THERMAL & STATISTICAL PHYSICS
SSP3133

STATISTICAL MECHANICS
(BASIC METHODS)

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Ensemble (also **statistical ensemble** or **thermodynamic ensemble**)
-introduced by Gibbs in 1878

-an **ensemble** is *an idealization consisting of a large number of mental copies (possibly infinitely many) of a system, considered all at once, each of which represents a possible state that the real system might be in.*

ENSEMBLE : Synonyms
1. totality, entirety, aggregate

ahn-**sahm**-b*uh*

There are three types of canonical ensemble:

- MICROCANONICAL
- CANONICAL
- GRAND CANONICAL

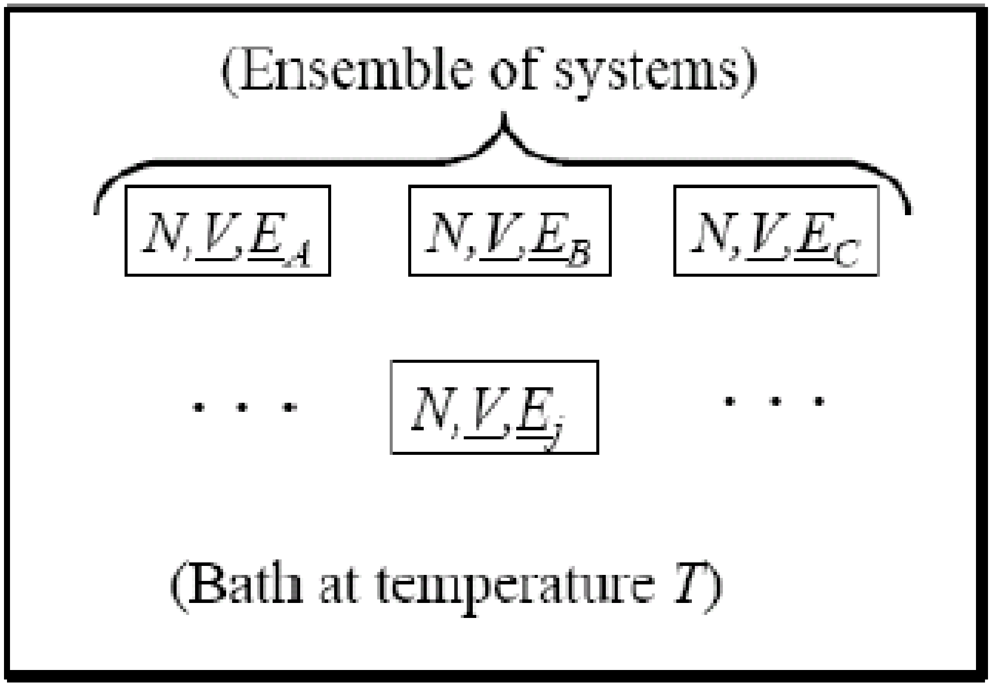
1. **Microcanonical ensemble**: the ensemble is isolated

-the energy of the system, U is constant.

-the total energy of the system does not fluctuate.

-the system can access only those of its micro-states that correspond to a given value E of the energy.

-The internal energy U of the system is then strictly equal to its energy, E.



1. In microcanonical ensemble, each system has constant N,V and E.

2. **Canonical ensemble**: the system is in thermal equilibrium with a heat reservoir at temperature *T*

