Statistical Thermodynamics

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Contents

1. Introduction

- **Mechanics : Study of position, velocity, force and energy**
  - **Classical Mechanics (Molecular Mechanics)**
    - **Molecules (or molecular segments) are treated as rigid object (point, sphere, cube,...)**
    - **Newton's law of motion**
  - **Quantum Mechanics**
    - **Molecules are composed of electrons, nuclei, ...**
    - **Schrodinger's equation → Wave function**

1. Introduction

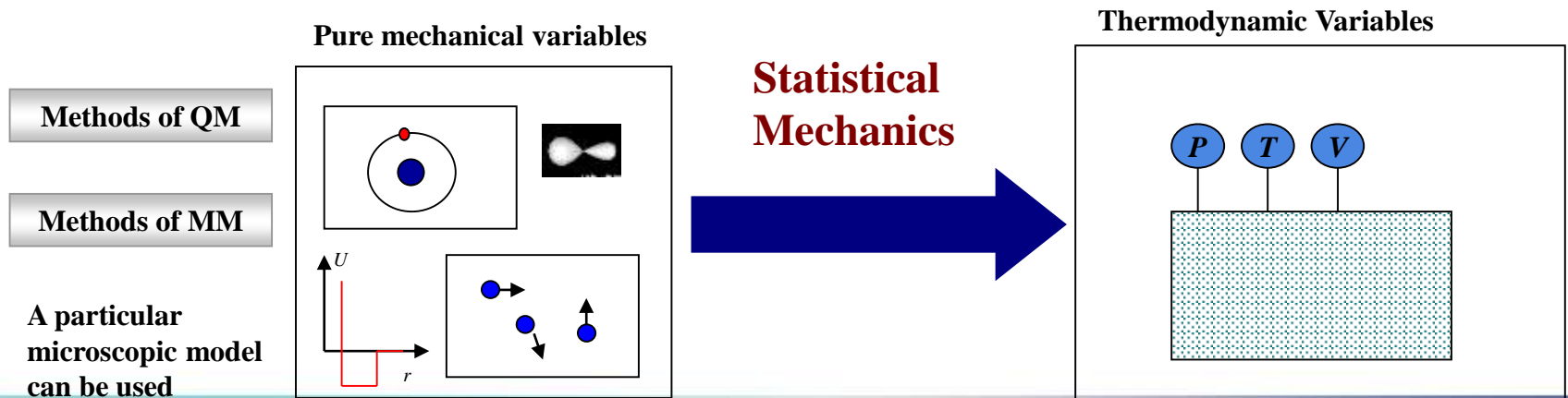- **Methodology of Thermodynamics and Statistical Mechanics**
  - **Thermodynamics**
    - **study of the relationships between _macroscopic_ properties**
      - Volume, pressure, compressibility, …
  - **Statistical Mechanics (Statistical Thermodynamics)**
    - **how the various macroscopic properties arise as a consequence of the _microscopic nature_ of the system**
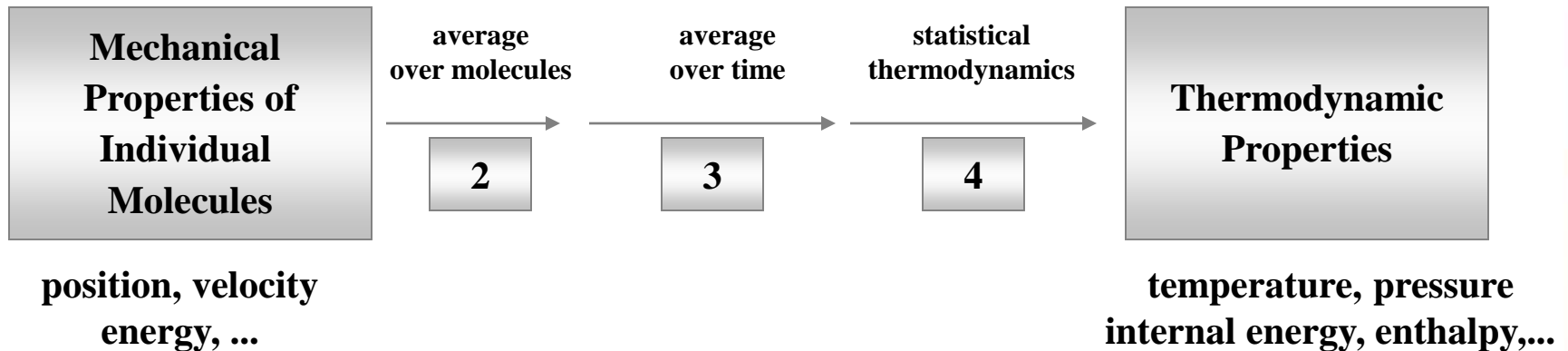   - Position and momenta of individual molecules (mechanical variables)
  - **Statistical Thermodynamics (or Statistical Mechanics) is a link between microscopic properties and bulk (macroscopic) properties**

Pure mechanical variables

Thermodynamic Variables

Statistical Mechanics

Methods of QM

Methods of MM

A particular microscopic model can be used

U

r

P T V

1.Introduction

- **Equilibrium Macroscopic Properties**
  - **Properties are consequence of average of individual molecules**
  - **Properties are invariant with time → Time average**

Mechanical Properties of Individual Molecules	average over molecules	average over time	statistical thermodynamics	Thermodynamic Properties
	2	3	4	

position, velocity energy, ...

**temperature, pressure internal energy, enthalpy,...**

1. Introduction

- **Description of States**
  - *Macrostates* : T, P, V, … (fewer variables)
  - *Microstates* : position, momentum of each particles ($\sim 10^{23}$ variables)
- **Fundamental methodology of statistical mechanics**
  - **Probabilistic approach : statistical average**
    - Most probable value
  - **Is it reasonable ?**
    - As N approaches very large number, then fluctuations are negligible
    - "Central Limit Theorem" (from statistics)
    - Deviation $\sim 1/N^{0.5}$

2. Distribution of Molecular States

- **Statistical Distribution**
  - **n : number of occurrences**
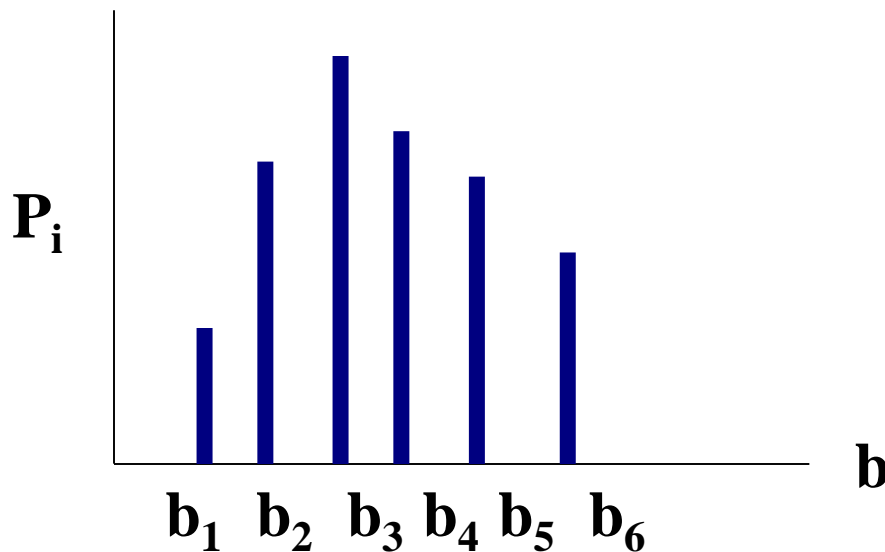 - **b : a property**

n_i

1 2 3 4 5 6

b
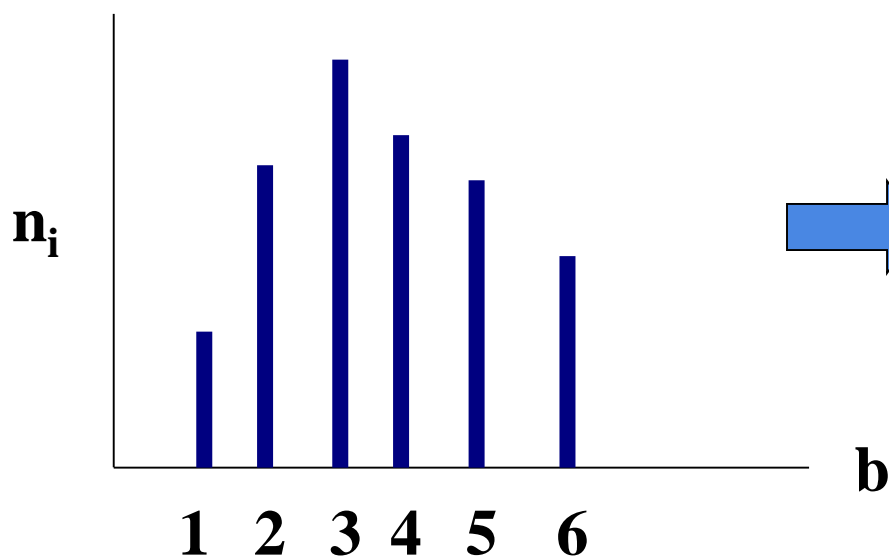
if we know "distribution"
we can calculate the average
value of the property **b**

