TOPIC: Canonical ensemble and Molecular Partition Fn:

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Dr. RKH:

$$Z(N,V,T) = \sum_j e^{-\beta E_j(N)}$$

: $E_j \rightarrow$ Energy levels of Hamiltonian

$$H(N) = \sum_{k=1}^{N} \frac{p_k^2}{2m_k} + V(r_1, r_2, r_k, r_N)$$

: when "N"-particles are approximated to be nearly non-interacting and fundamental $\Rightarrow$

$$H(N) \cong \sum_{i=1}^{N} H_i$$

$$\Rightarrow E_J = \underbrace{\varepsilon_i(1)}_{\text{Molecular level}} + \varepsilon_j(\underbrace{2}_{\text{co-ordinates of particles}}) + \cdots + \varepsilon_k(-) + \varepsilon_l(N)$$

$\Rightarrow$ Since Particles are distinguishable (Case-I)

$$Z(N,V,T) = \sum_J e^{-\beta E_J(N)}$$

$$= \sum_i \sum_j \cdots \sum_l e^{-\beta(\varepsilon_i + \varepsilon_j + \cdots + \varepsilon_l)}$$

$$Z(N,V,T) = \prod_{p=1}^{N} \left(\sum e^{-\beta \varepsilon_{ip}} \right) = \prod_{p=1}^{N} q_p$$

$$= q^N$$

since particles are fundamental and potentials are identical

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Iff Particles are indistinguishable (Case-II)
Means de-Broglie wavelength being larger than Mean-separations

$\forall$ $E_J \equiv \varepsilon_i(1) + \varepsilon_j(2) + \cdots + \varepsilon_l(N)$

$\equiv \varepsilon_i(2) + \varepsilon_j(1) + \cdots + \varepsilon_l(N)$

$\equiv$ Total $(N!)$ identical energy forms can be written

$\Rightarrow$ Actual Count

$= \dfrac{\text{Count of Permutations for distinguishable systems}}{(N!)}$

$\Rightarrow Z(N,V,T) = \left(q^N / N! \right)$

where $q \rightarrow$ Molecular Partition function

Molecular Partition function (q)

$$q = \sum_i e^{-\varepsilon_i / k_B T} \quad \text{where} \left(\frac{1}{k_B T}\right) = \beta$$

ε_i captures translational, rotational, vibrational and electronic energies.

$\Rightarrow$ $q = q_{trans}\, q_{vib}\, q_{rot}\, q_e$