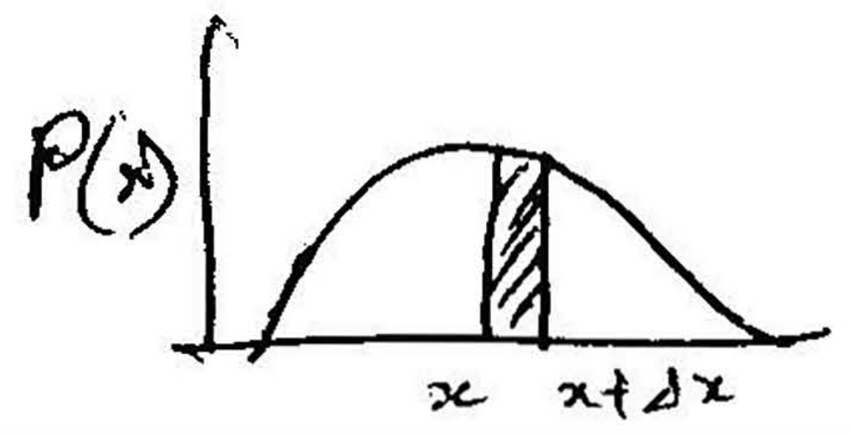
7

Review of last class:

- Defined probability.
- $P(A,B) = P(A\cap B) = P(A \text{ and } B) = P(A)\cdot P(B|A) = P(B)P(A|B)$; if independent $P(A|B) = P(A)$ or $P(B|A) =$

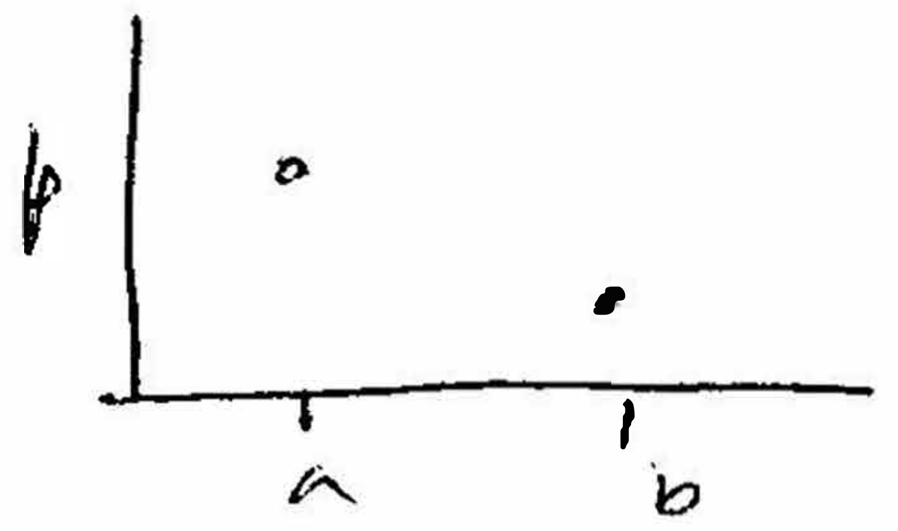
$= P(A)P(B)$

- $P(A \text{ or } B) = P(A\cup B) = P(A)+P(B) - P(A \text{ and } B)$ for mutually exclusive, $P(A\cup B) = P(A)+P(B)$
- Discrete and continuous pdf.

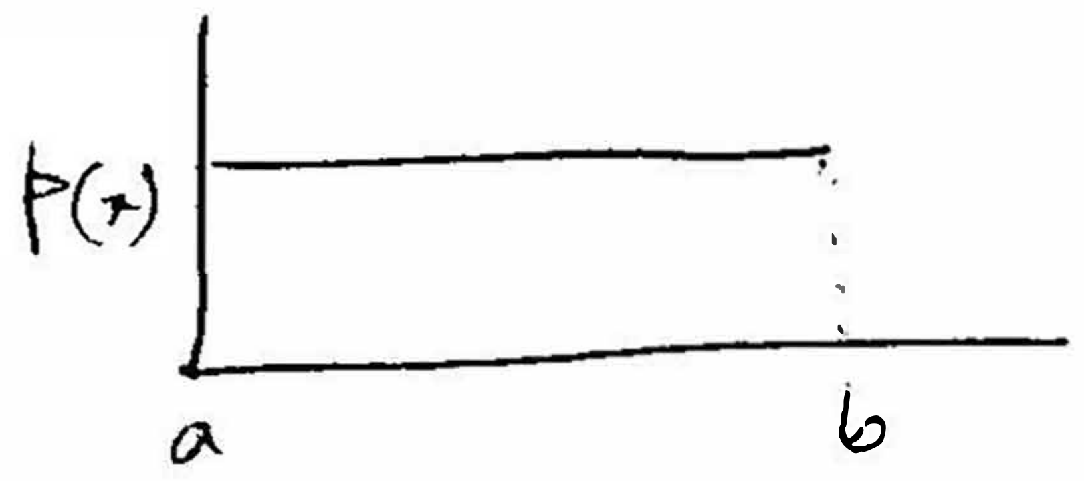


$P(x) = p(x)\cdot\Delta x$

⊙ Bernoulli distribution: for events with only two outcomes.



⊙ Uniform distribution:



$P(x) = \frac{1}{b-a}$

- Statistical quantities: average, ~~sta~~ variance, standard deviation, CV, fano factor etc.

average: $\langle x\rangle = \bar{x} = \sum_i x_i P(x_i)$, $\int x\, p(x)\, dx$

nth moment. $\langle x^n\rangle = \sum_i x_i^n P(x_i) = \int x^n p(x)\, dx$

Variance: $\langle(x_i - \langle x_i\rangle)^2\rangle = \langle x_i^2 - 2x_i\langle x_i\rangle + \langle x_i\rangle^2\rangle$

$= \langle x_i^2\rangle - 2\langle x_i\rangle^2 + \langle x_i\rangle^2$

$= \langle x_i^2\rangle - \langle x_i\rangle^2$

$=$ Second moment $-$ square of first moment

Standard deviation: $(\sigma) = \sigma_x = \sqrt{Var(x)} = \sqrt{\langle x_i^2\rangle - \langle x_i\rangle^2}$

$CV = \frac{\sigma_x}{\langle x\rangle}$, Fano factor: $= \frac{Var(x)}{\langle x\rangle}$

* Uniform distribution:

$$P(x) = \frac{1}{b-a} \qquad x \in \{a, b\}$$

$$= 0 \qquad x \notin \{a, b\}$$

$$\bar{x} = \int_a^b x\, P(x)\, dx = \int_a^b x \frac{1}{(b-a)} dx =$$

- Binomial distribution:

$$(p+q)^N = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} p^n . q^{(N-n)}$$

- Tossing of coins N no of times,
- Random walk of a brownian particle in 1D.

- What is the probability that out of N tossing n will be the heads?
- What is the probability that after N steps the drunk perso will be at net displacement, $x (= ml)$. Where m effective no. of steps in any direction, l length of steps.
  - Assumption: individual steps are uncorrelated or independent and step sizes are same.

<u>Calculation</u>:

- probability of head = p, prob. of tail = q in one toss.
- probability that n heads would come in a row, $= p^n$ (* independent even times multiplicatio
- Probability that (N-n) tail would come or (N-n) no. of times head would not come $= q^{(N-n)}$

- Now n heads ~~no (N-n~~ may appear in any order. how man diff. ways it may appear:

$$= \frac{N!}{n!(N-n)!}$$

· Thus the total probability

$$P(N,n) = \frac{N!}{n!(N-n)!} \cdot p^{n} q^{N-n}$$

for random walk in 1D.

n_2 = steps to the left $N = n_1 + n_2$

n_1 = steps to the right, $m = n_1 - n_2$; $-N \leq m \leq +N$

$$P(N,m) = \frac{N!}{n_1!\, n_2!} \cdot p^{n_1} \cdot q^{n_2}$$

$$= \frac{N!}{n_1!\,(N-n_1)!} \cdot p^{n_1} \cdot q^{(N-n_1)}$$

Average no. of steps to the right or av. no. of heads:

$$\bar{n}_1 = \langle n_1 \rangle = \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!} \cdot n_1 \cdot p^{n_1} \cdot q^{N-n_1}$$

$$= p \cdot \frac{\partial}{\partial p} \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!} \cdot p^{n_1} q^{N-n_1}$$

$n_1 p^{n_1}$
$= p\, \frac{\partial}{\partial p}(p^{n_1})$

$$= p \cdot \frac{\partial}{\partial p} (p+q)^{N}$$

$$= Np \cdot (p+q)^{N-1} \qquad p+q=1$$

$\boxed{\langle n_1 \rangle = Np}$ Similarly for $\langle n_2 \rangle$ = av. no. of steps to the left $= N \cdot q$.