2. Distribution of Molecular States

- **Normalized Distribution Function**

    → **Probability Distribution Function**

$$P_i(b_i) = \frac{n_i(b_i)}{n} = \frac{n_i(b_i)}{\sum\limits_i n_i(b_i)}$$

$$\sum\limits_i P_i(b_i) = 1$$

$$<b> = \sum\limits_i b_i P_i$$
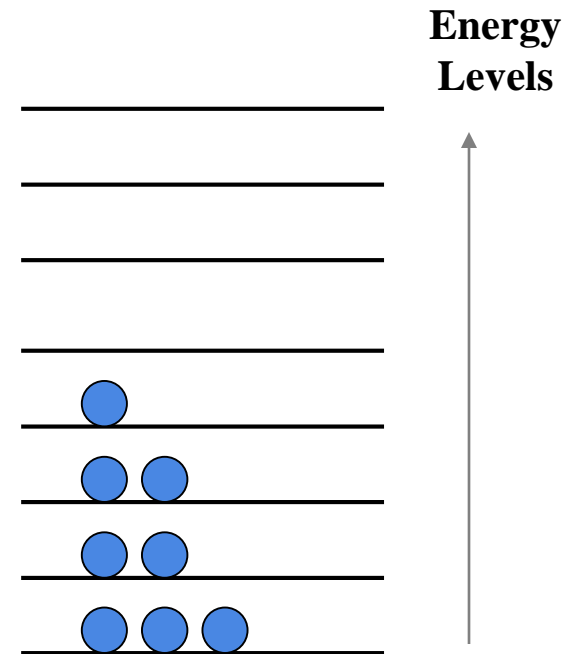
$$<F(b)> = \sum\limits_i F(b_i) P_i$$

Finding probability (distribution) function is the main task in statistical thermodynamics

2. Distribution of Molecular States

- **Quantum theory says ,**
  - **Each molecules can have only discrete values of energies**
- **Evidence**
  - **Black-body radiation**
  - **Planck distribution**
  - **Heat capacities**
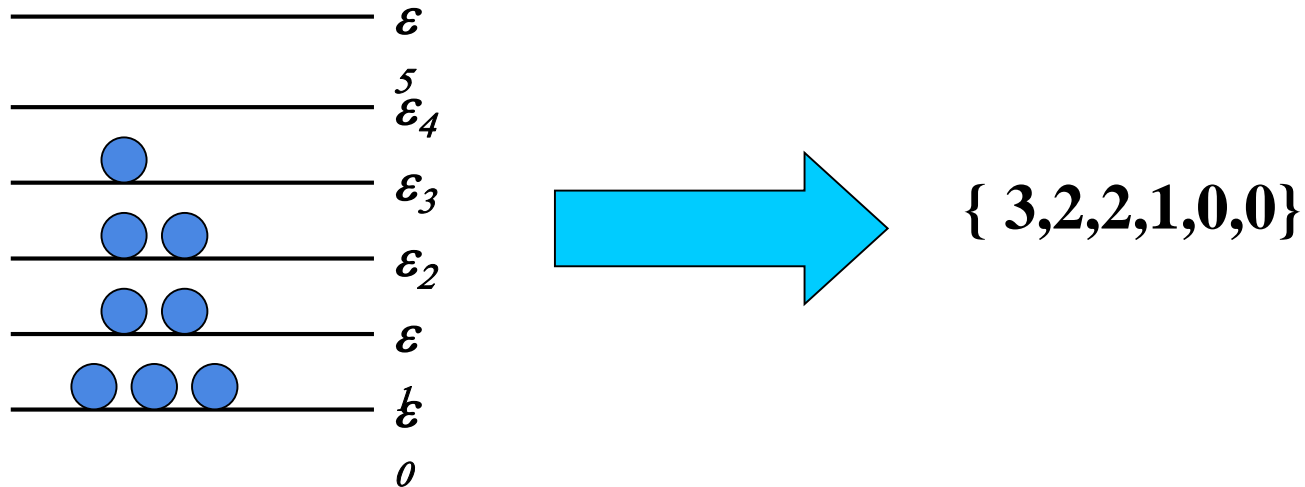 - **Atomic and molecular spectra**
  - **Wave-Particle duality**

Energy Levels

- **Configuration ....**

  - **At any instance, there may be n_o molecules at ε_0 , n_1 molecules at ε_1 , n_2 molecules at ε_2 , …**
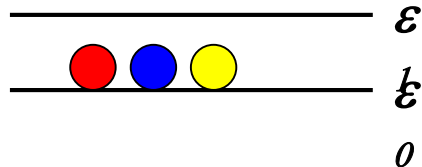
    ➔ {n_0 , n_1 , n_2 …} configuration

$$\varepsilon$$
$$\varepsilon_5$$
$$\varepsilon_4$$
$$\varepsilon_3$$
$$\varepsilon_2$$
$$\varepsilon$$
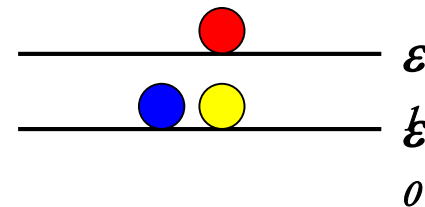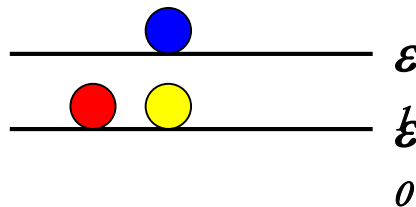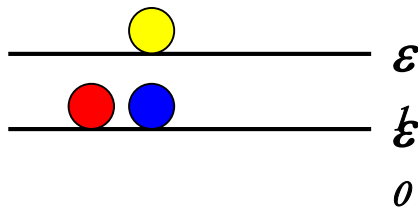$$\varepsilon_0$$

{ 3,2,2,1,0,0}

2. Distribution of Molecular States

- ## Weight ....
    - ### Each configurations can be achieved in different ways

- ### Example1 : {3,0} configuration → 1

- ### Example2 : {2,1} configuration → 3

2. Distribution of Molecular States

- **Calculation of Weight ....**
  - **Weight (W) : number of ways that a configuration can be achieved in different ways**
  - **General formula for the weight of $\{n_0 , n_1 , n_2 \dots\}$ configuration**

$$W = \frac{N!}{n_1! n_2! n_3! \dots} = \frac{N!}{\prod_i n_i!}$$

Example1
$\{1,0,3,5,10,1\}$ of 20 objects
W = 9.31E8

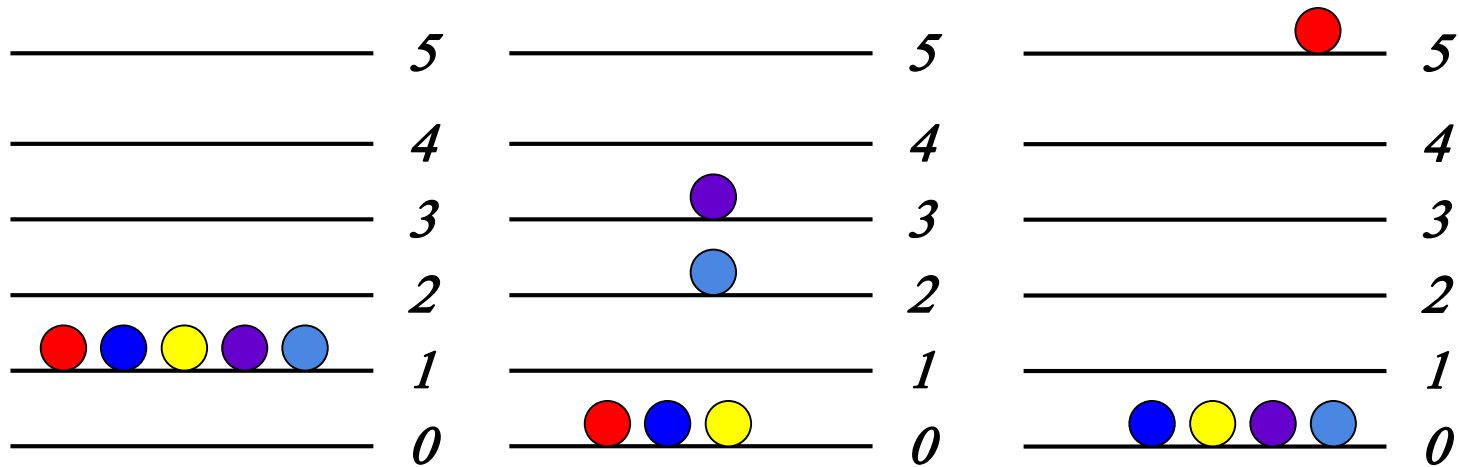**Example 2**
$\{0,1,5,0,8,0,3,2,1\}$ of 20 objects
W = 4.19 E10

- **All distributions of energy are equally probable**
- **If E = 5 and N = 5 then**

All configurations have equal probability, but possible number of way (weight) is different.

