2.14b

$$\Rightarrow \quad f(N,V) = -\lim_{T\to 0}\left[k_B\left(\frac{\partial}{\partial T}\left(T\ln Z\right)\right)_{N,V}\right]$$

$$= -\lim_{T\to 0}\left[k_B\left(\frac{\partial}{\partial T}\left(\underbrace{\cancel{T}\left(-\frac{E_0}{k_B\cancel{T}}\right)}_{T\text{ independent}}\right)\right)_{N,V}\right] = 0$$

$$\Rightarrow \quad \boxed{S = \left(\frac{\partial}{\partial T}\left(k_B T\ln Z\right)\right)_{N,V}} = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$$

$$\Rightarrow \quad F = -k_B T\ln Z + g(N,V)$$

Showing $g = 0$: as $T \to 0$, $Z \to e^{-\frac{E_0}{k_B T}}$

$$\Rightarrow F \to -k_B T\left(-\frac{E_0}{k_B T}\right) + g(N,V) = E_0 + g(N,V)$$

But by def'n:

$$F = E - TS \xrightarrow[T\to 0]{} E_0 = E_0 + g(N,V)$$

$$\Rightarrow \boxed{g(N,V) = 0}$$

$$\Rightarrow \boxed{F = -k_B T\ln Z} \checkmark$$

Fluctuations in $E \to 0$ as $V, N \to \infty$

~~$\Rightarrow$ replace $\langle E \rangle$ by "thermodynamic" E~~

$\Rightarrow$ drop brackets, $E \approx \langle E \rangle$ always

$$\boxed{E = -\left(\frac{\partial \ln Z}{\partial B}\right)_{N,V}}, \quad \boxed{B = \frac{1}{k_B T}}$$

$$\left(\frac{\partial E}{\partial T}\right)_{V,N} = C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = -\left(\frac{\partial^2 \ln Z}{\partial B^2}\right)_{V,N} \frac{dB}{dT}$$

$$\left(\frac{\partial}{\partial T}\right)_{V,N} = \left(\frac{\partial}{\partial B}\right)_{V,N} \frac{dB}{dT} = -\frac{1}{k_B T^2}\left(\frac{\partial}{\partial B}\right)_{V,N}$$

$$\Rightarrow -\frac{1}{k_B T}\left(\frac{\partial S}{\partial B}\right)_{V,N} = +\frac{1}{k_B T^2}\left(\frac{\partial^2 \ln Z}{\partial B^2}\right)_{V,N}$$

$$\Rightarrow \left(\frac{\partial S}{\partial B}\right)_{V,N} = -\frac{1}{T}\left(\frac{\partial^2 \ln Z}{\partial B^2}\right)_{V,N} = -k_B B\left(\frac{\partial^2 \ln Z}{\partial B^2}\right)_{V,N}$$

$$= -k_B\left(\frac{\partial}{\partial B}\left(B\frac{\partial \ln Z}{\partial B} - \ln Z\right)\right)_{V,N}$$

$$\Rightarrow S = k_B\left[\ln Z - B\left(\frac{\partial \ln Z}{\partial B}\right)_{N,V} + \cancel{f(N,V)}\right]$$

$S \to 0$ as $T \to 0$ $\Rightarrow$ $f = 0$

Free energy

$$\left(\frac{\partial F}{\partial T}\right)_{N,V} = -S = k_B\left[\beta\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V} - \ln Z\right]$$

$$\cancel{\Rightarrow -\frac{1}{k_B T^2}\left(\frac{\partial F}{\partial \beta}\right)_{N,V} = \beta\left(\frac{\partial \ln Z}{\partial \beta}\right)}$$

$$\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V} = \left(\frac{\partial \ln Z}{\partial T}\right)_{N,V}\frac{\partial T}{\partial \beta} = -\frac{1}{k_B \beta^2}\left(\frac{\partial \ln Z}{\partial T}\right)_{N,V}$$

$$\Rightarrow \left(\frac{\partial F}{\partial T}\right)_{N,V} = -\frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial T}\right)_{N,V} - k_B \ln Z$$

$$= -k_B\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_{N,V} + \ln Z\right]$$

$$= -k_B\left(\frac{\partial}{\partial T}\left[T \ln Z\right]\right)_{N,V}$$

$$\Rightarrow \boxed{F = -k_B T \ln Z + g(N,V)} \leftarrow \text{Gives all of thermodynamics}$$