· Now dispersion or variance?

$$\sigma_{m_1} = ? = \langle n_1^2 \rangle - \langle n_1 \rangle^2$$

$$\langle n_1^2 \rangle = \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!}\, n_1^2 p^{n_1} q^{N-n_1}$$

$$= \left(p \frac{\partial}{\partial p}\right)^2 \cdot \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!} \cdot p^{n_1} q^{N-n_1}$$

$n_1^2 p^{n_1}$

$= p \frac{\partial}{\partial p}(n_1 p^{n_1})$

$= \left(p \frac{\partial}{\partial p}\right)^2 \left[p^{n_1}\right]$

$$= \left(p\frac{\partial}{\partial p}\right)^2 \cdot (p+q)^N$$

$$= p\,\frac{\partial}{\partial p} \cdot \left[p\, N(p+q)^{N-1}\right]$$

$$= p \cdot \left[N(p+q)^{N-1} + pN(N-1)(p+q)^{N-2}\right]$$

$$= \cancel{p}\left[Np + p^2N(N-1)\right]$$

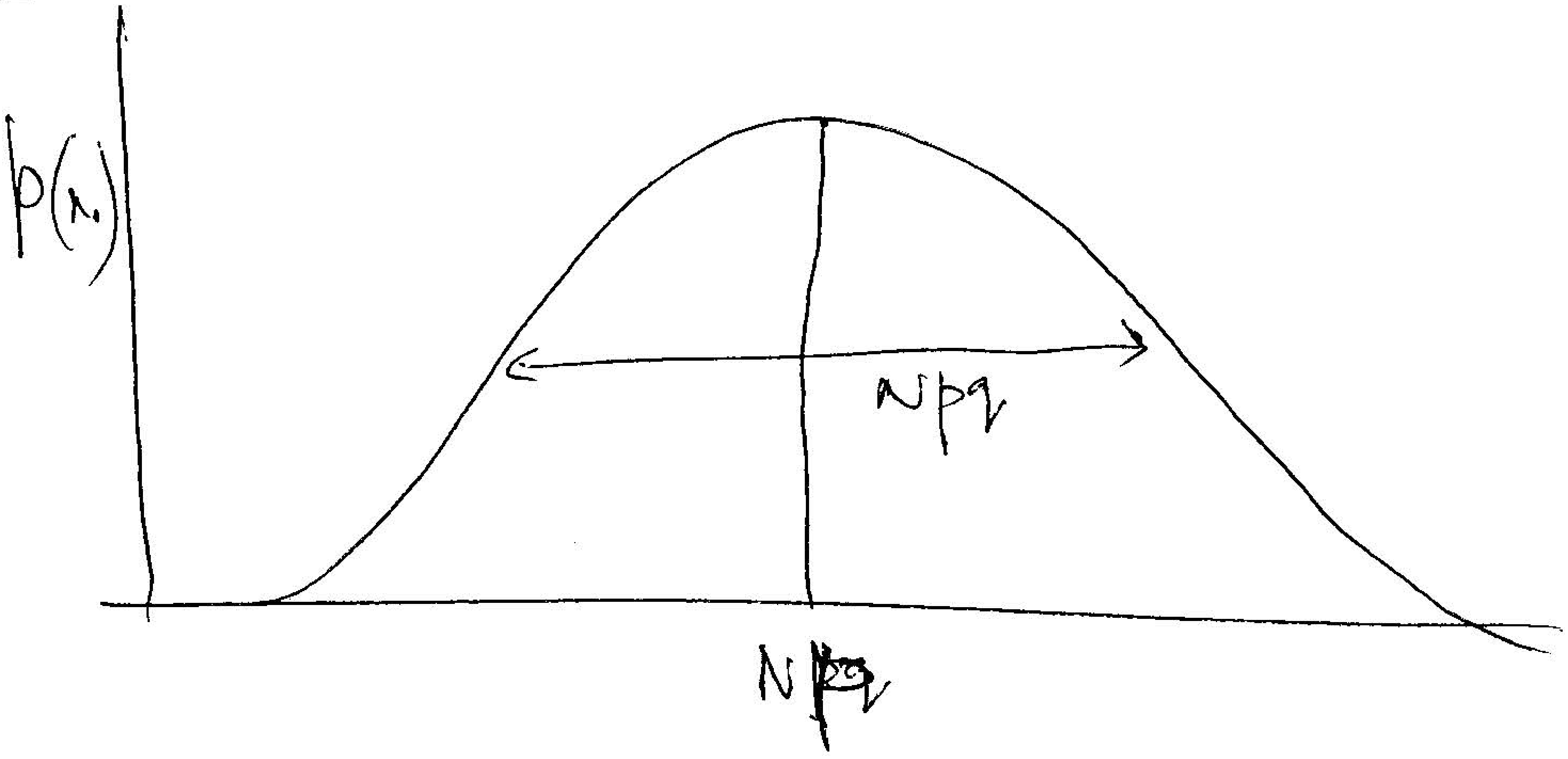
$$= \left[Np - Np^2 + N^2p^2\right]$$

$$= Np(1-p) + N^2p^2$$

$$= Npq + (Np)^2$$

$$= Npq + \langle n_1\rangle^2$$

$\boxed{\sigma_{n_1} = \langle n_1^2\rangle - \langle n_1\rangle^2 = Npq}$ Similarly, $\boxed{\sigma_{n_2} = Npq}$



B) Average m and dispersion in m

$\bar{m} = ?$ $\overline{\Delta m^2} = ?$ $m = n_1 - n_2 = n_1 - N + n_1 = 2n_1 - N$

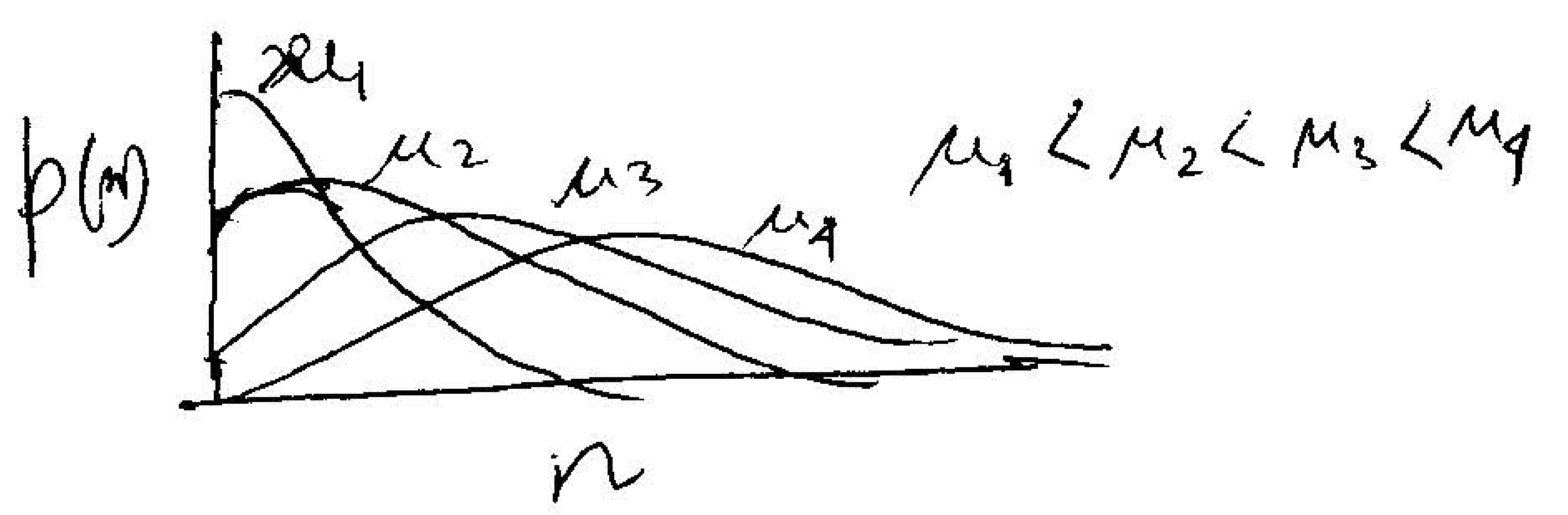
$\bar{m} = 2\bar{n}_1 - N = 2Np - N = (2p-1)N = [2p - p - q]N = (p-q)N$