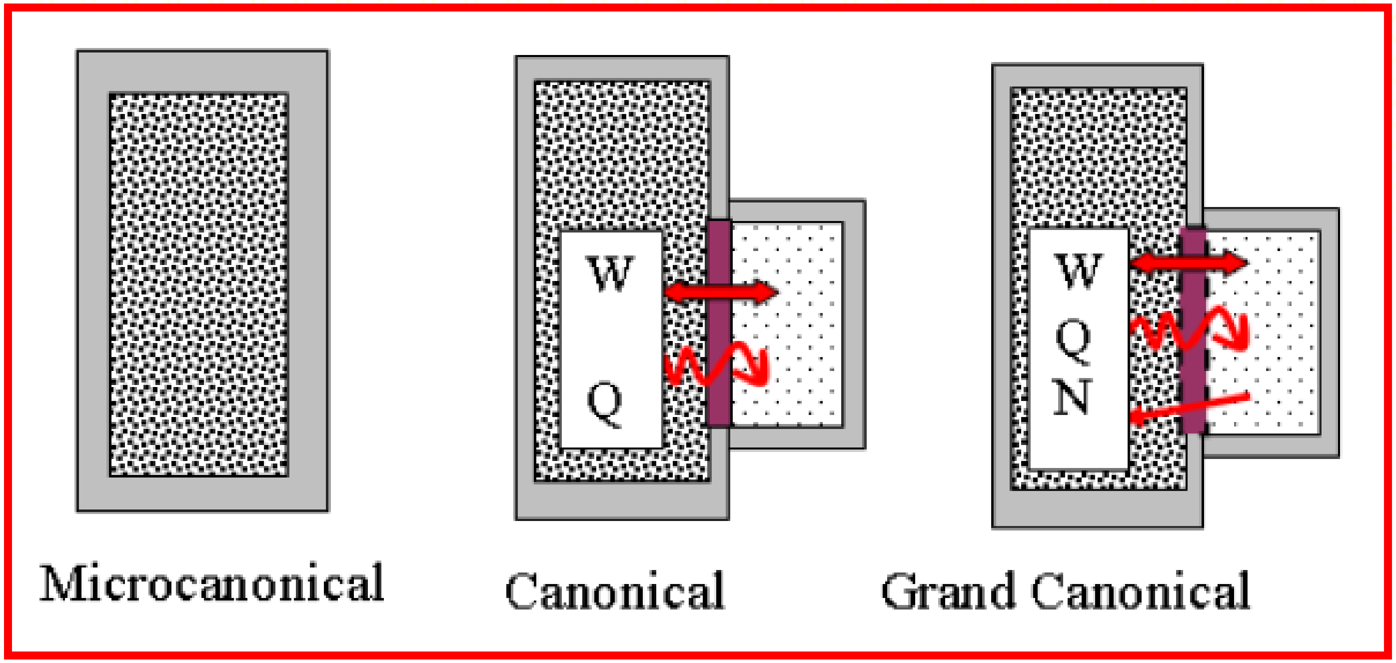
-the energy of the system, U is not a constant; the temperature is constant.

3. **Grand canonical ensemble**: the system is in contact with both a heat reservoir and a particle reservoir

-the U and N of the system are not constant

-the T and the μ are constant.

(The μ is the energy required to add a particle to the system.)



U constant;
N, V, E constant;
Isolated

U constant;
T not constant;
Heat reservoir

T , μ constant;
U, N not canstant;
Heat and particle reservoir

Probability of being in a certain state

Note: 1. probability, $p \propto \Omega$

2. $S = k \ln \Omega$

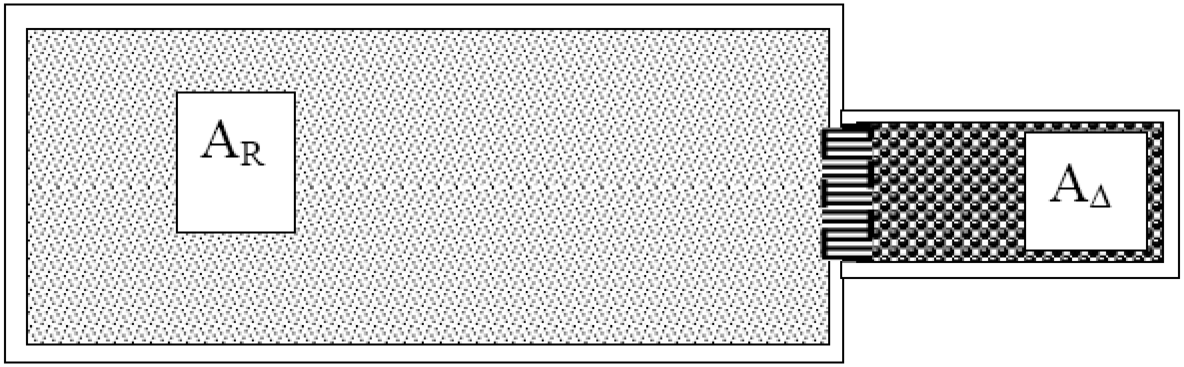
3. $\Delta S = \frac{1}{T}(\Delta U + P\Delta V - \mu \Delta N)$