$F \to 0$ as $T \to 0 \Rightarrow g = 0$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial^2 F}{\partial T^2}\right)_V, \quad E = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V},$$

Xeroxed

Lecture 3 ~~Continued~~

Energy fluctuations (Quantum)

$$\langle E^2 \rangle = \frac{\sum_i E_i^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$\langle E \rangle^2 = \left(\frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \right)^2$$

$$\left(\frac{\partial}{\partial \beta} \langle E \rangle \right)_{N,V} = - \underbrace{\frac{\sum_i E_i^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}} - \frac{\sum_i E_i e^{-\beta E_i}}{\left(\sum_i e^{-\beta E_i}\right)^2} \underbrace{\frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i}}$$

$$= - \sum_i E_i e^{-\beta E_i}$$

$$\Rightarrow \frac{\partial}{\partial \beta} \langle E \rangle = \cancel{\sum_i E_i^2 e^{-\beta E_i}} - \langle E^2 \rangle + \left(\frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \right)^2$$

$$= - \left(\langle E^2 \rangle - \langle E \rangle^2 \right)$$

~~$\Rightarrow$ RMS fluctuations $\Delta E = \sqrt{\langle (E - \langle E \rangle)^2 \rangle}$~~

So, $\langle E^2\rangle - \langle E\rangle^2 = -\left(\frac{\partial\langle E\rangle}{\partial B}\right)_{N,V} \propto N$

$\Rightarrow$ RMS fluctuations

$$\Delta E = \sqrt{(E-\langle E\rangle)^2} = \sqrt{\langle E^2\rangle - \langle E\rangle^2}$$

$$= \sqrt{-\frac{\partial\langle E\rangle}{\partial B}} \propto \sqrt{N} \quad (\langle E\rangle \propto N)$$

$$\Rightarrow \frac{\Delta E}{\langle E\rangle} \propto \frac{1}{\sqrt{N}} \to 0 \text{ as } N \to \infty$$

$\Rightarrow$ Energy fluctuations negligible

(best approximation you'll ever make)

$\Rightarrow$ Microcanonical Ensemble equivalent to canonical Ensemble

---

More on fluctuations: $B = \frac{1}{k_B T}$, $T = \frac{1}{k_B B}$

$$\left(\frac{\partial\langle E\rangle}{\partial B}\right)_{N,V} = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} \frac{\partial T}{\partial B}$$

$$= C_V\left(-\frac{1}{k_B B^2}\right) = -k_B T^2 C_V$$

So

$$\langle E^2\rangle - \langle E\rangle^2 = k_B T C_V \propto N \quad (C_V \propto N)$$

Distribution of Energies

probability : $p(E) = g(E)\, e^{-BE}$

$g(E)$ ← Density of states

$\Rightarrow \ln p = \ln g - BE$

Maximize: $\dfrac{\partial \ln p}{\partial E} = \dfrac{\partial \ln g}{\partial E} - B = 0$ at $E = E_{max} \approx \langle E\rangle$

$$\Rightarrow \left.\frac{\partial \ln g}{\partial E}\right|_{\langle E\rangle} = B$$

$$\Rightarrow \ln g \propto N$$

$$\frac{\partial^2 \ln p}{\partial E^2} = \frac{\partial^2 \ln g}{\partial E^2} \equiv -a \propto \frac{1}{N} \quad \left(\begin{matrix} \ln g \propto N \\ E \propto N \end{matrix}\right)$$

$$\frac{\partial^3 \ln p}{\partial E^3} = \frac{\partial^3 \ln g}{\partial E^3} \equiv b \propto \frac{1}{N^2}$$

$$\Rightarrow \ln p(E) = \ln p(\langle E \rangle) - \frac{1}{2} a (E - \langle E \rangle)^2 + \underbrace{\frac{b}{6} (E - \langle E \rangle)^3}_{\sim O\left(\frac{1}{\sqrt{N}}\right) \Rightarrow \text{neglect}} + \cdots$$

$$E - \langle E \rangle \sim \sqrt{N}$$

$$b \sim \frac{1}{N^2} \Rightarrow$$

~~can expand ln p in series; no~~

$$\cancel{\Rightarrow p(E) = \frac{e^{-\frac{1}{2} a (E - \langle E \rangle)^2}}{Z}}$$

$$(1) \quad p(E) = \underbrace{p(\langle E \rangle)\, e^{-\frac{1}{2} a (E - \langle E \rangle)^2}}_{\text{Gaussian}} \left(1 + O\left(\frac{1}{\sqrt{N}}\right)\right)$$

Note: As $N \to \infty$, can expand $\ln p(E)$ in series, but <u>not</u> $p(E)$ itself.