$\Delta m = (2n_1 - N) - (2\bar{n}_1 - N) = 2(n_1 - \bar{n}_1) = \cancel{2(n_1 - N)}\ 2\Delta n_1$

$(\Delta m)^2 = 4\Delta n_1^2$; $\overline{\Delta m^2} = 4\cdot\overline{\Delta n_1} = 4Npq$

Poission Distribution

$$P(n) = \frac{\mu^n}{n!} e^{-\mu}$$



When $N \to \infty$ and $p \to 0$ rare events typically follows Poission distributi

Binomial distribution.

$$P(n) = \frac{N!}{n!\,(N-n)!} \cdot p^n q^{N-n}$$

$$= \frac{N(N-1)(N-2)\cdots(N-n+1)(N-n)!}{n!\,(N-n)!} \cdot p^n \cdot q^{N-n}$$

$$= \cancel{(N-n)}\ \frac{N(N-1)(N-2)\cdots(N-n+1)}{n!} \cdot p^n \cdot q^{N-n}$$

$$\lim_{N\to\infty} (P(n)) = \frac{N^n}{n!} \cdot p^n \cdot q^N$$

$$= \frac{N^n}{n!} \cdot \frac{\mu^n}{N^n} \cdot (1-p)^N$$

$$p(n) = \frac{\mu^n}{n!} \cdot (1-p)^{\mu/p}$$

$\langle n \rangle = Np = \mu$

$\therefore p = \frac{\mu}{N}$

$N = \frac{\mu}{p}$

$$\lim_{p\to 0} [P(n)] = \frac{\mu^n}{n!} \cdot \lim_{p\to 0} (1-p)^{\mu/p}$$

$\lim_{y\to\infty} \left(1+\frac{x}{y}\right)^y = e^x$

$$\boxed{P(n) = \frac{\mu^n}{n!} \cdot e^{-\mu}}$$

$$\langle n \rangle = \sum_{n=0}^{\infty} n \cdot \frac{\mu^n}{n!} e^{-\mu}$$

$$= \mu \frac{d}{d\mu} \left[\sum_{n=0}^{\infty} \frac{\mu^n}{n!}\right] \cdot e^{-\mu}$$

$$= \mu \cdot e^{\mu} \cdot e^{-\mu}$$

$$= \mu$$

$$\langle n^2 \rangle = \sum_{n=0}^{\infty} n^2 \cdot \frac{\mu^n}{n!} e^{-\mu}$$

$$= \sum_{n=0}^{\infty} n \cdot \mu \frac{d}{d\mu} \cdot (\mu^n) \cdot \frac{1}{n!} \cdot e^{-\mu}$$

$$= \sum_{n=0}^{\infty} \mu \frac{d}{d\mu} (n \mu^n) \cdot \frac{1}{n!} e^{-\mu}$$

$$= \left(\mu \frac{d}{d\mu}\right)^2 \sum_{n=0}^{\infty} \frac{\mu^n}{n!} \cdot e^{-\mu}$$

$$= \mu \frac{d}{d\mu} \left[\mu \cdot e^{\mu}\right] \cdot e^{-\mu}$$

$$\langle n^2\rangle = \mu\left[e^{\mu}+\mu e^{\mu}\right]e^{-\mu}$$

$$= \mu + \mu^2$$

$$= \mu + \langle n\rangle^2$$

$$\overline{\Delta n^2} = \sigma_n^2 = \mathrm{Var}(n) = \mu$$

For large N

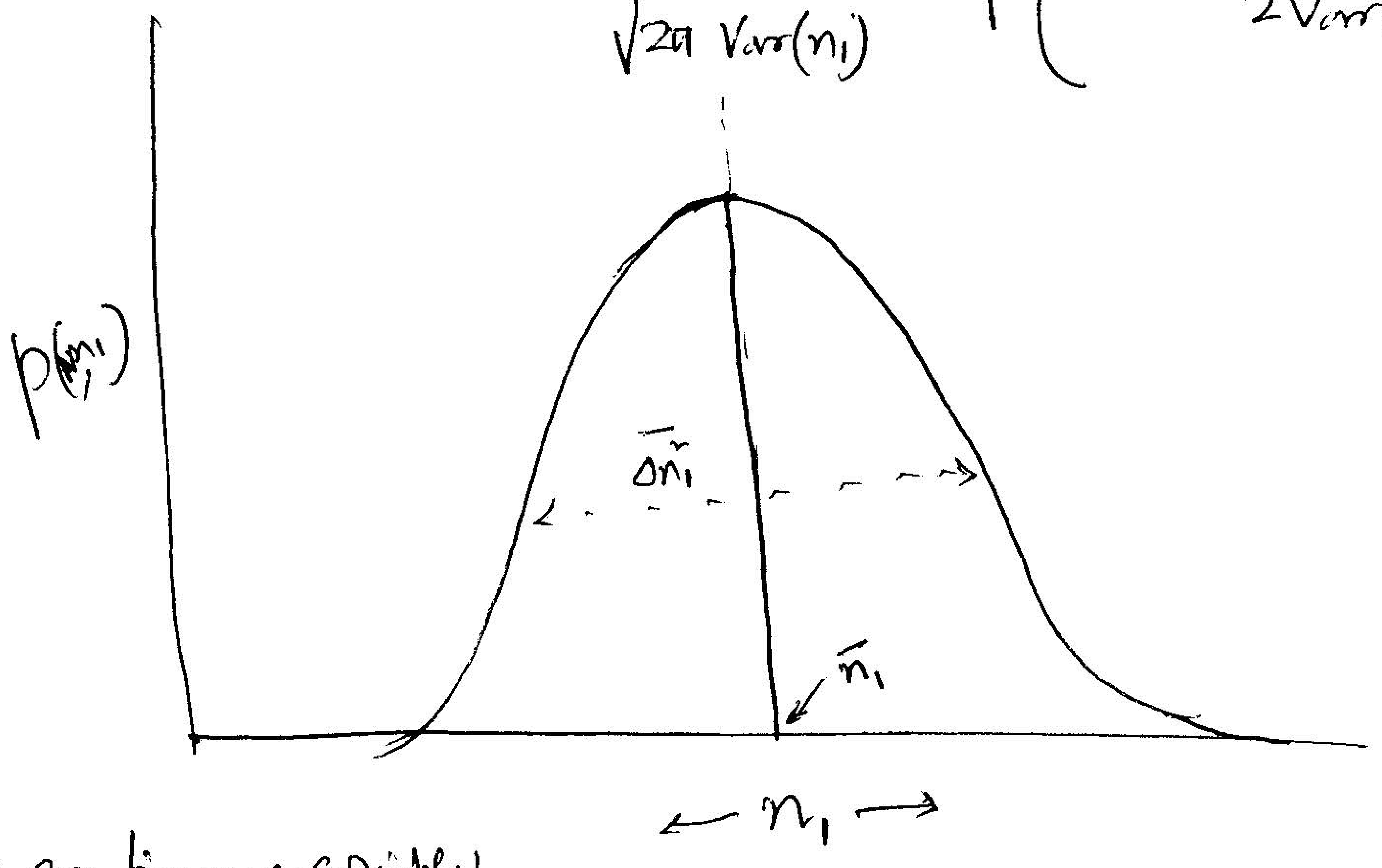
$$P(N, n_1) = \frac{1}{\sqrt{2\pi Npq}}\exp\left(-\frac{(n_1 - Np)^2}{2Npq}\right)$$

Since, $\bar{n}_1 = Np$, $\overline{\Delta n_1^2} = Npq$

$$P(N, n_1) = \frac{1}{\sqrt{2\pi \overline{\Delta n_1^2}}}\cdot\exp\left(-\frac{(n_1 - \bar{n}_1)^2}{2\overline{\Delta n_1^2}}\right)$$

Gen form

$$= \frac{1}{\sqrt{2\pi\, \mathrm{Var}(n_1)}}\cdot\exp\left(-\frac{(n_1 - \mathrm{Av}(n_1))^2}{2\,\mathrm{Var}(n_1)}\right)$$



for a continuous variable!

$$P(x) = \rho(x)\,dx$$

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\cdot\exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

μ = Average
σ = Std. deviation.