Consider a system $A_0 = A_R + A_\Delta$

A_R: reservoir

A_Δ: microscopic system

A_0: isolated from the rest of the universe



The number of the accessible states,

$$\Omega_0 = \Omega_R \, \Omega_\Delta$$

Let, r: one state of the A_Δ , therefore $\Omega_\Delta = 1$

The probability the system A_0 in that particular state,

$$P_r = \Omega_0 = \Omega_R \Omega_\Delta = \Omega_R = e^{\ln \Omega_R} = e^{S_R / k}$$

To be in the state r, the A_Δ takes ΔU, ΔV & ΔN from the A_R ----- reduce A_R entropy (1st Law)

$$\Delta S_R = -\frac{1}{T}(\Delta U + P\Delta V - \mu \Delta N)$$

Reservoir entropy

$$S_R = S_R^O - \frac{1}{T}(\Delta U + P\Delta V - \mu \Delta N)$$

S_R^O : initial reservoir's entropy

The probability eq,

$$P_r \propto \exp \frac{1}{k}\left[S_R^O - \frac{1}{T}(\Delta U + P\Delta V - \mu\Delta N)\right]$$

Or

$$P_r = C \exp -\frac{1}{kT}(\Delta U + P\Delta V - \mu\Delta N) \quad \ldots.(*)$$

C: constant

Consider TWO cases:

1. a group of particles that can occupy any of several different quantum states
   --- (classical statistics)

2. certain quantum state that could be occupied by various number of particles (quantum statistics)

Case 1:

1. a group of particles that can occupy any of several different quantum states
--- (classical statistics)

N: fixed $\Delta N = 0$
$P\Delta V << \Delta U$, --- ignored $P\Delta V$

Eq (*):

$$P_r = C \exp -\frac{1}{kT}(\Delta U + P\Delta V - \mu \Delta N) \quad \ldots(*)$$

C: constant

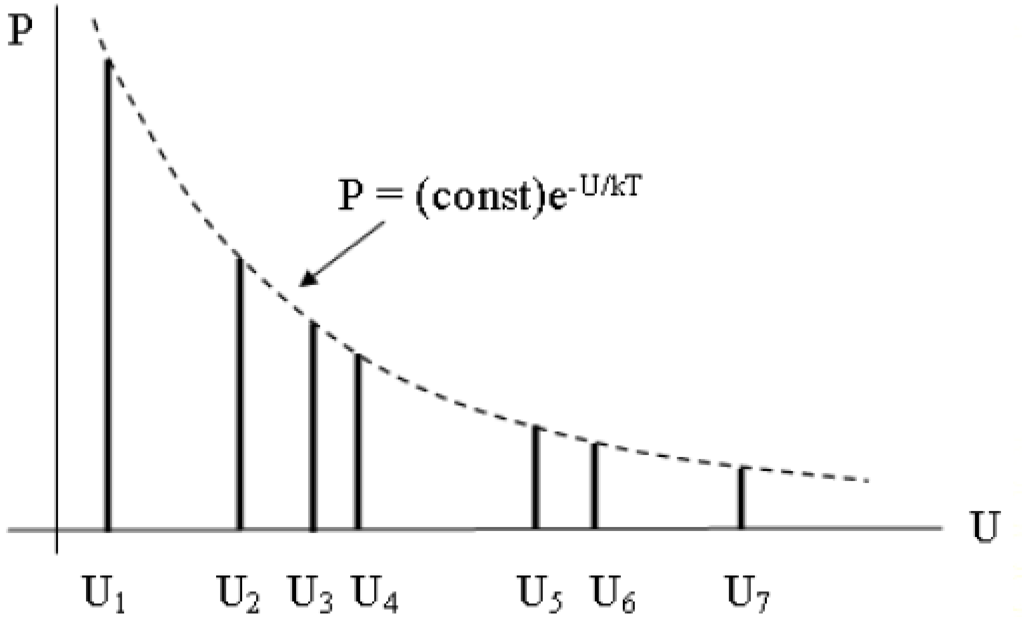
$$P_r = C \exp -\frac{1}{kT}(\Delta U)$$