Generic feature.

Calculate $\langle (E-\langle E\rangle)^2 \rangle$ from (1)

$$\langle (E-\langle E\rangle)^2 \rangle = \frac{1}{a} = k_B T^2 C_v$$

Earlier result

$$\Rightarrow \boxed{p(E) = \frac{e^{-\frac{(E-\langle E\rangle)^2}{2k_B T^2 C_v}}}{\sqrt{2\pi k_B T^2 C_v}}}$$

Calculations of Z,

1) Ideal monoatomic gas (classical)

$$Z = \frac{\int d^{3N} p_i \, e^{-\sum_i \frac{p_i^2}{2mk_BT}} \left[\int d^{3N} q_i = V^N\right]}{N!}$$

Indistinguishable particles

$$Z = \frac{V^N}{N!} \left(\int dp_i \, e^{-\frac{p_i^2}{2mk_BT}}\right)^{3N}$$

$$\boxed{Z = \frac{(mk_BT)^{\frac{3N}{2}} V^N}{N!}}$$

~~[illegible]~~ Constant factor to make dimensionless

$$\Rightarrow F = -k_BT \ln Z = Nk_BT \ln\left[\frac{h^3}{(mk_BT)^{3/2} V}\right] \cancel{+k_BT(\ln N-1)}$$

$$+ k_BT(N \ln N - N)$$

$$\boxed{F = Nk_BT\left[\ln\left[\frac{N}{V}\frac{h^3}{(mk_BT)^{3/2}}\right] - 1\right]}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = -Nk_B \ln\left(\frac{N}{V}\frac{h^3}{(mk_BT)^{3/2}}\right) + \frac{5}{2}Nk_B$$

$$\boxed{C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_B}$$

(3.7

$$\boxed{P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{N k_B T}{V}}$$

$$E = -\left(\frac{\partial \ln Z}{\partial B}\right)_{N,V} = \left(\frac{\partial}{\partial B}\left[\ln\left(B^{\frac{3N}{2}}\right)\right]\right)_{N,V} = \frac{3N}{2B} = \frac{3Nk_BT}{2}$$

$$= F + TS$$

$$H = E + PV = \frac{5}{2} N k_B T$$

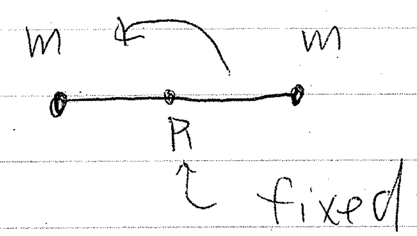
$$\Rightarrow \boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_{N,V} = \frac{5}{2} N k_B}$$

Ideal gases with internal molecular degrees

Internal molecular degrees of freedom in polyatomic ideal gases

Simplest example: ~~Ba~~ Diatomic molecules

Rigid rotor model:



Quantum mechanically:

Total Angular momentum $L^2 = \hbar^2 l(l+1) =$

Given l, $m_z = -l, -l+1, \dots l-1, l$: $2l+1$ m_z states

$$E(l) \equiv \text{Energy} = \frac{L^2}{2I} = \frac{\hbar^2 l(l+1)}{2I} \qquad I = \frac{1}{2}(2m)\left(\frac{R}{2}\right)^2 = \frac{mR^2}{4}$$

