TRINITY COLLEGE FOR WOMEN
NAMAKKAL
Department of Physics

Statistical Mechanics

23PPH04-EVEN Semester

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Introduction

❖Chemical Sciences and Statistical Physics are a collection of a number of macroscopically identical but essentially independent systems.

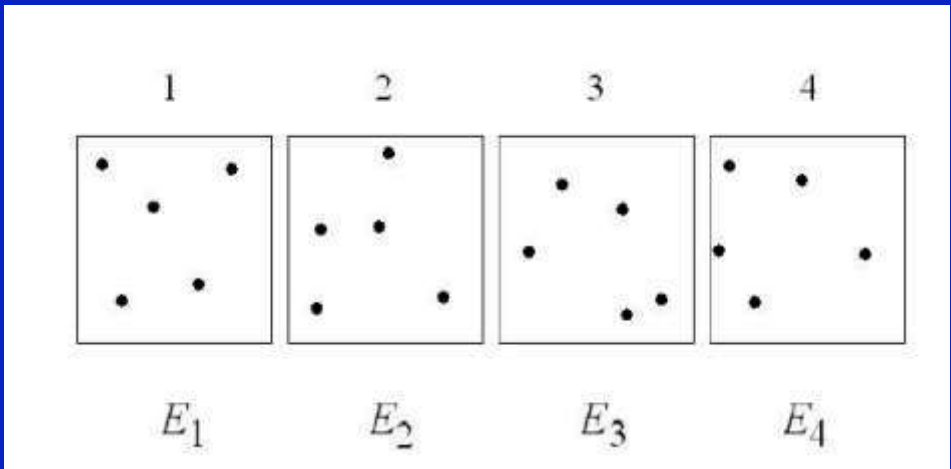
❖The System, is defined by the collection of a large number of particles

❖Same macroscopic conditions, like Volume, Energy, Pressure, Temperature and the total number of particles.

Microstates and Ensembles:

❖According to the quantum mechanics at any given moment, the system is in a superposition of distinct quantum states called microstates.

❖An ensemble on the other and is the collection of all possible microstates consistent with the externally controlled macroscopic parameter.



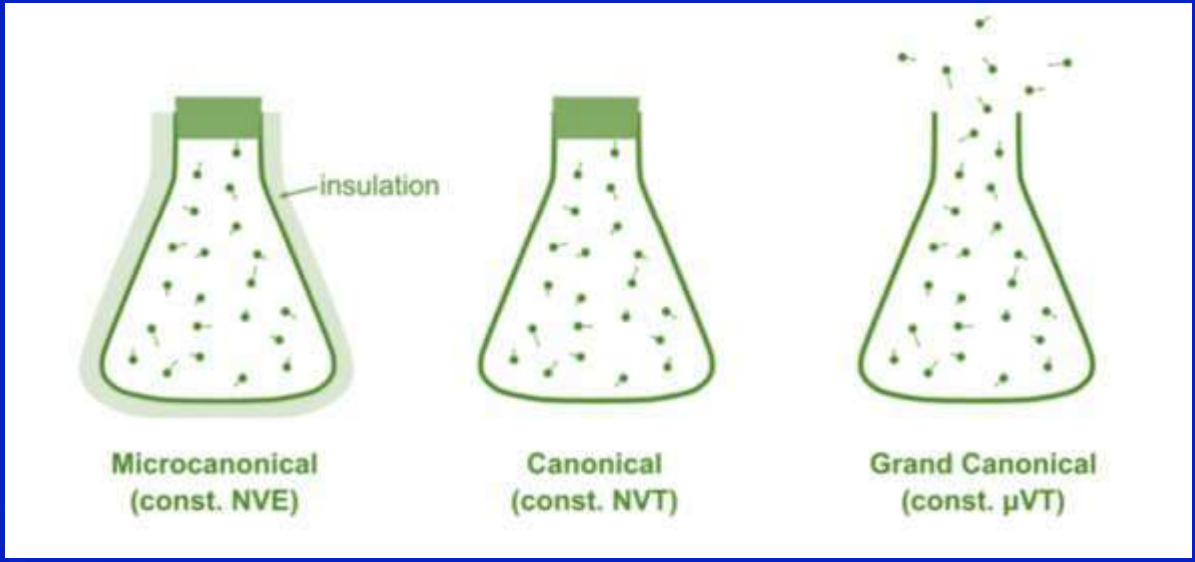
Fundamental postulate

- The probability density function is proportional to some function of the ensemble parameters and random variables.
- Thermodynamic state functions are described by ensemble averages of random variables.
- The entropy as defined by Giibb's entropy formula matches with the entropy as defined in classical thermodynamics

Types of Ensembles

There are three types of ensembles:

Micro-canonical Ensemble
Canonical Ensemble
Grand Canonical Ensemble



Micro-canonical Ensemble

- It is the collection of a large number of essentially independent systems having the same energy E, volume V and total number of particles N.

- Separated by rigid impermeable and insulated walls, such that the values of E, V & N are not affected by the mutual pressure of other systems.

Canonical Ensemble

- It's the collection of a large number of essentially independent systems having the same temperature T, volume V and the number of particles N.

- The equality of temperature of all the systems can be achieved by bringing all the systems in thermal contact.

- Hence, in this ensemble, the systems are separated by rigid, impermeable but conducting walls, the outer walls of the ensemble are perfectly insulated and impermeable though.

Grand Canonical Ensemble

- It is the collection of a large number of essentially independent systems having the same temperature T, volume V & chemical potential μ.

- The systems of a grand canonical ensemble are separated by rigid permeable and conducting walls.

Ensemble Average

❖Every statistical quantity has not an exact but an approximate value.

❖The average of a statistical quantity during motion is equal to its ensemble average.

❖Let R(x)*R*(*x*) be a statistical quantity along the x-axis and N(x)*N*(*x*) be the number of phase points in phase space, then **the ensemble average** of the statistical quantity R*R* is defined as,

$$\bar{R} := \frac{\int_{-\infty}^{\infty} R(x)N(x)\mathrm{d}x}{\int_{-\infty}^{\infty} N(x)\mathrm{d}x}$$

THANK YOU

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