But $\sum_r P_r = 1$ Therefore $C = \left(\sum_r e^{-\frac{U}{kT}}\right)^{-1}$

OPENCOURSEWARE

The probability of the microscopic system being in state r of energy U_r

$$P_r = C \exp - \frac{1}{kT}(U_r)$$



-the lower the energy of a state, the higher the probability that the system is in it.

Case 2:

2. certain quantum state that could be occupied by various number of particles (quantum statistics)

$$P_r = C \exp -\frac{1}{kT}(\Delta U + P\Delta V - \mu \Delta N) \quad \ldots.(*)$$

C: constant

-consider A_Δ as a single quantum state

Volume: fixed ($\Delta V=0$)

The probability the system is in configuration r,

$$P_r = C \exp -\frac{1}{kT}(\Delta U - \mu \Delta N)$$

$$P_r = Ce^{-\frac{1}{kT}(\Delta U - \mu \Delta N)}$$

Let n; number of particles in state r
ε_r; energy per particle in state r

$$P_r = Ce^{-\frac{1}{kT}n(\varepsilon_r - \mu)}$$

Since $\sum_r P_r = 1$

$$C = \left(\sum_r e^{-\frac{n}{kT}(\varepsilon_r - \mu)} \right)^{-1}$$

The ratio Let $P_i = C\,e^{-U_i/kT}$

And $P_j = C\,e^{-U_j/kT}$

P_i: the probability in state i

P_j: the probability in state j

$$\frac{P_i}{P_j} = \frac{Ce^{-\frac{U_i}{kT}}}{Ce^{-\frac{U_j}{kT}}} = e^{-(U_i - U_j)/kT}$$

U_0: ground state

U_1: excited state

& P_0: probability in the ground state

P_1: probability in the excited state

The ratio

$$\frac{P_1}{P_0} = \frac{Ce^{-\frac{U_1}{kT}}}{Ce^{-\frac{U_0}{kT}}} = e^{-(U_1 - U_0)/kT}$$

If $(U_1 - U_0) >> kT$

Then

$$\frac{P_1}{P_0} \approx 0$$

all the particles are in the ground state

-low probability of excitation

If $(U_1 - U_0) << kT$

$$\frac{P_1}{P_0} \rangle 0$$

-high probability of excitation

Defined excitation temperature, T_e as

$$T_e = \frac{1}{k}\left(U_1 - U_0\right)$$

for $T \ll T_e$ means $(U_1 - U_0) \gg kT$

Degeneracy

-when several quantum states all have the same energy—that energy level is *degenerate*

If n_r states all have energy U_r --- 'U_r is n_r-time degenerate'

P_{U_r}: The probability the system has energy U_r
P_r: the probability the system in state r

$$P_{U_r} = n_r P_r$$

Energy Band

The formula

$$\frac{P_1}{P_0} = \frac{Ce^{-\frac{U_1}{kT}}}{Ce^{-\frac{U_0}{kT}}} = e^{-(U_1 - U_0)/kT}$$

For a system to be in any single quantum state of energy U_1 to another quantum state of energy U_0