A Dominating Configuration

- **For large number of molecules and large number of energy levels, there is a <u>dominating configuration</u>.**

- **The weight of the dominating configuration is <u>much more larger</u> than the other configurations.**

W_i

$\{n_i\}$
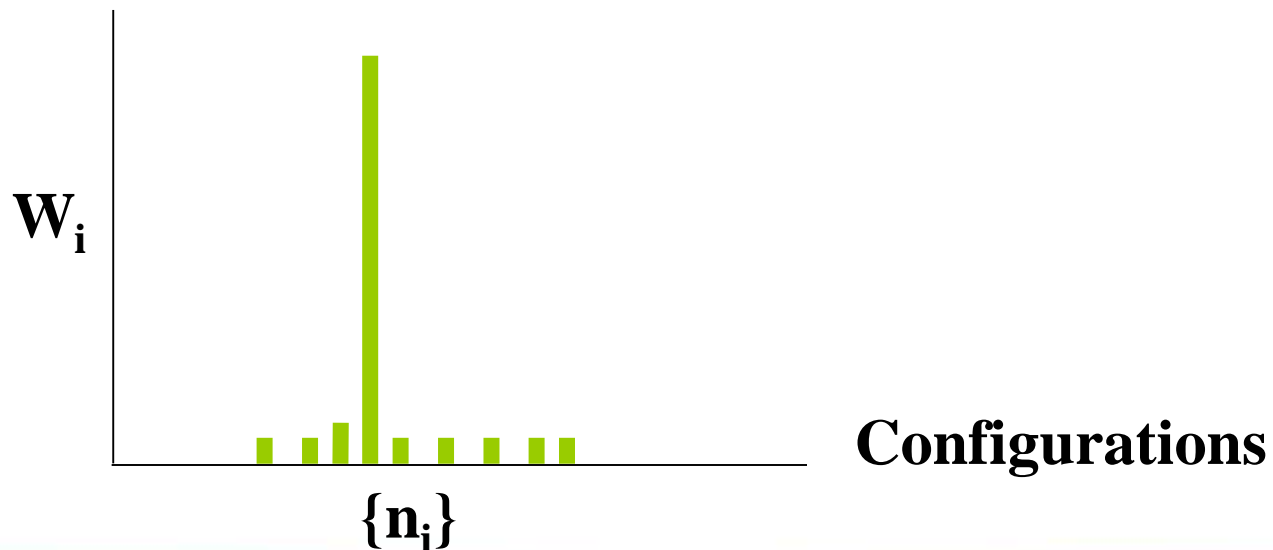
Configurations

Dominating Configuration
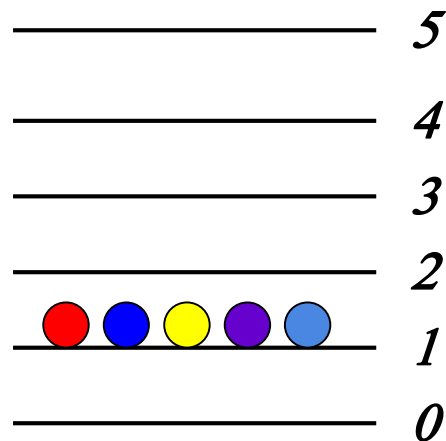
$W = 1 \ (5!/5!)$
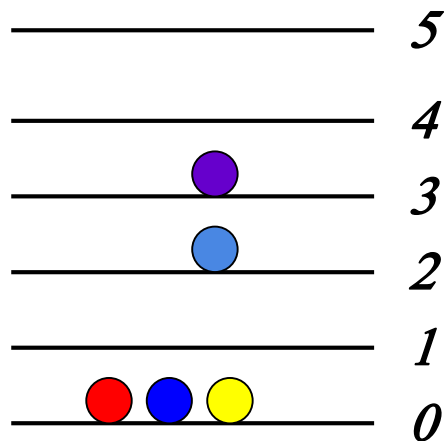
$W = 20 \ (5!/3!)$
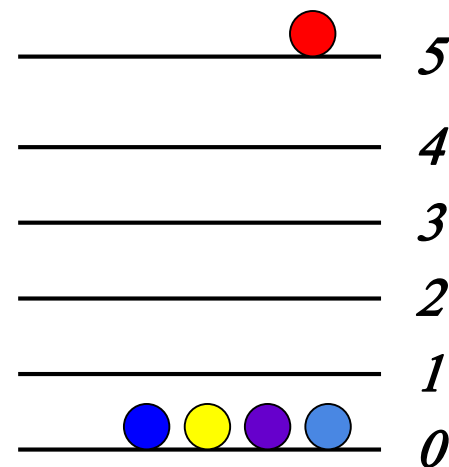
$W = 5 \ (5!/4!)$

→ **Difference in W becomes larger when N is increased !**

→ **In molecular systems ($N \sim 10^{23}$) considering the most dominant configuration is enough for average**

- ### **The Boltzmann Distribution**
  - **Task : Find the dominant configuration for given *N* and total energy *E***
  - **Method : Find maximum value of *W* which satisfies,**

$$N = \sum_i n_i$$

$$E = \sum_i \varepsilon_i n_i$$

$\Longrightarrow$
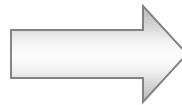
$$\sum_i dn_i = 0$$

$$\sum_i \varepsilon_i dn_i = 0$$

Stirling's approximation

- **A useful formula when dealing with factorials of large numbers.**

$$\ln N! = N \ln N - N$$

$$\ln W = \ln \frac{N!}{n_1! n_2! n_3! \dots} = \ln N! - \sum_i \ln n_i!$$

$$= N \ln N - N - \sum_i n_i \ln n_i + \sum_i n_i$$

$$= N \ln N - \sum_i n_i \ln n_i$$

Method of Undetermined Multipliers

- ## Maximum weight , W

  - → **Recall the method to find min, max of a function…**

    $d \ln W = 0$

    $$\left(\frac{\partial \ln W}{dn_i} \right) = 0$$

- ## Method of undetermined multiplier :

  - **Constraints should be multiplied by a constant and added to the main variation equation.**

Method of Undetermined Multipliers

undetermined multipliers

$$d \ln W = \sum_i \left(\frac{\partial \ln W}{dn_i} \right) dn_i + \alpha \sum_i dn_i - \beta \sum_i \varepsilon_i dn_i$$

$$= \sum_i \left\{ \left(\frac{\partial \ln W}{dn_i} \right) + \alpha - \beta \varepsilon_i \right\} dn_i = 0$$
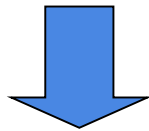
$$\left(\frac{\partial \ln W}{dn_i} \right) + \alpha - \beta \varepsilon_i = 0$$

Method of Undetermined Multipliers

$$\ln W = N \ln N - \sum n_i \ln n_i$$

$$\left(\frac{\partial \ln W}{\partial n_i} \right) = \frac{\partial N \ln N}{\partial n_i} - \sum_j \frac{\partial (n_j \ln n_j)}{\partial n_i}$$

$$\frac{\partial N \ln N}{\partial n_i} = \left(\frac{\partial N}{\partial n_i} \right) \ln N + N \times \frac{1}{N} \left(\frac{\partial N}{\partial n_i} \right) = \ln N + 1$$

$$\sum_j \frac{\partial (n_j \ln n_j)}{\partial n_i} = \sum_j \left\{ \left(\frac{\partial n_j}{\partial n_i} \right) \ln n_j + n_j \times \frac{1}{n_j} \left(\frac{\partial n_j}{\partial n_i} \right) \right\} = \ln n_i + 1$$
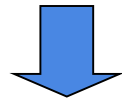
$$\frac{\partial \ln W}{\partial n_i} = -(\ln n_i + 1) + (\ln N + 1) = -\ln \frac{n_i}{N}$$

Method of Undetermined Multipliers

$$-\ln\frac{n_i}{N} + \alpha + \beta\varepsilon_i = 0 \longrightarrow \frac{n_i}{N} = e^{\alpha - \beta\varepsilon_i}$$

Normalization Condition

$$N = \sum_j n_j = Ne^{\alpha}\sum_j e^{-\beta\varepsilon_j}$$

$$e^{\alpha} = \frac{1}{\sum_j e^{-\beta\varepsilon_j}}$$

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_j e^{-\beta\varepsilon_j}}$$
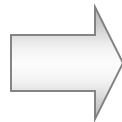
Boltzmann Distribution
(Probability function for energy distribution)

The Molecular Partition Function

- **Boltzmann Distribution**

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_j e^{-\beta \varepsilon_j}} = \frac{e^{-\beta \varepsilon_i}}{q}$$

- **Molecular Partition Function**

$$q = \sum_j e^{-\beta \varepsilon_j}$$

- **Degeneracies : Same energy value but different states (g_j-fold degenerate)**

$$q = \sum_{\substack{levels \\ j}} g_j e^{-\beta \varepsilon_j}$$

How to obtain the value of beta ?