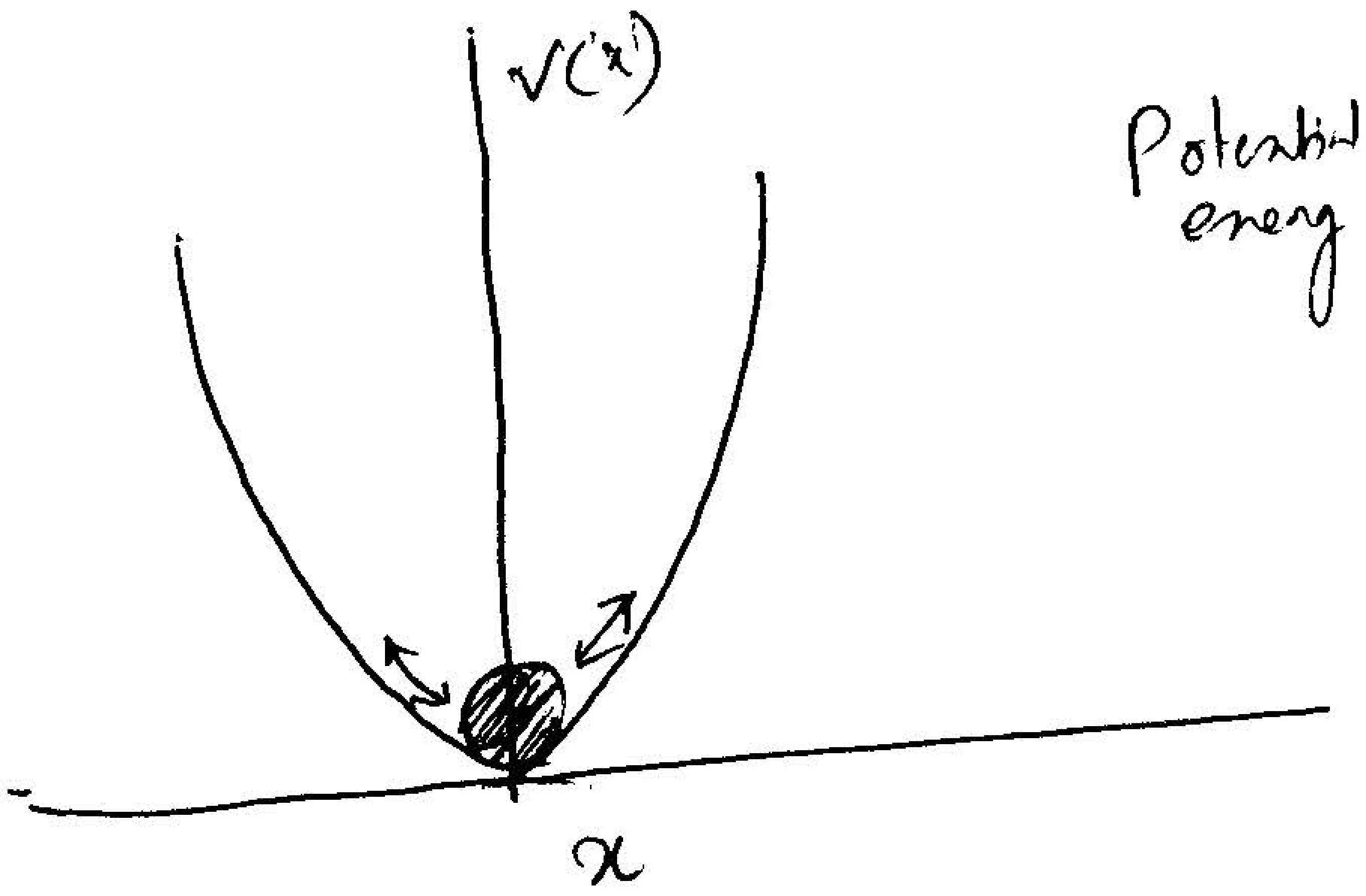
Principle of extremum predicts equilibrium

✓ Energetically a molecules attains its lowest energy state at equilibrium

✓ A macroscopic systems drives itself towards highest entropy.

States of equilibria: Stable, Neutral, Metastable and Unstable.

ⓐ Stable



Potential energy: $V(x) = \frac{1}{2} K x^2$, Force $F(x) = -\frac{dV}{dx} = -Kx$

For equilibrium to attains net force must be zero on the subject.

$$F(x) = 0 = -\frac{dV(x)}{dx} = 0$$

↑ Thus first derivative (extremum) is predictive of eqm.

✓ stable eqm, where potential energy has a global minima.

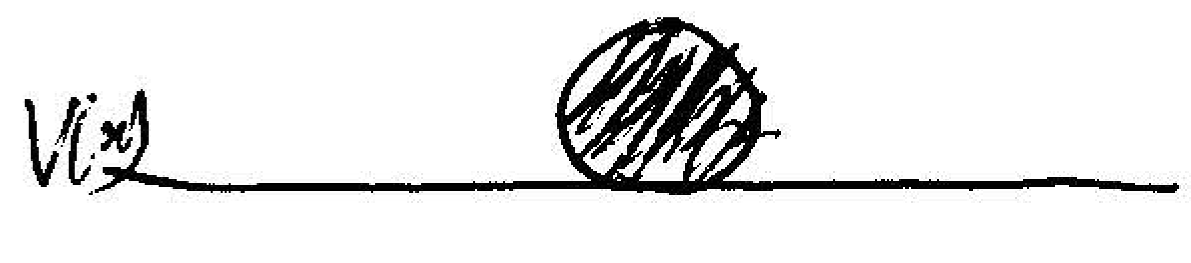
Equilibrium → $\frac{dV(x)}{dx} = 0$ & $\frac{d^2V(x)}{dx^2} > 0$ at $x = x^*$, eqn position

Global → $V(x) > V(x^*)$ for $x \neq x^*$

ⓑ Neutral equilibrium

✓ For potential energy surface is flat.

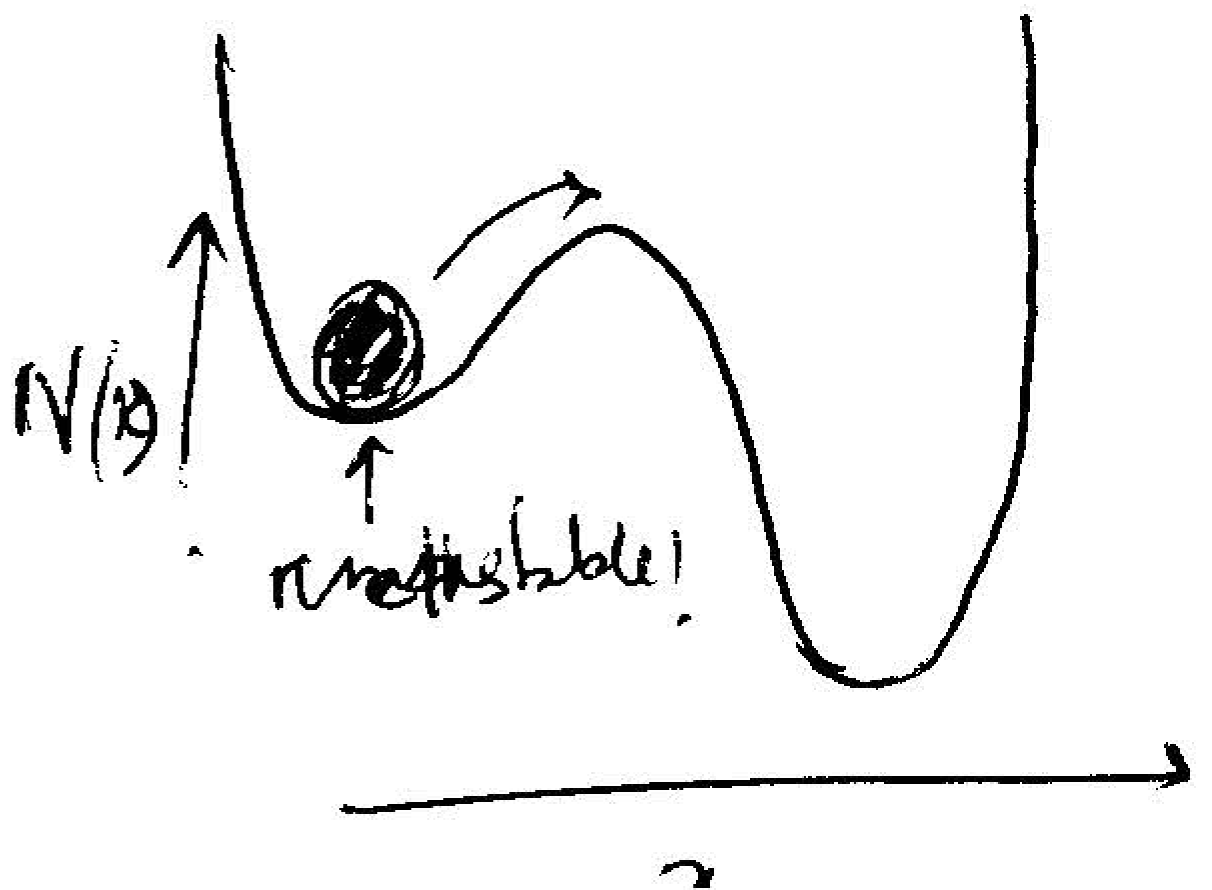
$V(x) =$ constant, $\frac{dV(x)}{dx} = 0$ for all x