$=$ moment of inertia

$$\Rightarrow Z = \underbrace{\int d^{3N}p_i \, d^{3N}q_i \, e^{-\sum_i \frac{p_i^2}{2m}}}_{\substack{\text{center of mass} \\ \text{degrees of freedom} \\ \shortparallel \\ Z_{\text{monoatomic}}}} \underbrace{\prod_{i=1}^{N} \sum_{l_i=0}^{\infty} g(l_i) \, e^{-\frac{E(l_i)}{k_B T}}}_{\equiv Z_r^N(T)}$$

$$Z_r(T) = \sum_{\ell=0}^{\infty} g(\ell)\, e^{-\frac{\hbar^2 \ell(\ell+1)}{2 I k_B T}}$$

$$= \sum_{\ell=0}^{\infty} (2\ell+1)\, e^{-\frac{T_0}{T}\ell(\ell+1)} \quad , \quad T_0 \equiv \frac{\hbar^2}{2 I k_B}$$

$T \ll T_0$, ~~lowest~~ $\ell = \cancel{0}\ 0, 1$ dominate

$$Z_r(T \ll T_0) = 1 + 3e^{-\frac{2T_0}{T}} + 5e^{-\frac{6T_0}{T}} + \cdots$$

$$\cancel{F = -k_B T \ln Z = -k_B T \ln Z_m - N k_B T \ln Z_r(T)}$$

$$\cancel{\Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = S_m + N k_B \ln Z_r(T) + \frac{N k_B T}{Z_r(T)}}$$

$T \gg T_0$: Z_r dominated by $\ell(\ell+1)\frac{T_0}{T} \approx \ell^2 \frac{T_0}{T} \sim 1$

$$\Rightarrow \ell \sim \left(\frac{T}{T_0}\right)^{1/2} \gg 1$$

$\Rightarrow$ approximate $\sum_\ell$ by $\int d\ell$

$$Z_r(T \gg T_0) \to \int_0^\infty e^{-\frac{T_0}{T}\ell(\ell+1)} (2\ell+1)\, d\ell$$

$$u \equiv \ell(\ell+1), \quad du = (2\ell+1)\, d\ell$$

$$\Rightarrow Z_r \to \int_0^\infty e^{-\frac{T_0}{T}u}\, du = \frac{T}{T_0} \quad \text{for } T \gg T_0$$

3.10

mono-atomic gas

$$F = -k_B T \ln Z = \overbrace{-k_B T \ln Z_m}^{\text{mono-atomic gas}} - N k_B T \ln Z_r$$

$$= F_m - N k_B T \ln Z_r$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = S_m + N k_B \frac{d}{dT}\left(T \ln Z_r\right)$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \underset{\frac{3}{2}Nk_B}{\underset{\shortparallel}{C_V^{\,m}}} + N k_B T \frac{d^2}{dT^2}\left(T \ln Z_r\right) \equiv C_V^{\,m} + N C_V^{\,r}$$

$$T \gg T_0 \Rightarrow Z_r = \frac{T}{T_0} \Rightarrow \ln Z_r = \ln\left(\frac{T}{T_0}\right)$$

$$\Rightarrow \frac{d}{dT}\left(T \ln Z_r\right) = \ln \frac{T}{T_0} + 1$$

$$\Rightarrow \frac{d^2}{dT^2}\left(T \ln Z_r\right) = \frac{1}{T}$$

$$\Rightarrow C_V^{\,r} = k_B, \quad T \gg T_0$$

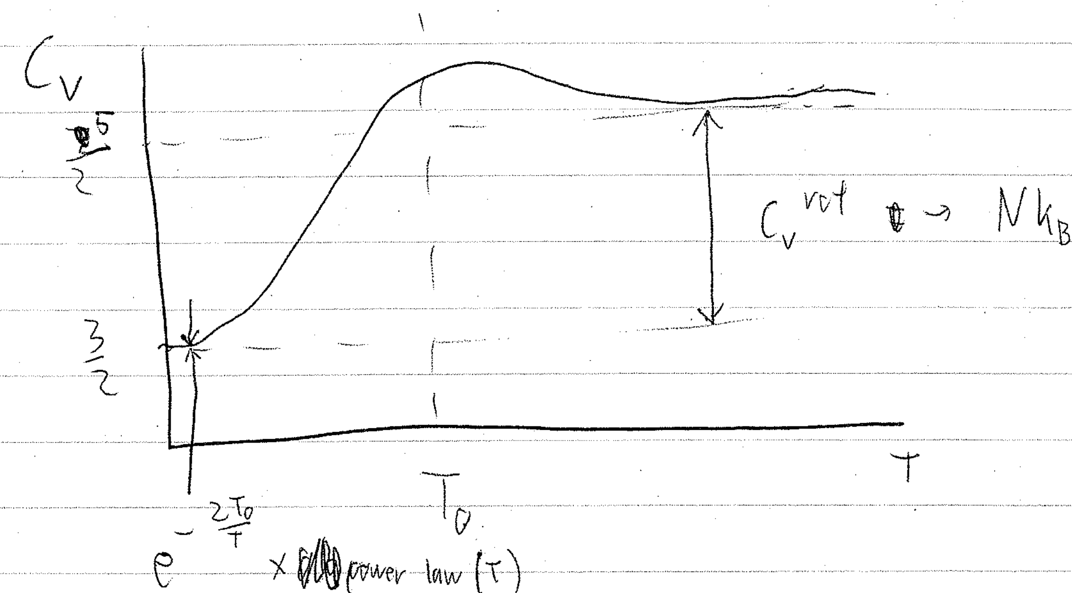
$$T \ll T_0 : \quad Z_r = 1 + 3e^{-\frac{2T_0}{T}} + O\left(e^{-\frac{6T_0}{T}}\right)$$