- **Assumption :** $\beta = 1/kT$

- **T→ 0 then q → 1**

- **T→ infinity then q → infinity**

- **The molecular partition function gives an indication of the <u>average number of states that are thermally accessible to a molecule at T</u>.**

2. Interacting Systems – Gibbs Ensemble

- **Solution to Schrodinger equation (Eigen-value problem)**
  - **Wave function**
  - **Allowed energy levels : E_n**

$$-\sum_i \frac{h^2}{8\pi^2 m_i}\nabla_i^2\Psi + U\Psi = E\Psi$$

- **Using the molecular partition function, we can calculate average values of property at given *QUANTUM STATE.***

- **Quantum states are changing so rapidly that the observed dynamic properties are actually time average over quantum states.**

Fluctuation with Time

states —
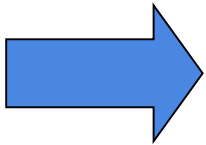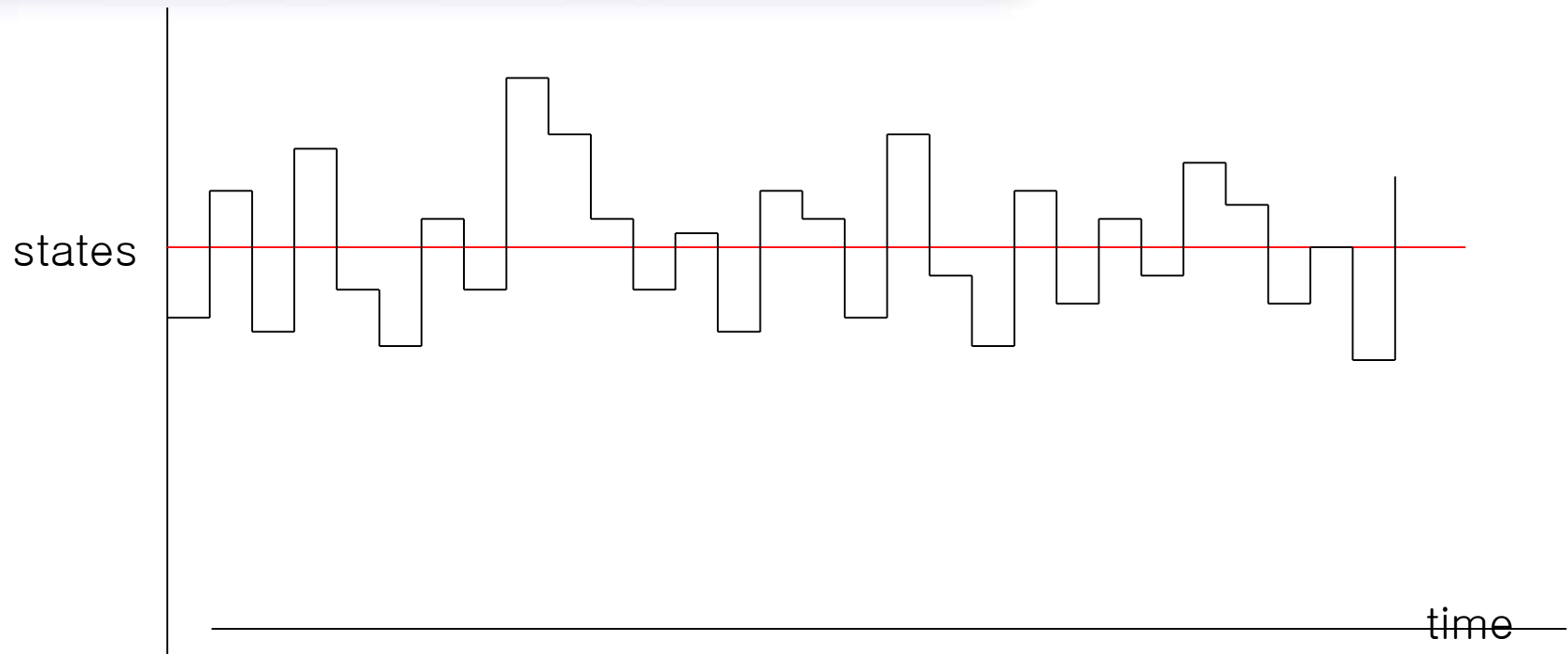
time

→ *Although we know most probable distribution of energies of individual molecules at given N and E (previous section – molecular partition function) it is almost impossible to get time average for interacting molecules*

Thermodynamic Properties

- **Entire set of possible quantum states**

$$\Psi_1, \Psi_1, \Psi_1, \ldots \Psi_i, \ldots$$

$$E_1, E_2, E_3, \ldots, E_i, \ldots$$

- **Thermodynamic internal energy**

$$U = \lim_{\tau \to \infty} \frac{1}{\tau} \sum_i E_i \Delta t_i$$

Difficulties

- **Fluctuations are very small**
- **Fluctuations occur too rapidly**

→**We have to use alternative, abstract approach.**

→**Ensemble average method (proposed by Gibbs)**

Alternative Procedure

- ## **Canonical Ensemble**
  - **Proposed by J. W. Gibbs (1839-1903)**
  - **Alternative procedure to obtain average**
  - **Ensemble : Infinite number of mental replica of system of interest**

Large reservoir (constant T)

All the ensemble members have the same (n, V, T)

Energy can be exchanged but particles cannot

Number of Systems : N
N → ∞
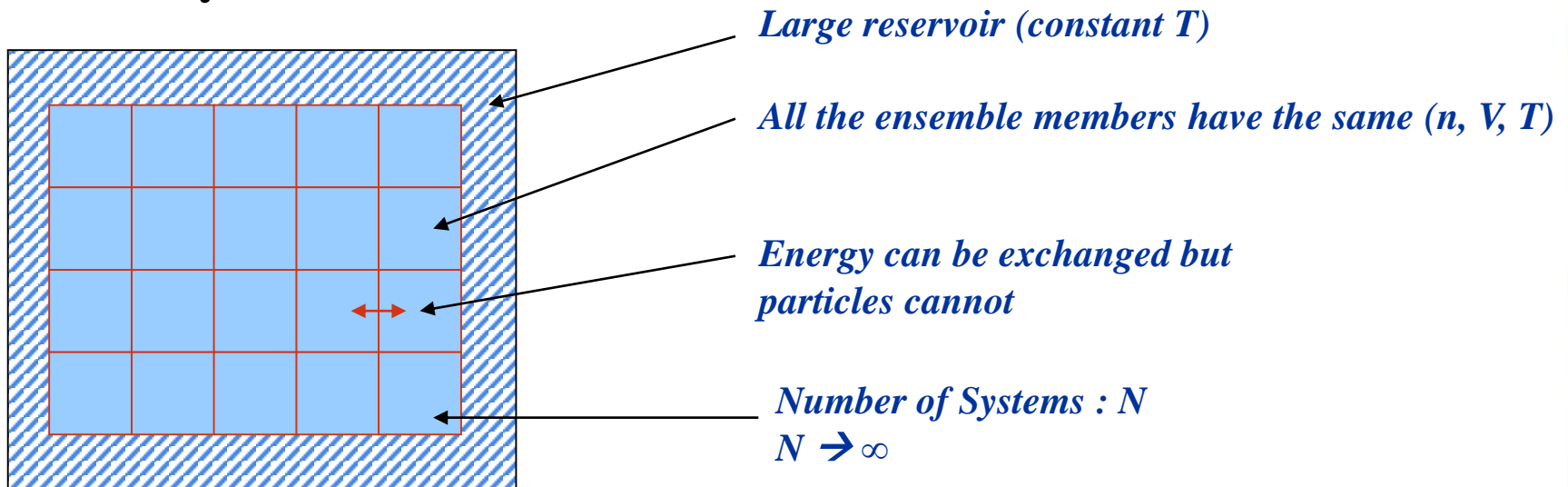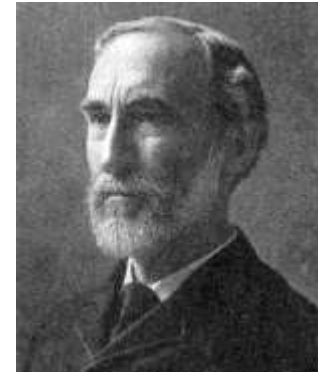
Two Postulate