ⓒ Metastable equilibrium:

✓ Stable to small perturbation but unstable to large perturbation

→ locally stable.

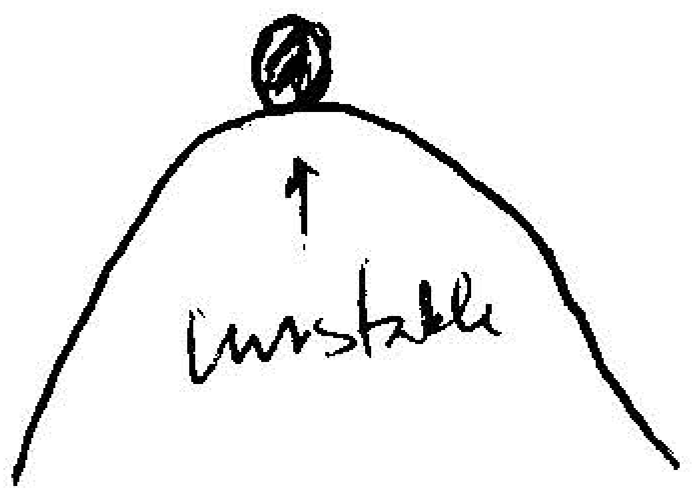


$\frac{dV(x)}{dx} = 0$, $\frac{d^2V(x)}{dx^2} > 0$ for $x = x^*$

$V(x) > V(x^*)$ for small $|x - x^*|$

$V(x) < V(x^*)$ for large $|x - x^*|$

ⓓ Unstable state:



- $\frac{dV(x)}{dx} = 0, \quad \frac{d^2V(x)}{dx^2} < 0 \quad$ at $x = x^*$
- $V(x) < V(x^*)$ for all $x \neq x^*$

Conclusion: ~~Max~~ Extremum of potential energy predicts the equilibrium state.

? Now how one would predict the equilibrium or most probable state for ~~a~~ random variable?

Case Study: Tossing four coins and asking the question. What the probability of obtaining a given number of heads (or tails) after tossing the coins?

$$\text{Probability} = \frac{\#\text{ of ways an event can occur}}{\text{total }\#\text{ of ways}}$$

For tossing 4 coins, total # of ways heads can be arranged: $2^4 = 16$, with $N = 4$.

No. of heads (n)	Multiplicity (W)	Probability (P)	ln W
0	$\binom{4}{0} = 1$	1/16	0
1	$\binom{4}{1} = 4$	4/16	1.4
2	$\binom{4}{2} = 6$	6/16	1.8
3	$\binom{4}{3} = 4$	4/16	1.4
4	$\binom{4}{4} = 1$	1/16	0

Most probable state is the 2 heads w 2 tails as it has highest probability (P). Now it has also maximum multiplicity (W). Thus most probable state can be predicted by maximizing the multiplicity factor.

$$\left.\frac{dW}{dn}\right|_{n^*} = 0 \qquad n^* \text{ is the most probable state.}$$

~~Mul~~ ✓ All the different arrangements ~~a~~ given multiplicity factor represents ~~is call~~ are called microstate. Ex. $\{HHTH,\ HTHH,\ THHH,\ HHHT\} = W$

✓ The state a given multiplicity factor ~~res~~ represent is call macrostate. Ex. for the microstate ~~ste~~ above the macrostate is one tail w three heads.

The logarithum f W is also predictive f equilibrium.

Now we know macroscopic state tries to attain a state which has maximum entropy, Thus maximum entropy predicts the equilibrium of system.

? Is there any connection between microstates or multiplicity factor and entropy?

Boltzman's postulate was entropy is connected to the 'disorderness of the macroscopic system.

$$\boxed{S = k\ln\Omega \text{ or } S = k\ln W}$$

W, the multiplicity factor is the measure of disorderdness!

~~✓ Thus maximizing~~ ✓ Thus maximization f entropy may lead to equilib distribution. ~~for~~

How?

$$\ln x! = x\ln x - x$$ for large x, Sterling's approximation.

$$x! = \exp(x\ln x - x)$$
$$= \exp(\ln x^x - x)$$
$$= x^x e^{-x}$$
$$= \left(\frac{x}{e}\right)^x$$

$$W = \frac{N!}{n_1!\, n_2!\, n_3!\, n_1! \cdots n_t!}$$

if total trials are N, and total t possible outcomes are there.

$$N = n_1 + n_2 + \cdots n_t$$

$$= \frac{(N/e)^N}{(n_1/e)^{n_1}(n_2/e)^{n_2}\cdots(n_t/e)^{n_t}}$$

$$= \frac{N^N}{n_1^{n_1}\, n_2^{n_2}\cdots n_t^{n_t}}$$

$$= \frac{1}{(n_1/N)^{n_1}\cdot(n_2/N)^{n_2}\cdots(n_t/N)^{n_t}}$$

$$= \frac{1}{p_1^{n_1} p_2^{n_2} \cdots p_t^{n_t}}$$

taking natural log

$$\ln W = -\sum_{i=1}^{t} \ln p_t^{n_i}$$

$$= -\sum_{i=1}^{t} n_i \ln p_i$$

$$\frac{1}{N} \ln W = -\sum_{i=1}^{t} \frac{n_i}{N} \ln p_i$$

$$= -\sum_{i=1}^{t} p_i \ln p_i$$

$$\ln W = -N \sum_{i=1}^{t} p_i \ln p_i = \frac{S}{k} \qquad [S = k \ln W]$$

or.