$$\Rightarrow \ln Z_r = 3e^{-\frac{2T_0}{T}} + O\left(e^{-\frac{4T_0}{T}}\right)$$

$$\cancel{\Rightarrow \frac{d^2 (T \ln Z_r)}{dT^2} = T_0 \frac{d}{dT}\left(\frac{e^{-\frac{2T_0}{T}}}{T^2}\right) =}$$

$$\cancel{\Rightarrow \frac{d^2\, T \ln Z_r}{dT^2} \rightarrow \frac{12 T_0^2}{T^2} e^{-\frac{2T_0}{T}}}$$

$$\Rightarrow C_V^{\,r} = k_B T \frac{d^2}{dT^2}\left(T \ln Z_r\right) \longrightarrow \frac{12 T_0^2 k_B}{T^2} e^{-\frac{2T_0}{T}}$$

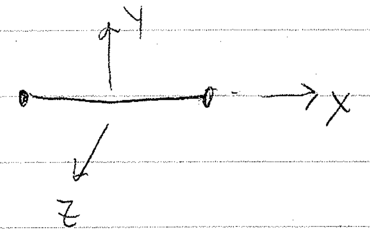


$T \ll T_0$ $\quad \Delta C_V \propto e^{-\frac{\Delta E}{k_B T}}$: characteristic of system with "gap" ΔE

here, $\Delta E = 2k_B T_0 = \frac{\hbar^2}{2I} l(l+1)\Big|_{l=1} = \frac{\hbar^2}{I}$

$T \gg T_0$: $\quad C_V^{rot} \to Nk_B = \frac{1}{2}k_B$ / degree of freedom (L_y, L_z)

Equipartition theorem in classical limit



General rule: $\quad T \ll T_{quantum}$: Quantum effects important

$T \gg T_{quantum}$: Classical limit recovered.

4.1

$$Z(T,N,V) = Z_m(T,N,V)\, Z_r^N(T) \quad , \quad Z_r(\beta) = \underbrace{\sum_{\ell=0}^{\infty}(2\ell+1)e^{-\beta\ell(\ell+1)\frac{\hbar^2}{2I}}}_{\text{Independent of } N,V}$$

$$\Rightarrow E(N,V,T) = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V}$$

$$= E_m(N,V,T) + N\underbrace{\left(-\frac{\partial \ln Z_r}{\partial \beta}\right)_{N,V}}_{\text{Independent of } N,V}$$

$$\cancel{\tfrac{3}{2}Nk_BT +} \quad = E_r'(T)$$

$$\Rightarrow E = Nk_B\left[\frac{3}{2}T + \left(-\frac{\partial \ln Z_r}{\partial \beta}\right)\right] \quad : \text{Independent of } V$$

$$F = -k_BT\ln Z = -k_BT\ln Z_m(N,V,T) \underbrace{-Nk_BT\ln Z_r(T)}_{\text{independent of } V}$$

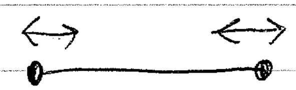
$$\Rightarrow P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = P_m = \frac{Nk_BT}{V}$$

