{1}{1+e^{-\beta\Delta}} = n}$$

with $\Delta = 2\mu_B B$

$$\frac{1}{n} = 1 + e^{-\beta\Delta} \quad \text{and} \quad e^{-\beta\Delta} = 1 - \frac{1}{\bar{n}}$$

and so $\boxed{\beta\Delta = \ln((1-\bar{n})/\bar{n})}$

Then

$$M = \langle N_\uparrow - N_\downarrow \rangle \mu_B$$

$$= N\left(1 - 2\frac{N_\downarrow}{N}\right)\mu_B$$

$$= N\left(1 - 2\,\frac{1}{1+e^{-\beta\Delta}}\right)\mu_B$$

$$= N\left(\frac{1 - e^{-\beta\Delta}}{1+e^{-\beta\Delta}}\right)\mu_B$$

$$\boxed{M = N \tanh(\beta \mu_B B)\,\mu_B}$$

Finally

$$\chi = \frac{\partial \langle M\rangle}{\partial H} \simeq \frac{\partial \langle M\rangle}{\partial B} = N \operatorname{sech}^2(\beta \mu_B B)\,\mu_B^2\,\beta$$

$$\boxed{\chi = \frac{N\mu_B^2}{kT}\operatorname{sech}^2(\beta\mu_B B)}$$

this describes the fluctuations in $\langle M\rangle$. Qualitatively it is maxmal when $B=0$, and the system can't decide what configuration it is in.