$$\frac{(S/N)}{k} = -\sum_{i=1}^{t} p_i \ln p_i$$

$$\boxed{\frac{S_N}{k} = -\sum_{i=1}^{t} p_i \ln p_i}$$

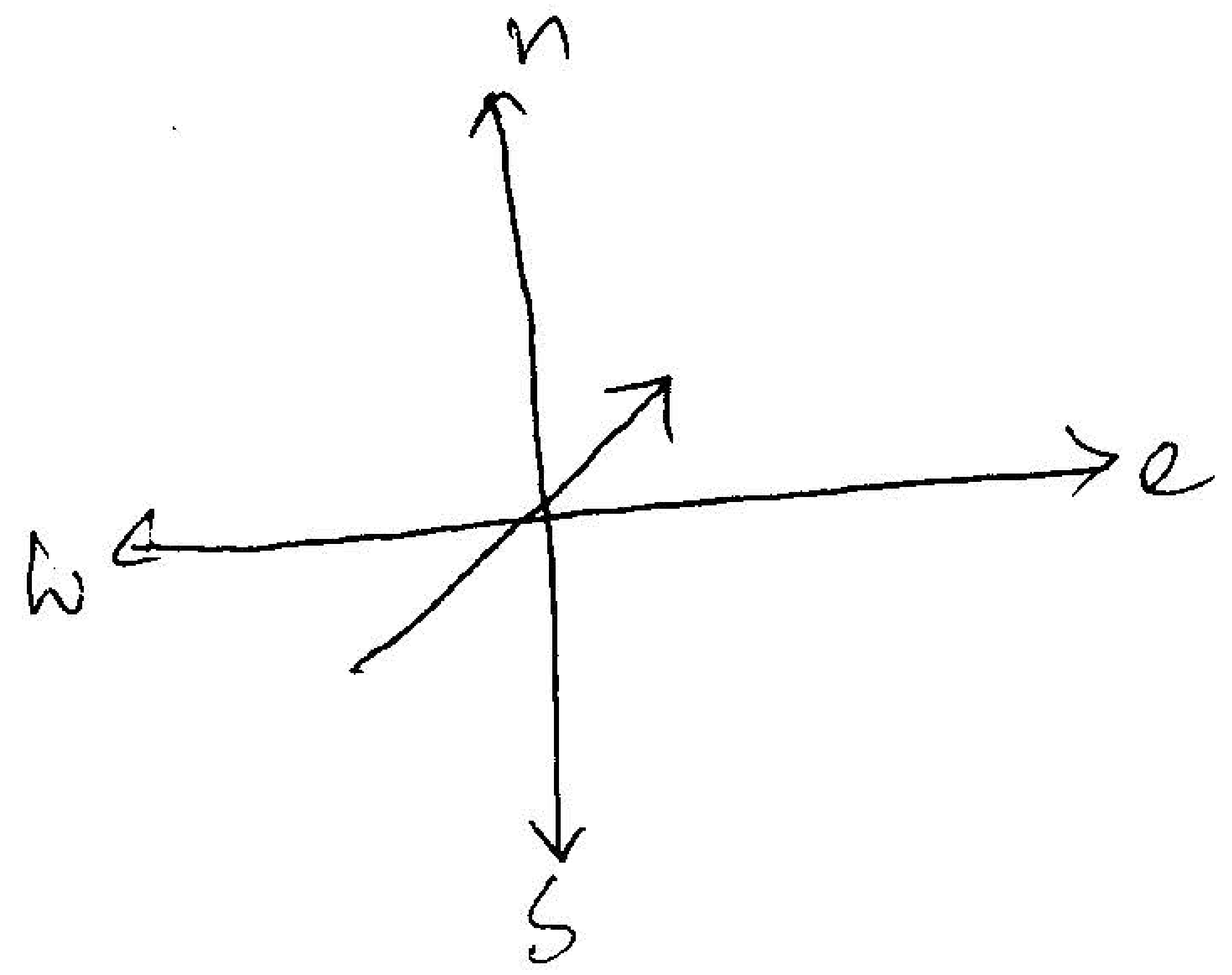
Relation between entropy per trial ($S_N = \frac{S}{N}$) and probability of an outc

- Perfectly ordered state: means there is only one arrangement.
  → fully deterministic → $p_i = 1$
  $S_N = 0$: entropy of a fully ordered state is zero.

- Entropy cannot be negative, $S \geq 0$.. as $0 \leq p_i \leq 1$.

Now what kind of system will have highest entropy.
or why dipoles try to orient randomly?

- k is entropy per molecule?

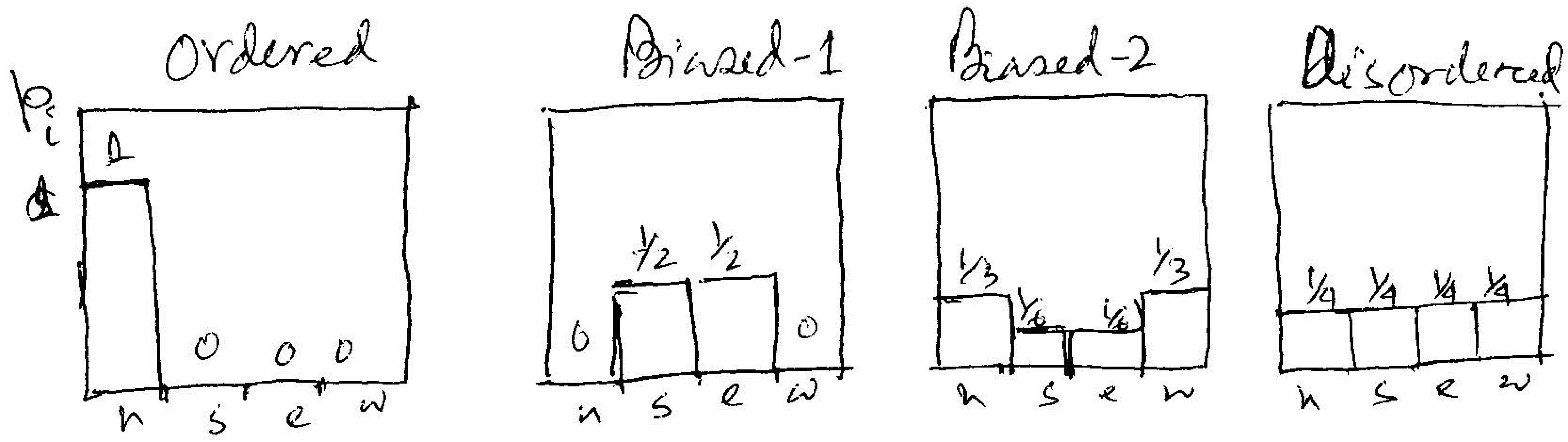


A pencil is rotated on a paper with marked quandrents.

$P(n) = \frac{n_n}{N}$, $P(s) = \frac{n_s}{N}$, $P(e) = \frac{n_e}{N}$, $P(w) = \frac{n}{N}$

n_n, n_s, n_e, n_w are no. of times outcomes were n, s, e, and w respectively, out of N total trials.

various probability ~~of~~ 'structure'



$S = -\sum_i p_i \ln p_i$ assuming $k=1$

$S = 0$

$S = -\left[\frac{1}{2}\ln\frac{1}{2} + \frac{1}{2}\ln\frac{1}{2}\right] = 0.69$

$S = -2\left[\frac{1}{3}\ln\frac{1}{3} + \frac{1}{2}\ln\frac{1}{6}\right] \simeq 1.33$

$S = -4\left[\frac{1}{4}\cdot\ln\frac{1}{4}\right] \simeq 1.39$

- → Entropy for the disordered state is maximum.
- → Highest entropy predicts flat distribution [unconstrained system]
- → In general if there are "t" no. of equally probable outcomes then $\boxed{S = \ln t}$
- → Relative "flatness" of distribution can be measured by entropy.

What is the nature of probability distribution for a system with out any constraint?

- Maximum entropy leads to the equilibrium distribution for a system.
- $S = -k\sum_{i=1}^{t} p_i \ln p_i$ needs to be maximized subject to the constraint that total ~~to~~ probability = 1
- Constraint: $g(p_j) = \sum_{i=1}^{t} p_i = 1$ 't' is the number of various outcomes.

Applying Lagrange multiplier method;

~~$\sum_{i=1}^{t}\left[\left(\frac{\partial S}{\partial p_i}\right)_{j\neq i} - \alpha\left(\frac{\partial g}{\partial p_i}\right)\right] dp_i = 0$~~

$$\sum_{i=1}^{t}\left[\left(\frac{\partial S}{\partial p_i}\right)_{j\neq i} - \alpha\left(\frac{\partial g}{\partial p_i}\right)_{j\neq i}\right] dp_i = 0.$$

$$\left(\frac{\partial S}{\partial p_i}\right)_{j\neq i} = -[1+\ln p_i] \;; \quad \left(\frac{\partial g}{\partial p_i}\right)_{j\neq i} = 1$$

Thus,

$$-(1+\ln p_i^*) - \alpha = 0$$

p_i^* = eq^m distribution

$k = 1$

$$\ln p_i^* = -(1+\alpha)$$

$$\boxed{p_i^* = e^{-(1+\alpha)}}$$

α is unknown.

To determine α we use the constraint,

$$\sum_{i=1}^{t} p_i^* = 1 = \sum_{i=1}^{t} e^{-(1+\alpha)} = t\,e^{-(1+\alpha)}$$

$$e^{-(1+\alpha)} = \frac{1}{t}$$

Thus $$\boxed{p_i^* = \frac{1}{t}}$$

- Since t is constant. it predicts a flat distribution for an unconstrained system. This is ~~true~~ applicable for an isolated system.