$\Rightarrow PV = Nk_BT$ ~~indepen~~ all Temperatures

$$\Rightarrow C_p = \left(\frac{\partial}{\partial T}(E+PV)\right)_{P,N} = \left(\frac{\partial E}{\partial T}\right)_{N,V} + \left(\frac{\partial}{\partial T}(Nk_BT)\right)_{N,P}$$

$$\boxed{C_P = C_V + Nk_B}$$ all temperatures

Vibrational modes:



Quantum harmonic oscillator:

$$Z = Z_m \left(Z'_{rot}(T)\right)^N \left(Z'_{vib}(T)\right)^N$$

Z_{vib}: $\quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega$

$$Z'_{vib} = \sum_{n=0}^{\infty} e^{-\frac{\hbar\omega}{k_B T}\left(n+\frac{1}{2}\right)} = e^{-\frac{\hbar\omega}{2k_B T}} \sum_{n=0}^{\infty} e^{-n\frac{\hbar\omega}{k_B T}}$$

$\hookrightarrow$ Geometric series: $\displaystyle\sum_{n=0}^{\infty} r^n = \frac{1}{1-r}$

$$\Rightarrow Z'_{vib} = \frac{e^{-\frac{\hbar\omega}{2k_B T}}}{1 - e^{-\frac{\hbar\omega}{k_B T}}} = \frac{1}{e^{\frac{\hbar\omega}{2k_B T}} - e^{-\frac{\hbar\omega}{2k_B T}}} = \frac{1}{2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)}$$

$$\longrightarrow \begin{cases} \dfrac{k_B T}{\hbar\omega}, & k_B T \gg \hbar\omega \quad \left(\doteq \displaystyle\int_0^{\infty} e^{-\left(n+\frac{1}{2}\right)\frac{\hbar\omega}{k_B T}}\, dn\right) \\[2ex] e^{-\frac{\hbar\omega}{2k_B T}}\left(1 + \cancel{k_B T} e^{-\frac{\hbar\omega}{k_B T}}\right), & k_B T \ll \hbar\omega \end{cases}$$

(4.3

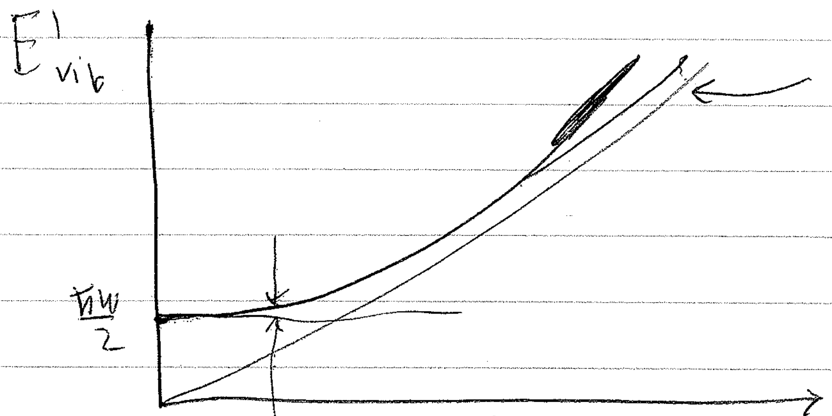
$$\ln z'_{vib} = -\ln 2 - \ln\left(\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right)$$

$$E = -\left(\frac{\partial \ln z}{\partial \beta}\right)_{N,V} = E_m + E_{rot} + N E'_{vib} \cancel{= N(\tfrac{3}{2}k_B + (T) + E'_v}$$

$$= N\left(\tfrac{3}{2}k_B T + E'_r(T) + E'_{vib}(T)\right)$$

$$E'_{vib} = -\left(\frac{\partial \ln z'_{vib}}{\partial \beta}\right)_{N,V} = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)$$

$$\rightarrow \begin{cases} \dfrac{1}{\beta} = k_B T, & k_B T >> \hbar\omega \\ \dfrac{\hbar\omega}{2}\left(1 + 2e^{-\frac{\hbar\omega}{k_B T}}\right), & k_B T >> \hbar\omega \end{cases}$$



$$\Delta E = \hbar\omega e^{-\frac{\hbar\omega}{k_B T}} \triangleq (E_1 - E_0) \times \underbrace{e^{-\frac{\hbar\omega}{k_B T}}}$$ probability that 1st level is excited