Fist Postulate

*The **long time average** of a mechanical variable M is equal to the **ensemble average** in the limit N ➜ ∞*

time

E_1 E_2 E_3 E_4 E_5
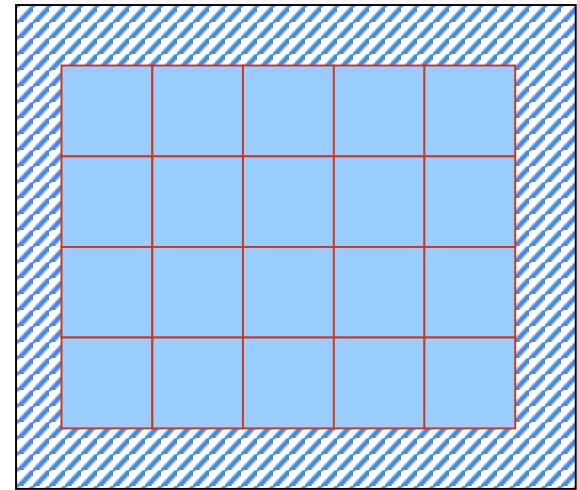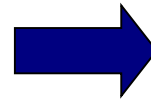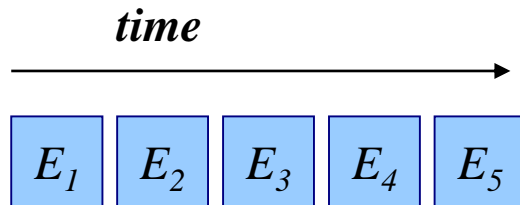
Second Postulate (Ergodic Hypothesis)

*The systems of ensemble are **distributed uniformly** for **(n,V,T) system***
***Single isolated system** spend equal amount of time*

Averaging Method

- **Probability of observing particular quantum state *i***

$$P_i = \frac{\tilde{n}_i}{\sum\limits_i \tilde{n}_i}$$

- **Ensemble average of a dynamic property**

$$<E> = \sum\limits_i E_i P_i$$

- **Time average and ensemble average**

$$U = \lim_{\tau \to \infty} \sum E_i \Delta t_i = \lim_{n \to \infty} \sum\limits_i E_i P_i$$

How to find Most Probable Distribution ?

- **Calculation of Probability in an Ensemble**
  - **Weight**

$$\Omega = \frac{\tilde{N}!}{\tilde{n}_1!\tilde{n}_2!\tilde{n}_3!...} = \frac{\tilde{N}!}{\prod_i \tilde{n}_i!}$$

  - **Most probable distribution = configuration with maximum weight**

  - **Task : find the dominating configuration for given *N* and *E***
    - **Find maximum *Ω* which satisfies**

$$\tilde{N} = \sum_i \tilde{n}_i \qquad \Longrightarrow \qquad \sum_i d\tilde{n}_i = 0$$

$$E_t = \sum_i E_i \tilde{n}_i \qquad \qquad \sum_i E_i d\tilde{n}_i = 0$$

Canonical Partition Function

- **Similar method (Section 2) can be used to get most probable distribution**

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}$$

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Q}$$

$$Q = \sum_j e^{-\beta E_j} \qquad \longrightarrow \qquad \textit{Canonical Partition Function}$$

How to obtain beta ?
– Another interpretation

$$dU = d(\sum_i E_i P_i) = \sum_i E_i dP_i + \sum_i P_i dE_i$$

$$dU = \delta q_{rev} - \delta w_{rev} = TdS - pdV$$

$$\sum_i P_i dE_i = \sum_i P_i \left(\frac{\partial E_i}{\partial V}\right)_N dV = -PdV = -\delta w_{rev}$$

$$\sum_i E_i dP_i = -\frac{1}{\beta}(\sum_i \ln P_i dP_i + \ln Q \sum_i dP_i) = -\frac{1}{\beta}\sum_i \ln P_i dP_i = TdS = dq_{rev}$$

The only function that links heat (path integral) and state property is TEMPERATURE.

$$\beta = 1/kT$$

Properties from Canonical Partition Function

- **Internal Energy**

$$U = <E> = \sum_i E_i P_i = = \frac{1}{Q} \sum_{i(qs)} E_i e^{-\beta E_i}$$

$$\left(\frac{\partial Q}{\partial \beta} \right)_{N,V} = -\sum_{i(qs)} E_i e^{-\beta E_i}$$

$$U = -\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{N,V} = -\left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V}$$

Properties from Canonical Partition Function

- ## Pressure

$$(\delta w_i)_N = P_i dV = F_i dx$$

$$(dE_i)_N = -F_i dx = -P_i dV = -\delta w_i$$

$$P_i = -\left(\frac{\partial E_i}{\partial V}\right)_N$$

$$P = <P> = \sum_i P_i \mathrm{P}_i$$

$$P = \frac{1}{Q}\sum_i P_i e^{-\beta E_i} = \frac{1}{Q}\sum_i \left(\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{\beta,N} = \frac{\beta}{Q}\sum_i \left(\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i}$$

$$P = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\ln V}\right)$$

Small Adiabatic expansion of system
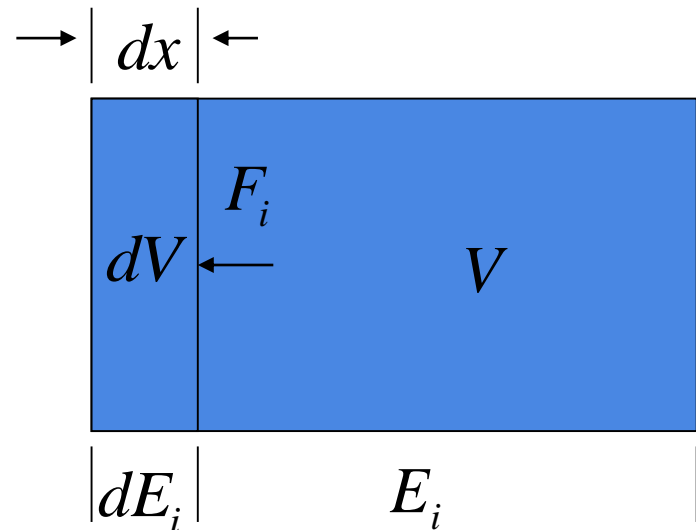
Thermodynamic Properties from Canonical Partition Function

$$U = kT(\frac{\partial \ln Q}{\partial \ln T})_{V,N}$$

$$S = k\left(\ln Q + (\frac{\partial \ln Q}{\partial \ln T})_{V,N} \right)$$

$$H = kT\left((\frac{\partial \ln Q}{\partial \ln T})_{V,N} + (\frac{\partial \ln Q}{\partial \ln V})_{T,N} \right)$$

$$A = -kT \ln Q$$

$$G = -kT\left(\ln Q - (\frac{\partial \ln Q}{\partial \ln V})_{T,N} \right)$$

$$\mu_i = -kT\left(\frac{\partial \ln Q}{\partial N_i} \right)_{T,V,N_{j \neq i}}$$

Grand Canonical Ensemble

- ## **Ensemble approach for open system**
  - ### Useful for open systems and mixtures
  - ### Walls are replaced by permeable walls

Large reservoir (constant T)

All the ensemble members have the same (V, T, μ_i)

Energy and particles can be exchanged

Number of Systems : N
N ➔ ∞
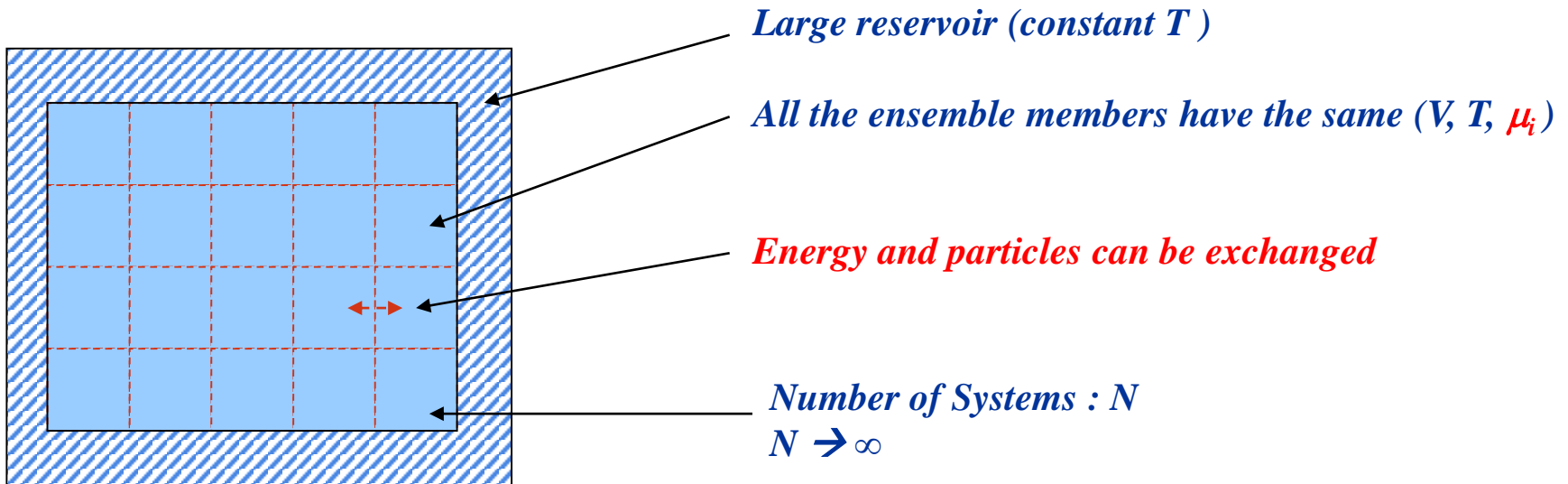
Grand Canonical Ensemble