- This also suggests all the outcomes are equally probable. This is called law of equal a priori probability.

Now what will be the nature of probability at eqm. if there are additional constraint?

Again, $$S = -k \sum_{i=1}^{t} p_i \ln p_i \quad \cdots \text{①}$$

$$\sum_{i=1}^{t} p_i = 1 \quad \cdots \text{②}$$

The other constraint is the average ~~of~~ ~~certain~~ of a quantity of interest must have certain value.

For example, A die with 't' no. of faces and on each side a number is printed. Say on ith side the number printed is ϵ_i.

Total no. of rolls = N, n_i = no. of times ith side was the outcome,

$$N = \sum_{j=1}^{t} n_j$$

The total 'score' after N rolls, $E = \sum_{i=1}^{t} \epsilon_i n_i$

Average score per roll, $\langle \epsilon \rangle = \frac{E}{N}$.

Now using probability definition of average, $\langle \epsilon \rangle = \sum_{i=1}^{t} \epsilon_i p_i$

where, $p_i = \frac{n_i}{N}$.

$$\langle \epsilon \rangle = \frac{E}{N} = \sum_{i=1}^{t} \epsilon_i p_i \quad \cdots \text{③}$$

? What is the probability distribution p_i^* that results the average 'score' $\langle \epsilon \rangle$?

Thus there ~~are two~~ is another constraint, given by eqn ③.

We use the usual method of Lagrange multiplier to maximize entropy subject to two constraints given by ② and ③.

$$\left(\frac{\partial S}{\partial p_i}\right)_{i \neq j} - \alpha \left(\frac{\partial g}{\partial p_i}\right)_{i \neq j} - \beta \left(\frac{\partial h}{\partial p_i}\right)_{i \neq j} = 0 \quad \text{for all } i.$$

assuming $k = 1$,

$$-1 - \ln p_i^* - \alpha - \beta \epsilon_i = 0.$$

$$\therefore p_i^* = e^{-(1+\alpha+\beta\epsilon_i)}$$

to eliminate α we use the conservation of probability constraint.

$$p_i^* = \frac{p_i^*}{\sum_{i=1}^{t} p_i^*} = \frac{e^{-(1+\alpha+\beta\epsilon_i)}}{\sum_{i=1}^{t} e^{-(1+\alpha+\beta\epsilon_i)}} = \frac{e^{-\beta\epsilon_i}}{\sum_{i=1}^{t} e^{-\beta\epsilon_i}} \quad \cdots \; \textcircled{4}$$

This distribution is known as Boltzmann distribution law.

The ~~q~~ denominator, $\sum_{i=1}^{t} e^{-\beta\epsilon_i} = q$, is called partition function.

Basic postulate of statistical mechanics:

Law of equal apriori probability: All the accessible microstates of an isolated system at equilibrium are equally probable.

~~Thus the probability for an isolated system at equilibrium.~~

~~$P = \frac{C}{\Omega}$~~ ~~where C is constant and Ω is the no. of micro state representing a given macrostate.~~

Ensemble: An ensemble in statistical mechanics represents a collection of "mental copies" of same macroscopic system (represented by macroscopic thermodynamic variables such as T, P, V, E etc) each of it is given by different microstates.

Microcanonical ensemble: Represents ~~as~~ a collection of isolated systems with fixed number of particles (N), fixed volume (V) & fixed energy (E).

Canonical Ensemble: Fixed N, V, T. Here the system is allowed to exchange energy with the surrounding. Represents Closed system.

Grand-Canonical ensemble: Fixed. μ, V, T. (μ: chemical potential) Here both mass & energy exchange are allowed. Thus deals with an open system.

Thus according to Law of equal apriori probability for microcanonical ensemble the probability can be give as.

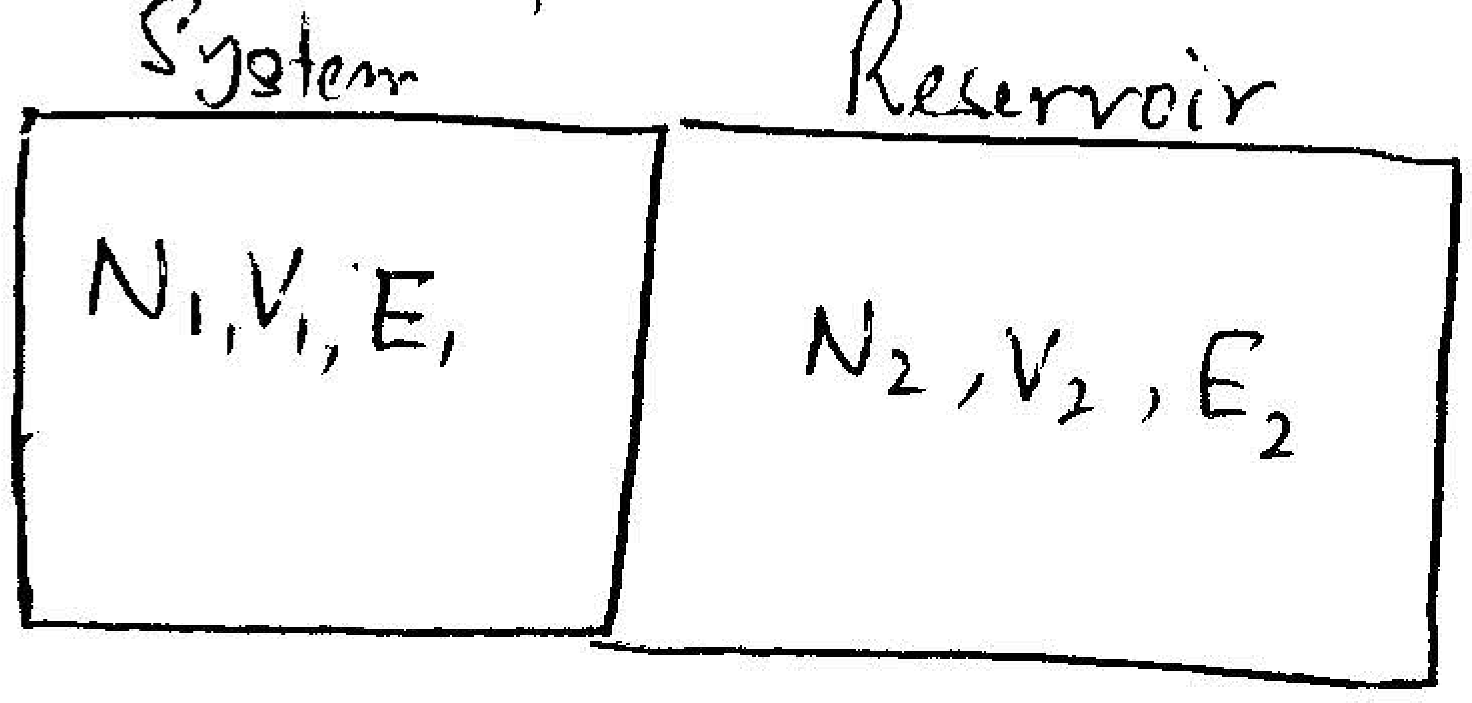
$$P = \frac{1}{\Omega} \quad \text{for} \quad E' \leq E \leq E+\Delta E$$

$$= 0 \quad \text{otherwise}.$$

Ω: No of microstates for the macrostate of interest.

Now using this postulate we can derive the equilibrium probability distribution for other ensembles.

Condition for thermal equilibrium between a system and reservoir.



These two macrostates are allowed to exchange thermal energy between them. ~~Have long~~ Now what is the condition for the thermal equilibrium

# of Microstates: for the system: $\Omega_s(N_1, V_1, E_1)$

" " " reservoir: $\Omega_R(N_2, V_2, E_2)$

The # microstates for the joint system: $\Omega(N, V, E)$

*Now the joint system becomes an isolated system together.

$E = E_1 + E_2$ & $E_2 \gg E_1$ ~~result~~ $\frac{E_1}{E} = \frac{E-E_2}{E} = 1 - \frac{E_2}{E} \ll 1$

(Since E_2 is for the reservoir).

$$\Omega(N, V, E) = \Omega_s(N_1, V_1, E_1) \times \Omega(N_2, N_2, E_2)$$

$$= \Omega_s(E_1)\,\Omega_R(E_2)$$

N & V's can be left out as they are fixed.