Classical Equipartition: $\frac{1}{2}k_B T$ / Quadratic degree of freedom

$$H_{class} = \frac{1}{2}m\omega^2 x^2 + \frac{1}{2}m\dot{x}^2 \ : \ 2 \text{ Quadratic d.o.f.}$$

$$\Rightarrow E = k_B T \quad \checkmark$$

(4.4

Note: E still independent of V, P

(at fixed N) ~~temperature~~

$PV = N k_B T$ still

$\Rightarrow \cancel{C_p = C_V + N k_B}$ ~~s~~

$$\Rightarrow C_p = \left(\frac{\partial}{\partial T}(E + PV)\right)_{N,P} = \left(\frac{\partial E}{\partial T}\right)_{N,P} + \left(\frac{\partial}{\partial T}(N k_B T)\right)_{N,P}$$

E independent of P, V

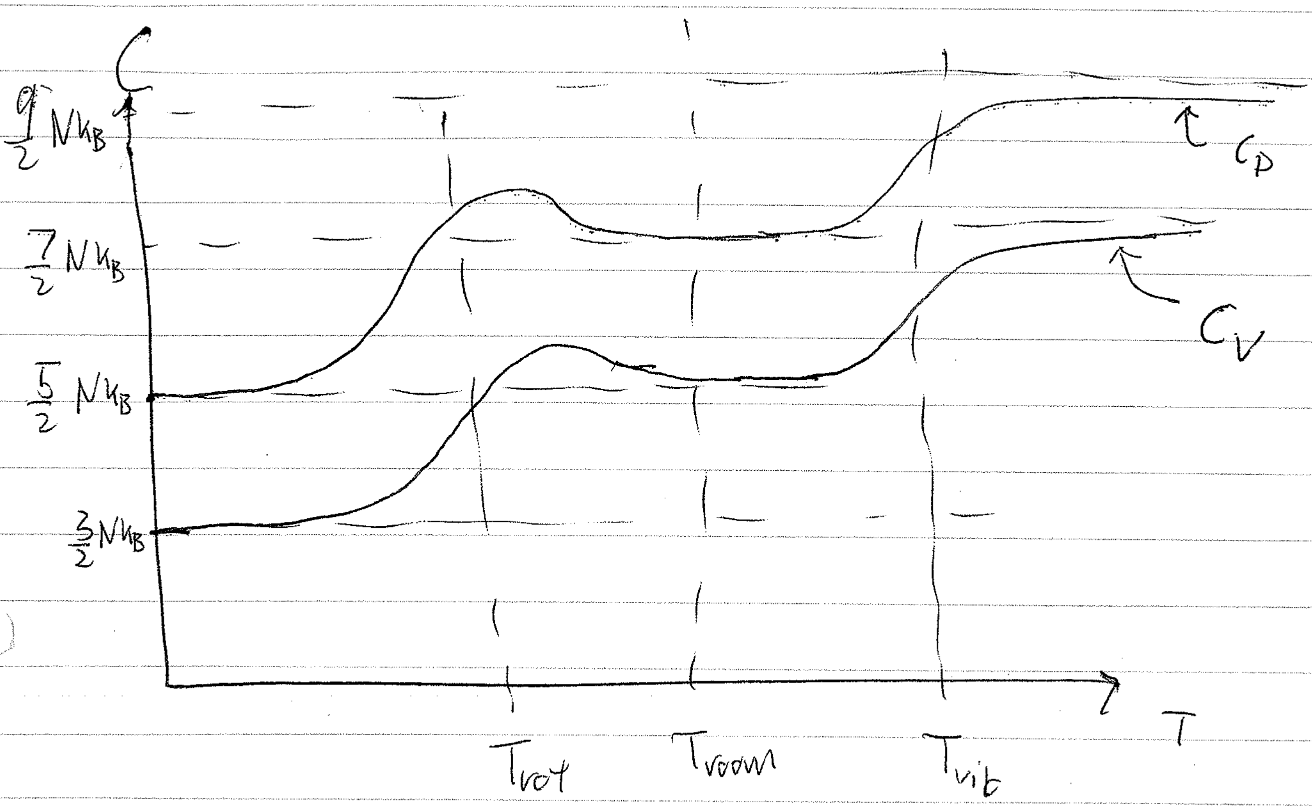
$$= \left(\frac{\partial E}{\partial T}\right)_{N,V} + N k_B$$