- **Similar approach as Canonical Ensemble**
  - We cannot use second postulate because *systems are not isolated*
  - After equilibrium is reached, we place walls around ensemble and treat each members the same method used in canonical ensemble

After equilibrium

T,V,μ

T,V,N_1 T,V,N_3 T,V,N_5

T,V,N_2 T,V,N_4
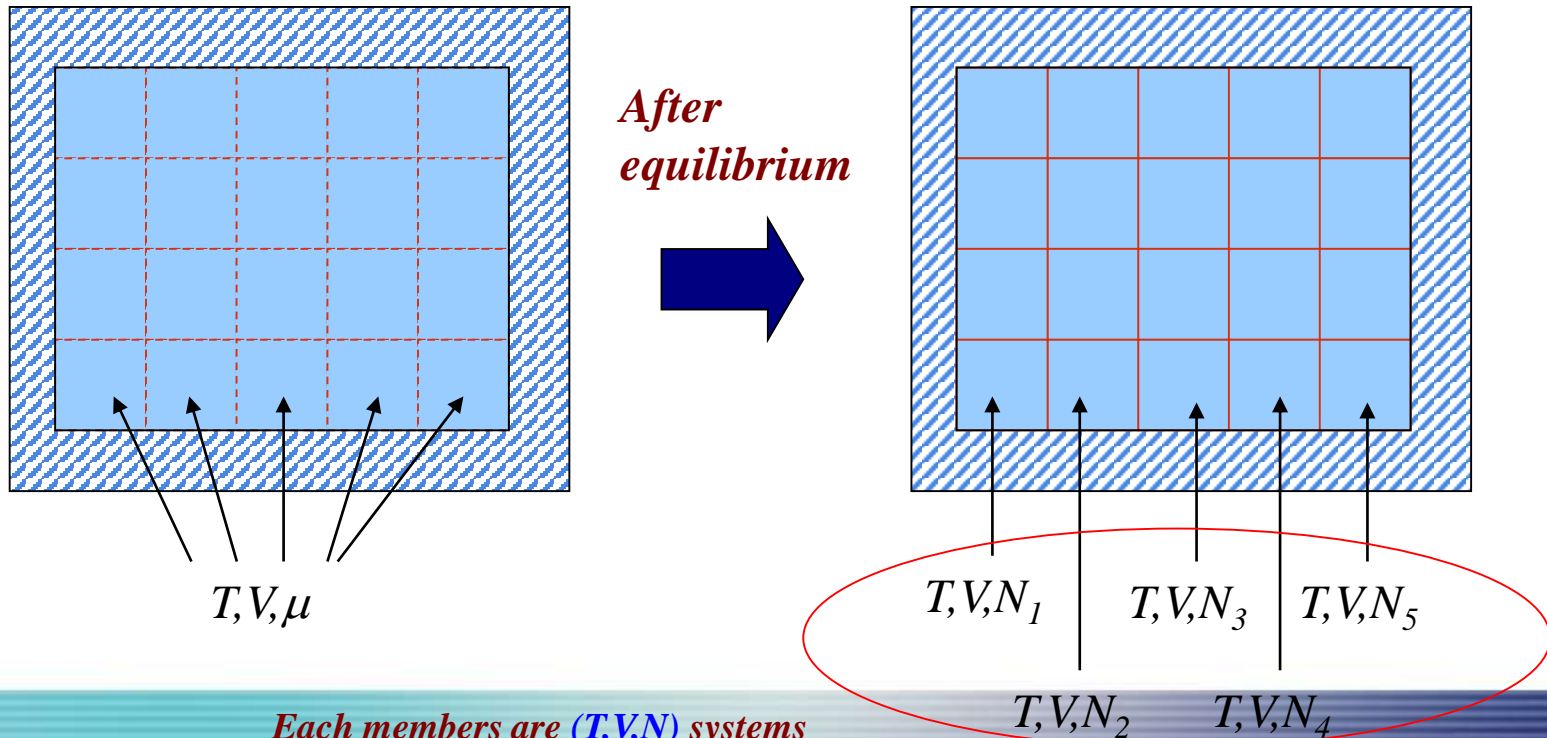
Each members are (T,V,N) systems
→Apply canonical ensemble methods for each member

Grand Canonical Ensemble

- **Weight and Constraint**

Number of ensemble members

Number of molecules after fixed wall has been placed

$$\Omega = \frac{\left[\sum_{j,N} n_j(N)\right]!}{\prod_{j,N} n_j(N)!}$$

$$\mathcal{N} = \sum_{j,N} n_j(N)$$

$$E_t = \sum_{j,N} n_j(N) E_j(V,N)$$

Method of undetermined multiplier with α, β, γ

$$N_t = \sum_{j,N} n_j(N) N$$

$$n_j^*(N) = \mathcal{N} e^{-\alpha} e^{-\beta E_j(N,V)} e^{-\gamma N}$$

$$P_j(N) = \frac{\overline{n_j(N)}}{\mathcal{N}} = \frac{n_j^*(N)}{\mathcal{N}} = \frac{e^{-\beta E_j(N,V)} e^{-\gamma N}}{\sum_{j,N} e^{-\beta E_j(N,V)} e^{-\gamma N}}$$

Grand Canonical Ensemble

- **Determination of Undetermined Multipliers**

$$U = \langle E \rangle = \sum_{j,N} P_j(N) E_j(N,V)$$

$$dU = \sum_{j,N} E_j(N,V) dP_j(N) + \sum_{j,N} P_j(N) dE_j(N,V)$$

$$\Xi = \sum_{j,N} e^{-\beta E_j(N,V)} e^{-\gamma N}$$

$$dU = -\frac{1}{\beta} \sum_{j,N} \left[\gamma N + \ln P_j(N) + \ln \Xi \right] dP_j(N) + \sum_{j,N} P_j(N) \frac{\partial E_j(N,V)}{\partial V} dV$$

$$dU = TdS - pdV - \mu dN$$

Comparing two equation gives,

$$\beta = \frac{1}{kT} \qquad \gamma = -\frac{\mu}{kT}$$

$$\Xi = \sum_{j,N} e^{-E_j(N,V)/kT} e^{N\mu/kT}$$

Grand Canonical Partition Function

4. Classical Statistical Mechanics

- **The formalism of statistical mechanics relies very much at the microscopic states.**
    - **Number of states , sum over states**
    - **convenient for the framework of quantum mechanics**
- **What about "Classical Sates" ?**
    - **Classical states**
        - **We know *position* and *velocity* of all particles in the system**
    - **Comparison between Quantum Mechanics and Classical Mechanics**

| QM Problem | $H\psi = E\psi$ | $\longrightarrow$ | *Finding probability and discrete energy states* |

| CM Problem | $F = ma$ | $\longrightarrow$ | *Finding position and momentum of individual molecules* |

Newton's Law of Motion

- **Three formulations for Newton's second law of motion**
  - **Newtonian formulation**
  - **Lagrangian formulation**
  - **Hamiltonian formulation**

$$H(\mathbf{r}^N, \mathbf{p}^N) = \text{KE(kinetic energy)} + \text{PE(potential energy)}$$

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_i \frac{\mathbf{p}_i}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$

$$\left[\frac{\partial H}{\partial \mathbf{r}_i} \right] = -\dot{\mathbf{p}}_i \qquad \frac{\partial \mathbf{r}_i}{\partial t} = \frac{\mathbf{p}_i}{m_i} \qquad \mathbf{r} = \mathbf{r}(r_x, r_y, r_z)$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{p} = \mathbf{p}(p_x, p_y, p_z)$$

$$\left[\frac{\partial H}{\partial \mathbf{p}_i} \right] = \dot{\mathbf{r}}_i \qquad \frac{\partial \mathbf{p}_i}{\partial t} = \mathbf{F}_i \qquad \mathbf{F}_i = \sum_{\substack{j=1 \\ j \neq i}} \mathbf{F}_{ij}$$

Classical Statistical Mechanics

- **Instead of taking replica of systems, use abstract "phase space" composed of momentum space and position space (total *6N*-space)**

$\mathbf{p}^N$

t_2

Γ_2

t_1

Phase space

Γ_1

$$\Gamma = \left\{ \mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, ..., \mathbf{p}_N, \mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_3, ..., \mathbf{r}_N \right\}$$