-normally a system can has many excited states and many ground states

-solution

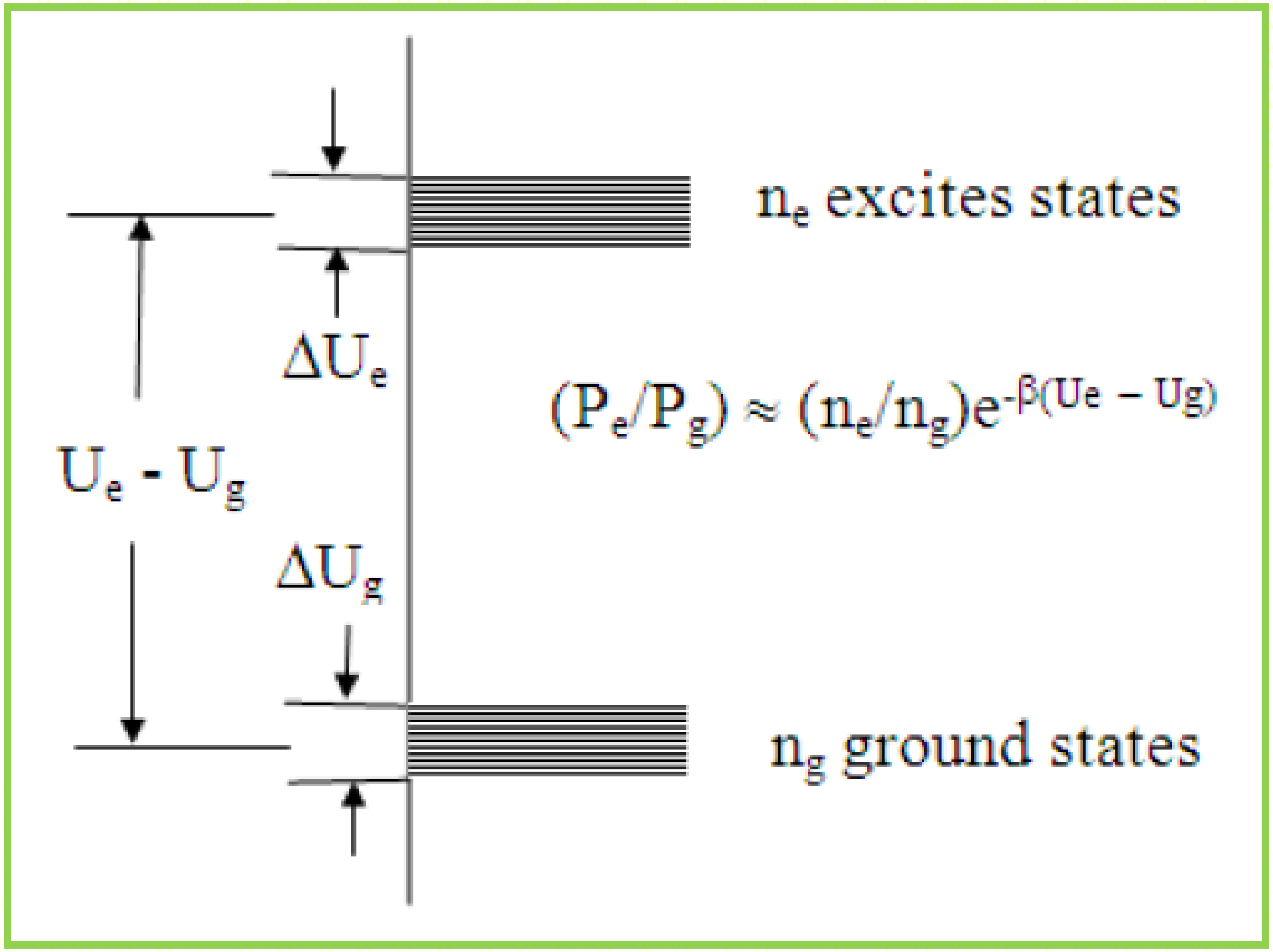
$$\frac{P_{\text{any excited st}}}{P_{\text{any ground st}}} = \frac{\sum_{e} Ce^{-\frac{Ue}{kT}}}{\sum_{g} Ce^{-\frac{U_g}{kT}}} = \frac{\sum_{e} e^{-\beta U_e}}{\sum_{g} e^{-\beta U_g}}$$

