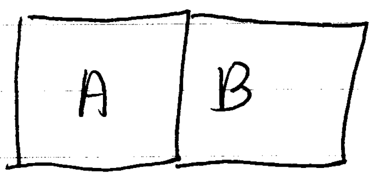
DIFFERENT CONSTRAINTS	$\longleftrightarrow$	DIFFERENT ENSEMBLE
N, V, E		CANONICAL
N, V, T		CANONICAL (VARIABLE E_T)
μ, V, T		GRAND CANONICAL (VARIABLES E AND N)
N, P, T		PRESSURE ENSEMBLE (VARIABLE V AND E)

NONINTERACTING SYSTEMS

$$Q = \sum_n e^{-\beta E_n}$$



FOR TWO SYSTEMS

$$E_{ABmn} \cong E_{An} + E_{Bm} + I_{ABmn}$$

FOR IDEAL GAS-TYPE SYSTEMS

$$E_{ABmn} \cong E_{An} + E_{Bm}$$

$$Q = \sum_m \sum_n e^{-\beta E_{An} - \beta E_{Bm}} = q_A \, q_B$$

$$q_A = \sum_n e^{-\beta E_{An}}$$

$$Q = q_A \, q_B \quad \text{IF } A = B \quad Q = q^2$$

FOR N SYSTEMS

$$Q = q^N$$ DISTINGUISHABLE

FOR N PARTICLES

$$Q = \frac{1}{N!} q^N$$ INDISTINGUISHABLE

NON INTERACTING (IDEAL) PARTICLES.
(WEAK APPROXIMATION)

FOR N molecules

$$Q = \frac{1}{N!} q_{mol}^N$$

$$E_{mol} = E_{TRA} + E_{ROT} + E_{vib} + E_{elec.}$$

$$q_{mol} = q_T \, q_R \, q_V \, q_E$$

THIS IS BETTER APPROX. SINCE THERE IS NO INTERFERENCE BETWEEN DEGRESS OF FREEDOM

TRANSLATIONAL MOTION

QM → PARTICLE IN a BOX

$$E_n = \frac{h^2}{8mL^2} n^2$$

$$\Delta E_{n,n+1} = \frac{h^2}{2mL^2}(2n+1)$$

$$\frac{h^2}{2mL} \sim 10^{-15}\ \mathrm{cm}^{-1} \triangleq 10^{-38}\ \mathrm{J}$$

FOR $L \sim 10^{-2}\ \mathrm{m}$

FOR MACRO L WE HAVE A CONTINIUM OF ENERGY

$$\sum e^{-\beta E_n} \longrightarrow \int_0^\infty e^{-\frac{\beta h^2}{8mL^2} n^2} dn$$

$$\boxed{\int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}}$$

$$q_T = \int_0^{\infty} e^{-\frac{\beta h^2}{8mL^2}x^2}\,dx$$

$$= \frac{1}{2}\sqrt{\frac{\pi\, 8mL^2}{\beta h^2}} = \frac{1}{2}\frac{L}{h}\sqrt{8m k_B T \pi}$$

$$\boxed{q_T = \frac{L}{\Lambda}}$$ 1-d

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$ THERMAL WAVELENGTH

FROM KINETIC THEORY

$$\frac{1}{2}\frac{\bar{p}^2}{m} = \frac{1}{2}k_B T \implies \bar{p}^2 \simeq m k_B T$$

$$\Lambda \simeq \frac{h}{\bar{p}}$$

In 3-d

$$\boxed{q_T = \frac{V}{\Lambda^3} = (2\pi m k_B T)^{3/2} \frac{V}{h^3}}$$

ROTATIONAL MOTION

$$q_R = \sum_{J=0} (2J+1)\, e^{-\beta hcBJ(J+1)}$$

$$\xrightarrow[\text{APPROX}]{} \int_0^{\infty} (2X+1)\, e^{-\beta hcB\, X(X+1)}\, dX$$

$$q_R = \frac{1}{hc\beta B} = \frac{k_B T}{hcB}$$

$$q_R = \frac{T}{\Theta_R}$$

$$\boxed{\Theta_R = \frac{hcB}{k_B}}$$ ROTATIONAL TEMPERATURE

SYMMETRY CONSIDERETIONS

HOMONUCLEAR
HETERONUCLEAR DIATOMIC MOLECULES

σ

$$\boxed{q_R = \frac{T}{\sigma \Theta_R}}$$

AT LOW TEMPERATURES THE INTEGRAL IS NOT A GOOD APPROXIMAION OF THE SUM !

POLYATOMIC MOLECULES

ALL MOLECULES HAVE 3 PRINCIPAL AXIS OF ROTATION !

$$\Longrightarrow I_i$$

$$q_R = \frac{\sqrt{\pi}}{\sigma}\left[\frac{1}{\beta h c B_A}\right]^{1/2} \sqrt{\frac{1}{\beta h c B_B}}\, \sqrt{\frac{1}{\beta h c B_C}}$$

WHERE $B_i = \dfrac{h}{8\pi^2 c\, I_i}$

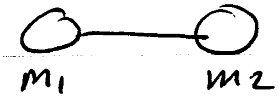
$k_B T \simeq \Delta E_{ROT}$ AT ROOM TEMP

$\Rightarrow$ DISTRIBUTION AND POPULATION OF HIGHER ROTATIONAL ENERGY LEVELS

NOTE:

$$\boxed{P_i = \frac{e^{-\beta \varepsilon_i}}{\sum_{n=0}^{\infty} e^{-\beta \varepsilon_n}}} = \boxed{\frac{e^{-\beta(\varepsilon_i - \varepsilon_0)}}{1 + \sum_{n=1}^{\infty} e^{-\beta(\varepsilon_n - \varepsilon_0)}}}$$

THE PARTION FUNCTION ONLY DEPEND ON THE ENERGY DIFFERENCES!



ROTATIONAL MOTION

DIATOMIC MOLECULE

$$E_J = B J(J+1) hc \quad J = 0, 1, 2, \ldots$$

$$B = \frac{h}{8\pi^2 c I}$$

$$I = \mu R^2 \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$g_J = 2J + 1$$

$$q_R = \sum_{J=0} (2J+1)\, e^{-\beta \cdot hcBJ(J+1)}$$

$$\longrightarrow \int_0^{\infty} (2x+1)\, e^{-\beta hcBx(x+1)}\, dx$$

$$\frac{d}{dx} e^{-\beta hcBx(x+1)} = -\beta hcB(2x+1)$$

$$\boxed{q_R = \frac{1}{\beta hcB} = \frac{k_B T}{hcB}}$$

VIBRATIONAL PARTITION FUNCTION

HO — QM

$$E_n = hc\bar{\nu}\left(\frac{1}{2} + n\right) \quad n = 0, 1, \dots$$

$$q_V = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-\frac{\beta hc\bar{\nu}}{2}} \sum_{n=0}^{\infty} e^{-\beta hc\bar{\nu} n}$$

$$= e^{-\beta\frac{hc\bar{\nu}}{2}} \sum_{n=0}^{\infty} \left[e^{-\beta hc\bar{\nu}}\right]^n$$

$$\sum_{n=0}^{\infty} X^n = \frac{1}{1-X} \simeq 1 - X + \dots$$

$$q_R = \frac{e^{-\beta\frac{hc\bar{\nu}}{2}}}{1 - e^{-\beta hc\bar{\nu}}} \longrightarrow \frac{1}{1 - e^{-\beta hc\bar{\nu}}}$$

$E_0 \neq 0$

ENERGY SHIFT

$\Rightarrow E_0 = 0$