$\mathbf{r}^N$
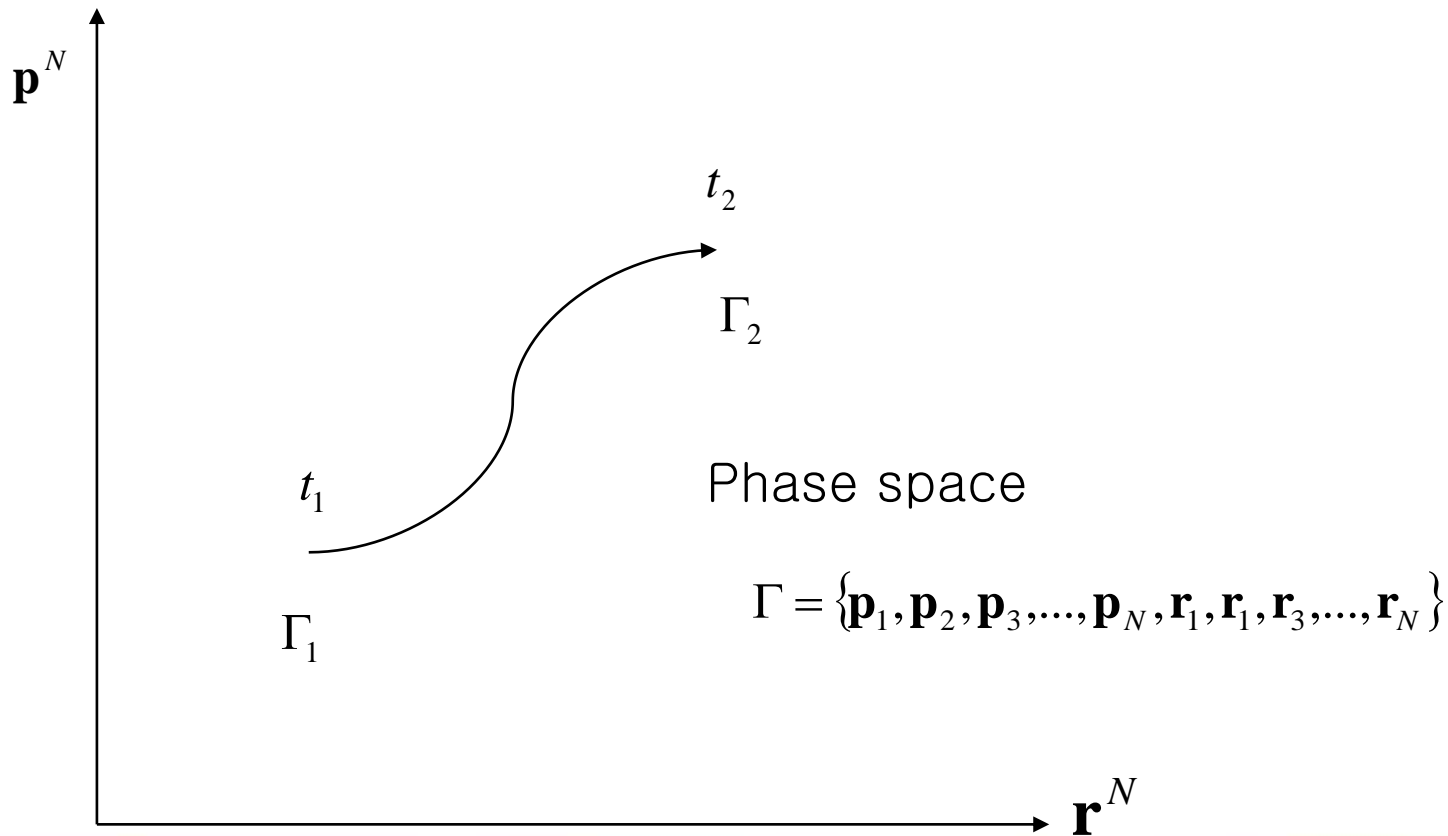
Classical Statistical Mechanics

- " Classical State " : defines a cell in the space (small volume of momentum and positions)

$$\text{"Classical State"} \propto dq_x dq_y dq_z dr_x dr_y dr_z = d^3 p \, d^3 r \text{ for simplicity}$$

- **Ensemble Average**

$$U = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} E(\Gamma) d\tau = \lim_{n \to \infty} \int \mathcal{P}_N(\Gamma) E(\Gamma) d\Gamma$$

$$\mathcal{P}_N(\Gamma) d\Gamma \longrightarrow$$ Fraction of Ensemble members in this range (Γ to $\Gamma + d\Gamma$)

Using similar technique used for Boltzmann distribution

$$\mathcal{P}_N(\Gamma) d\Gamma = \frac{\exp(-H/kT) d\Gamma}{\int ... \int \exp(-H/kT) d\Gamma}$$

Classical Statistical Mechanics

- **Canonical Partition Function**

Phase Integral

$$\mathcal{T} = \int ... \int \exp(-H/kT) d\Gamma$$

Canonical Partition Function

$$Q = c \int ... \int \exp(-H/kT) d\Gamma$$

Match between Quantum and Classical Mechanics

$$c = \lim_{T \to \infty} \frac{\sum_i \exp(-E_i/kT)}{\int ... \int \exp(-H/kT) d\Gamma}$$

$$\longrightarrow \qquad c = \frac{1}{N! h^{NF}}$$

For rigorous derivation see Hill, Chap.6 ("Statistical Thermodynamics")

Classical Statistical Mechanics

- **Canonical Partition Function in Classical Mechanics**

$$Q = \frac{1}{N!h^{NF}} \int ... \int \exp(-\mathbf{H}/kT)d\Gamma$$

Example) Translational Motion for Ideal Gas

$$H(\mathbf{r}^N, \mathbf{p}^N) = \text{KE(kinetic energy)} + \text{PE(potential energy)}$$

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_i \frac{\mathbf{p}_i}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$$

$$H = \sum_i^{3N} \frac{p_i^2}{2m_i}$$

No potential energy, 3 dimensional space.

$$Q = \frac{1}{N! h^{3N}} \int ... \int \exp\left(-\sum_i \frac{p_i^2}{2m_i}\right) dp_1 ... dp_N \, dr_1 ... dr_N$$

$$= \frac{1}{N! h^{3N}} \left[\int_{-\infty}^{\infty} \exp\left(-\frac{p}{2m_i}\right) dp \right]^{3N} \left[\int_0^V dr_1 dr_2 dr_3 \right]^N$$

$$= \frac{1}{N!} \left[\frac{2\pi m k T}{h^2} \right]^{3N/2} V^N$$

We will get ideal gas law
pV= nRT

Semi-Classical Partition Function

- **The energy of a molecule is distributed in different modes**
  - **Vibration, Rotation (Internal : depends only on T)**
  - **Translation (External : depends on T and V)**
- **Assumption 1 : Partition Function (thus energy distribution) can be separated into two parts (internal + center of mass motion)**

$$Q = \sum \exp\left(-\frac{E_i^{CM} + E_i^{\text{int}}}{kT}\right) = \sum \exp\left(-\frac{E_i^{CM}}{kT}\right) \sum \exp\left(-\frac{E_i^{\text{int}}}{kT}\right)$$

$$Q = Q_{CM}(N,V,T) Q_{\text{int}}(N,T)$$

Semi-Classical Partition Function

- **Internal parts are density independent and most of the components have the same value with ideal gases.**

$$Q_{\text{int}}(N, \rho, T) = Q_{\text{int}}(N, 0, T)$$

- **For solids and polymeric molecules, this assumption is not valid any more.**

Semi-Classical Partition Function

- **Assumption 2 : for T>50 K , classical approximation can be used for translational motion**

$$H_{CM} = \sum_i \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m} + U(r_1, r_2, ..., r_{3N})$$

$$Q = \frac{1}{N!h^{3N}} \int ... \int \exp\left(-\sum_i \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2mkT}\right) dp^{3N} \int ... \int (-U/kT) dr^{3N}$$

$$= \frac{\Lambda^{-3N}}{N!} Z$$

Configurational Integral

$$\Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$

$$Z = \int ... \int (-U/kT) dr_1 dr_2 ... dr_{3N}$$

$$Q = \frac{1}{N!} Q_{\text{int}} \Lambda^{-3N} Z$$
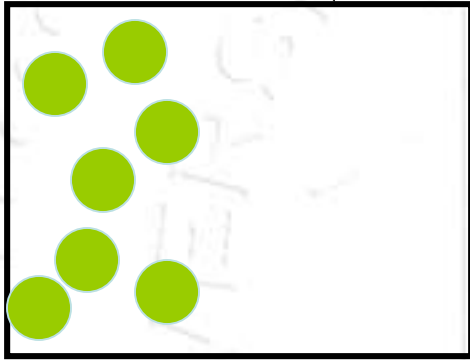
Another, Different Treatment
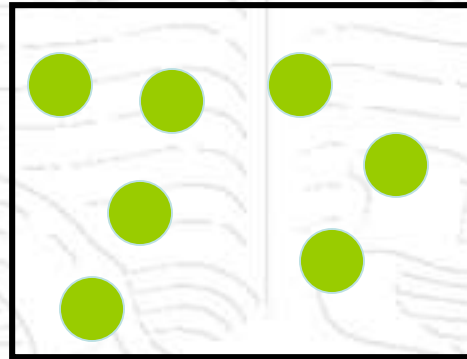
Statistical Thermodynamics: the basics

- Nature is quantum-mechanical

- Consequence:
  - Systems have discrete quantum states.
  - For finite "closed" systems, the number of states is finite (but usually very large)

- Hypothesis: **In a closed system, every state is equally likely to be observed.**

- Consequence: **ALL of equilibrium Statistical Mechanics and Thermodynamics**

Does the basis assumption lead to something that is consistent with classical thermodynamics?