$$\Rightarrow \boxed{C_p = C_V + N k_B} \quad \text{still}$$

4.6

Summary of diatomic gas:

$$T_{rot} \equiv \frac{\hbar^2}{2Ik_B} \ll T_{vib} \equiv \frac{\hbar\omega}{k_B}$$



$$\gamma = \frac{C_p}{C_v} \simeq \begin{cases} \frac{5}{3}, & T \ll T_{rot} \\ \frac{7}{5}, & T_{rot} \ll T \ll T_{vib} \\ \frac{9}{5}, & T_{rot} \ll T_{vib} \ll T \end{cases}$$

Numerical estimate: $I = \frac{m_0 r^2}{2}$

$k_B T_{rot} = \frac{\hbar^2}{m_0 r^2}$, $E_{Rydberg} = \frac{\hbar^2}{2m_e}k^2 \sim 13.6\,\text{eV} \sim k_B(1.5\times10^5\,\text{K})$ $(1\,\text{eV} \sim 11{,}000\,\text{K})$, $k \sim \frac{1}{a_0} \sim \frac{1}{r}$

Bohr radius

(4.5

$$F = -k_B T \ln Z = F_m + F_{rot} + N F'_{vib}$$

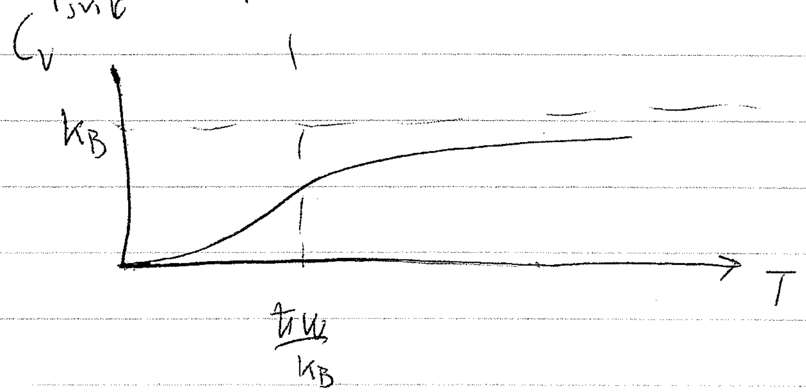
$$F'_{vib} = k_B T \ln 2 + k_B T \ln\left(\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right)$$

$$S'_{vib} = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = -k_B\Big[\ln 2 + \ln\left(\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right) - \frac{\hbar\omega}{2k_BT}\coth\left(\frac{\hbar\omega}{2k_BT}\right)\Big]$$

$$\rightarrow \begin{cases} 0, & T \to 0 \\ k_B \ln\left(\frac{k_B T}{\hbar\omega}\right), & T \to \infty \end{cases}$$

$$C_V^{1,vib} = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \left(\frac{\partial E'_{vib}}{\partial T}\right)_{N,V} = \frac{\hbar^2\omega^2}{k_B T^2 \sinh^2\left(\frac{\hbar\omega}{2k_BT}\right)}$$

$$\rightarrow \begin{cases} k_B, & T \to \infty \\ \frac{\hbar^2\omega^2}{k_B T^2} e^{-\frac{\hbar\omega}{k_BT}}, & T \to 0 \end{cases}$$



4.7

$$\Rightarrow k_B T_{rot} \simeq \frac{\hbar^2}{m_e a^2} \frac{m_e}{m_o} \sim k_B (1.5 \times 10^{5} \, {}^\circ K) \frac{m_e}{m_o}$$

$$\frac{m_e}{m_o} \sim \frac{m_e}{16 m_p}, \quad \frac{m_e}{m_p} \approx \frac{1}{6\pi^5} \text{ (6 sig. figures)}$$

$$\approx \frac{1}{2 \times 10^3}$$

$$\Rightarrow \boxed{T_{rot} \sim \frac{1.5 \times 10^{5} \, {}^\circ K}{3 \times 10^4} \sim 5 \, {}^\circ K}$$

$\Rightarrow$ ~~ld~~ $T_{vib} \sim 10^3 \, {}^\circ K$