Assume U_g & U_e constant

$$\frac{P_{\text{any excited st}}}{P_{\text{any ground st}}} = \frac{(\sum_{e} 1)\, e^{-\frac{U_e}{kT}}}{(\sum_{g} 1)\, e^{-\frac{U_g}{kT}}} = \frac{n_e\, e^{-\beta U_e}}{n_g\, e^{-\beta U_g}}$$

n_e: number of excited states

n_g: number of ground states


n_e excites states
ΔU_e
$(P_e/P_g) \approx (n_e/n_g)e^{-\beta(U_e - U_g)}$
U_e - U_g
ΔU_g
n_g ground states

The Equipartition Theorem

-to determine the mean value of energy stored in any degree of freedom

-applies only to systems whose energy in the form

$$U = b\,q^2$$

q: coordinate or momentum variables (x, p_x, L_x,…)

The probability for a microscopic component is in a certain state s, with energy E_s, is

$$P_s = Ce^{-\beta Es}$$

Where

$$C = (\Sigma e^{-\beta Es})^{-1}$$

$$P_s = (\Sigma e^{-\beta Es})^{-1} e^{-\beta Es}$$

Let's take a particle (can be electron)

Energy in a degree of freedom $E = bq^2$

-deg of freedom: x-portion of KE $= 1/(2m)\, p_x^2$

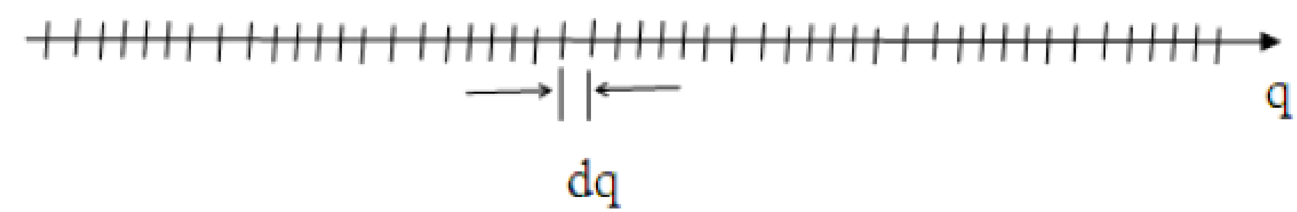
-deg of freedom: y-portion of PE $= ½\, ky^2$

The probability for a microscopic component is in a certain state s, with energy E_s, is

$$P_s = (\Sigma e^{-\beta E s})^{-1} e^{-\beta E s}$$

The mean value of the energy

$$\overline{E} = \sum_{s} P_S E_S = \left(\sum_{s} e^{-\beta E_s} \right)^{-1} \sum_{s} e^{-\beta E_s} E_S$$



Note: number of quantum states in interval dq $\propto$ dq

Number of states $= C\,dq$,

C: constant

Large number $\Sigma \rightarrow \int$

$$\overline{E} = \left[\int_{-\infty}^{\infty} dq e^{-\beta b q^2}\right]^{-1} \int_{-\infty}^{\infty} dq\, e^{-\beta b q^2}\left(bq^2\right)$$

Integrating (replace $(bq^2)\,dq = (1/2)\,d\,(bq^2)$)

$$\int_{-\infty}^{\infty} dq\, e^{-\beta b q^2}\left(bq^2\right) = 0 + \frac{1}{2\beta}\int_{-\infty}^{\infty} dq\, e^{-\beta b q^2}$$

$$\bar{E} = \left[\int_{-\infty}^{\infty} dq e^{-\beta b q^2} \right]^{-1} \frac{1}{2\beta} \int_{-\infty}^{\infty} dq e^{-\beta b q^2}$$

$$\bar{E} = \frac{1}{2\beta} = \frac{1}{2} kT$$

If there are υ degrees of freedom, then the mean internal energy per molecule will be given by

$$U = (\upsilon\ k\ T)/2$$

Where T is the absolute temperature, k is Boltzmann's constant

Or

The mean internal energy associated with each degree of freedom of a monoatomic ideal gas is the same.

The components of velocity can be either linear or angular.

A LITTLE CAPTION OF
TANGKUBAN PARAHU, INDONESIA (2009)

REFERENCES:

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