Systems 1 and 2 are weakly coupled such that they can exchange energy.

What will be E_1?

E_1 | $E_2 = E - E_1$
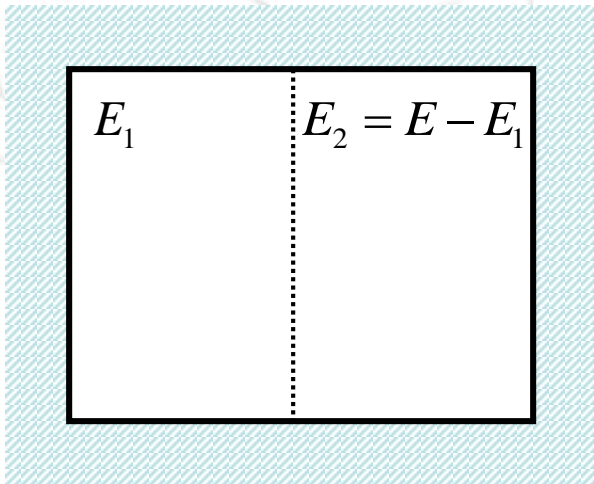
$$\Omega(E_1, E - E_1) = \Omega_1(E_1) \times \Omega_2(E - E_1)$$

BA: each configuration is equally probable; but the number of states that give an energy E_1 is not know.

$$\Omega(E_1, E - E_1) = \Omega_1(E_1) \times \Omega_2(E - E_1)$$

$$\ln\Omega(E_1, E - E_1) = \ln\Omega_1(E_1) + \ln\Omega_2(E - E_1)$$

$$\left(\frac{\partial \ln\Omega(E_1, E - E_1)}{\partial E_1} \right)_{N_1, V_1} = 0$$

$$\left(\frac{\partial \ln\Omega_1(E_1)}{\partial E_1} \right)_{N_1, V_1} + \left(\frac{\partial \ln\Omega_2(E - E_1)}{\partial E_1} \right)_{N_2, V_2} = 0$$

Energy is conserved!
$dE_1 = -dE_2$

$$\left(\frac{\partial \ln\Omega_1(E_1)}{\partial E_1} \right)_{N_1, V_1} = \left(\frac{\partial \ln\Omega_2(E - E_1)}{\partial E_2} \right)_{N_2, V_2}$$

This can be seen as an equilibrium condition

$$\beta \equiv \left(\frac{\partial \ln\Omega(E)}{\partial E} \right)_{N, V}$$

$$\beta_1 = \beta_2$$

Entropy and number of configurations

Conjecture: $$S = \ln \Omega$$

Almost right.

- **Good features:**

    - Extensivity

    - Third law of thermodynamics comes for free
- **Bad feature:**
    - It assumes that entropy is dimensionless but (for unfortunate, historical reasons, it is not…)

We have to live with the past, therefore

$$S = k_B \ln \Omega(E)$$

With $k_B = 1.380662 \ 10^{-23}$ J/K

In thermodynamics, the absolute (Kelvin) temperature scale was defined such that

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$$

$$dE = TdS - pdV + \sum_{i=1}^{n} \mu_i dN_i$$

But we found (defined):

$$\beta \equiv \left(\frac{\partial \ln \Omega(E)}{\partial E}\right)_{N,V}$$

And this gives the "statistical" definition of temperature:

$$\frac{1}{T} \equiv k_B \left(\frac{\partial \ln \Omega(E)}{\partial E} \right)_{N,V}$$

In short:

Entropy and temperature are both related to the fact that we can COUNT states.

Basic assumption:
1. leads to an equilibrium condition: equal temperatures
2. leads to a maximum of entropy
3. leads to the third law of thermodynamics

Number of configurations
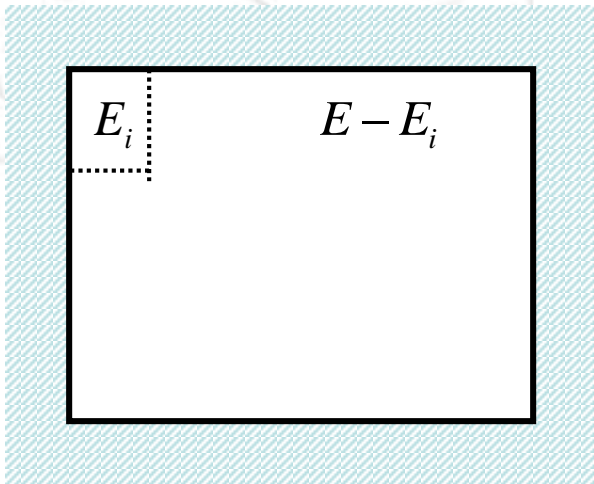
How large is Ω?

- For macroscopic systems, super-astronomically large.

- For instance, for a glass of water at room temperature:

$$\Omega \approx 10^{2 \times 10^{25}}$$

- Macroscopic deviations from the second law of thermodynamics are not forbidden, but they are extremely unlikely.

Canonical ensemble

Consider a small system that can exchange heat with a big reservoir

$1/k_BT$

$$\ln\Omega\left(E - E_i\right) = \ln\Omega\left(E\right) - \frac{\partial\ln\Omega}{\partial E}E_i + \cdots$$

E_i $E - E_i$

$$\ln\frac{\Omega\left(E - E_i\right)}{\Omega\left(E\right)} = -\frac{E_i}{k_BT}$$

Hence, the probability to find E_i:

$$P\left(E_i\right) = \frac{\Omega\left(E - E_i\right)}{\sum_j\Omega\left(E - E_j\right)} = \frac{\exp\left(-E_i/k_BT\right)}{\sum_j\exp\left(-E_j/k_BT\right)}$$

$$P\left(E_i\right) \propto \exp\left(-E_i/k_BT\right)$$

Boltzmann distribution

Example: ideal gas

$$Q(N,V,T \ldots$$

Free energy:

$$\beta F$$

Pressure:

$$P = -\left(\frac{\partial \ldots}{\partial V}\right)_T \quad \rho V$$

Thermo recall (3)

Helmholtz Free energy:

$$dF = -SdT - pdV$$

Pressure

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

Energy:

$$\left(\frac{\partial F/T}{\partial 1/T}\right) = \left(\frac{\partial \beta F}{\partial \beta}\right) = E$$
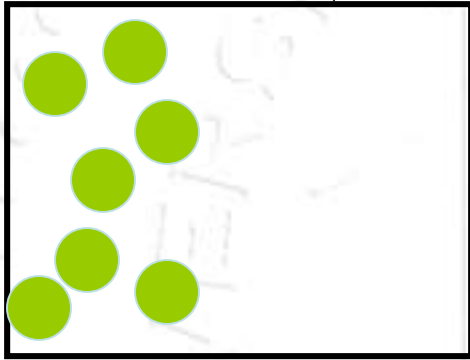
$$E = \left(\frac{\ }{\partial \beta}\right) = \frac{\ }{\Lambda}\frac{\partial}{\partial \beta} = \frac{3}{2}Nk_B T$$
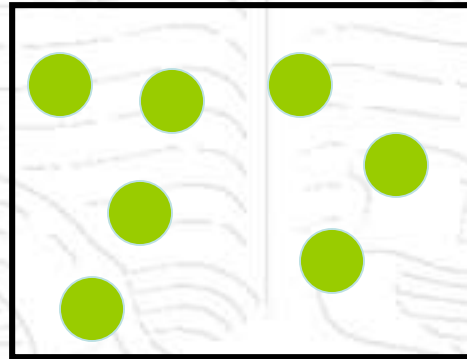
Ensembles

- Micro-canonical ensemble: E, V, N

- Canonical ensemble: T, V, N

- Constant pressure ensemble: T, P, N

- Grand-canonical ensemble: T, V, μ

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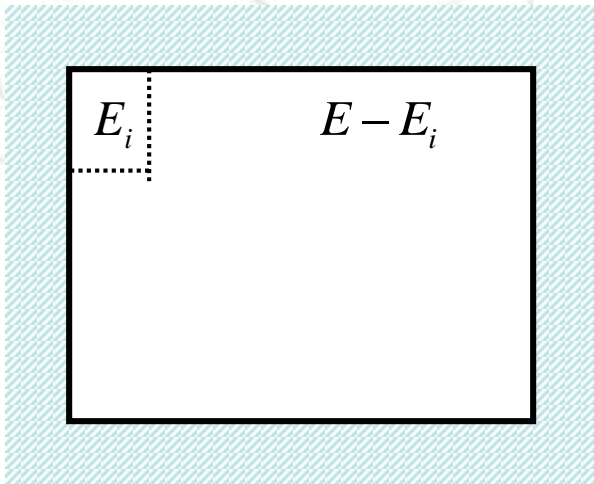
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