# VIVEKANANDA COLLEGE THAKURPUKUR KOLKATA-700063

NAAC accredited 'A' GRADE

Topic: Canonical Ensemble

Course Title: Statistical Mechanics

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# STATISTICAL MECHANICS

How is stat. phy different from Q. Mech in terms of usage of probability?

# Stat Mech uses probability as because of "IGNORANCE" about the system containing large no. of particles $N >> 1 \sim 10^{22}$

# Q. Mech uses probability as a "PRACTICE" based on the two basic principles of nature, which are Uncertainty Principle & De Broglie Hypothesis.

Till now, our study on canonical ensembles & their application on different system can be summarised as:

# Canonical ensemble corresponds to exact replicas of the system with varying energy between 0 to $\infty$ with $T =$ constt., $N =$ constt and $V =$ constt.

# Canonical distribution function is given by

$$P_r = e^{-\beta E_r} \Big/ \sum_r e^{-\beta E_r}$$ for system with non degenerate energy levels.

$$= g_r e^{-\beta E_r} \Big/ \sum_r g_r e^{-\beta E_r}$$ for system with levels $E_r$ with degeneracy $g_r$.

# The partition function is the key function – from which all thermodynamic properties can be derived. Canonical Partition funct for different system are:

| System | Canonical Partition Funct. |
| --- | --- |
| Quantum Mechanical (non degenerate) | $Z = \sum_r e^{-\beta E_r}$ |
| ,, ,, (degenrate) | $Z = \sum_r g_r e^{-\beta E_r}$ |
| ,, ,, (with DOS $g(E)$) | $Z = \int_0^\infty g(E) e^{-\beta E} dE$ |
| Classical System | $Z_N(V,T) = \frac{1}{N! h^{3N}} \int e^{-\beta H(q,p)} d^{3N}q \, d^{3N}p$ |

# The partition function of a non-interacting system is factorizable i.e

$$Z_N(V,T) = \frac{1}{N!}\left[\frac{1}{h^3}\int e^{-\beta H_i(q_i,p_i)} d^3q_i \, d^3p_i\right]^N = \frac{1}{N!}\left[Z_1(V,T)\right]^N$$

where $Q_1(V,T)$ is the single particle partition function.

# Thermodynamic Properties from partition function:

**2-level System**

Partition Function $Z = Z_1^N = (1+e^{-\beta E})^N$

Helmholtz Free Energy $A = -NkT\ln(1+e^{-\beta E})$

Internal Energy $U = N\epsilon / (1+e^{\beta E})$

**Classical Ideal Gas**

Partition Funct. $Z_N(V,T) = \cancel{\frac{1}{N!}\left[\frac{V}{h^3}(2\pi mkT)^{3/2}\right.}$

$$= \frac{1}{N!}\left[\frac{V}{h^3}(2\pi mkT)^{3/2}\right]^N$$

Helmholtz free Energy

$$A = NkT\left[\ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right) - 1\right]$$