Now equilibrium requires maximization of Ω for the joint system w.r.to the energy of the system. Thus,

$$\left.\frac{\partial\Omega}{\partial E_1}\right|_{\substack{E_1 = E_1^* \\ E_2 = E_2^*}} = 0$$

(with const N, V)

where E_1^* & E_2^* are the eqm energies of the appropriate system.

$$\rightarrow \left.\frac{\partial\Omega_s(E_1)}{\partial E_1}\right|_{E_1^*}\Omega_R(E_2^*) + \Omega_s(E_1^*)\cdot\left.\frac{\partial\Omega_R(E_2)}{\partial E_2}\right|_{E_2^*}\cdot\frac{\partial E_2}{\partial E_1} = 0$$

Since, $E_2 + E_1 = E$, $\frac{\partial E_2}{\partial E_1} = -1$,

$$\rightarrow \frac{1}{\Omega_s(E_1^*)}\left.\frac{\partial\Omega_s(E_1)}{\partial E_1}\right| = \frac{1}{\Omega_R(E_2^*)}\cdot\left.\frac{\partial\Omega_R(E_2)}{\partial E_2}\right|$$

$$\rightarrow \quad \left.\frac{\partial \ln \Omega_S(E_1)}{\partial E_1}\right|_{E_1^*, N_1, V_1} = \left.\frac{\partial \ln \Omega_R(E_2)}{\partial E_2}\right|_{E_2^*, N_2, V_2} = \beta \text{ , a constant.} \quad \cdots ①$$

From thermodynamics we have

$$dE = dU = TdS - PdV + \mu dN \quad \text{leading to}$$

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

now applying $S = k \ln \Omega$

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

$$\rightarrow \quad \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} = \frac{1}{kT} \quad \cdots ②$$

Thus comparing ① & ②, $\beta = \frac{1}{kT}$.

This concludes that exchange of energy would go on between system and reservoir untill they reach a common temperature which must be fixed.

Similar arguments can be made for system that exchanges other quantities such as mass etc.

What is the equibrium probability distribution for canonical ~~system~~ ensemble?

Canonical ensemble allows the system to exchange energy with the reservior/surrounds. Now the system with the reservoir together makes it microcanonical system where law of equal a priori probability holds at equilibrium.

E_S : energy of the system.

E_R : " " reservior. $\qquad E = E_S + E_R$ = constant.

Ω_S : # of microstates for the system

Ω_R : # of " " " reservoir.

Now probability that the system will be with energy E_i must be same as probability that the ~~syste~~ reservior with energy $(E-E_i)$.

Thus,

$$P(E_i) = P_i \propto \Omega_R(E-E_i)$$ as probability must proportional to the # of microstates.

Now, $E_i \ll E$, $S = R\ln\Omega$

$$S = R\ln\Omega_R(E-E_i)$$

$$= k\ln\Omega_R(E) - \frac{\partial[R\ln\Omega_R(E)]}{\partial E_i} E_i + \frac{1}{2}\frac{\partial^2(R\ln\Omega_R(E))}{\partial E^2} \cdot E_i^2 - \dots$$

$$= R\ln\Omega_R(E) - \frac{\partial[R\ln\Omega_R(E)]}{\partial E} \cdot E_i + O(E_i^2)$$

$$\approx R\ln\Omega_R(E) - \frac{E_i}{T}$$ as, $\frac{R\partial\ln\Omega}{\partial E} = \frac{1}{T}$

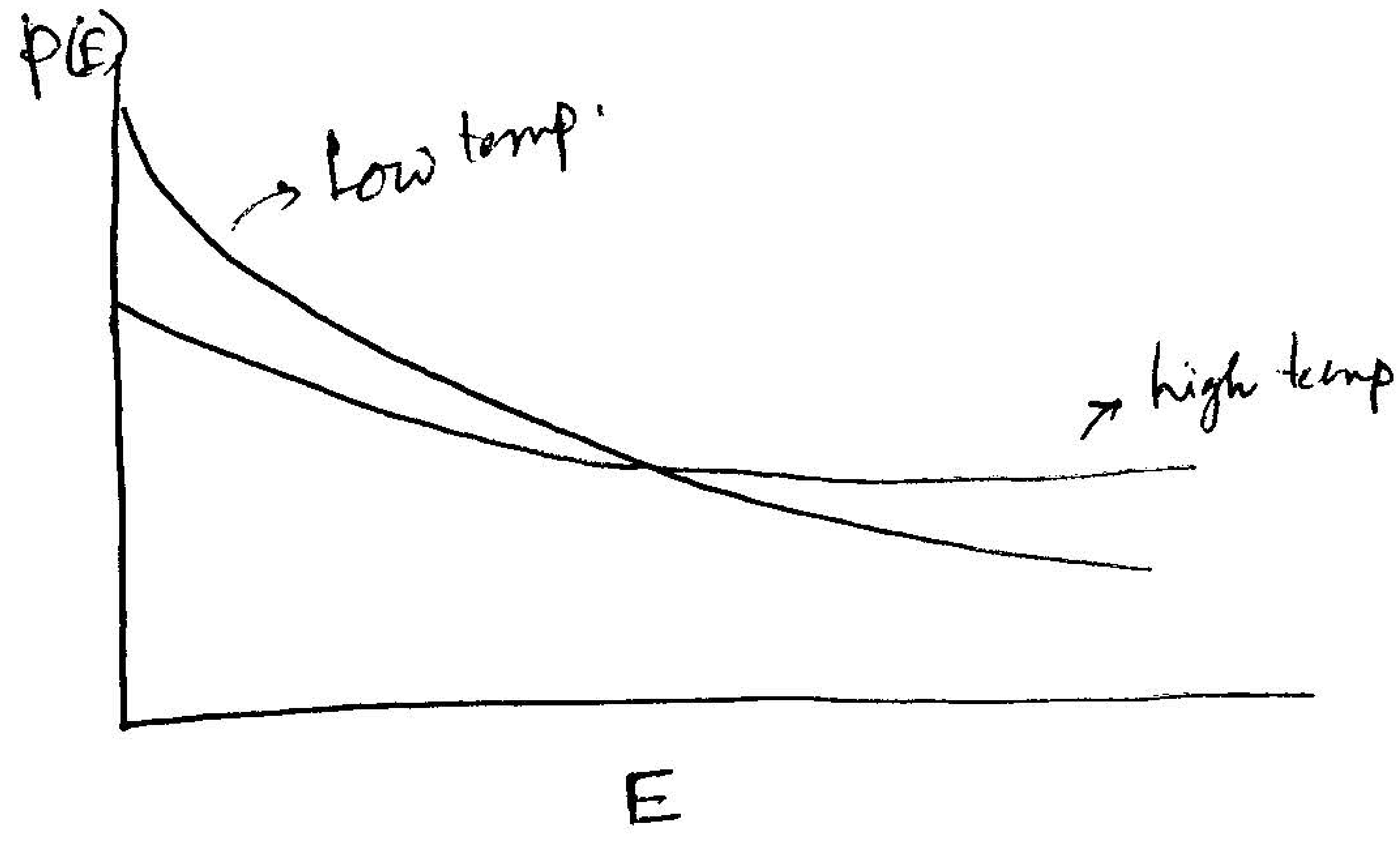
$$\ln\Omega_R(E-E_i) = \ln\Omega_R(E) - \frac{E_i}{RT}$$

$$\Omega_R(E-E_i) = \Omega_R(E) \cdot e^{-E_i/RT}$$

Thus, $$P(E_i) \propto e^{-E_i/RT}$$

$$P(E_i) = \frac{e^{-E_i/RT}}{}$$ ← Boltzmann distribution for

$$q = \sum_{i=1}^{t} e^{-E_i/RT} = \sum_{i=1}^{t} e^{-\beta E_i}$$ is called partition function.



According to Boltzmann distribution probability of system with lower energy is more than system with high energy. In other words low energy states are more probable than the high energy state. Since total energy is conserved, more no. of system with low energy leads to bigger no. of "possible arrangements" as compared to distributing higher amt of energy only to a few state.

Q The partition function q represents total no. of accessible states.

Often in partition function calculation "ground state" energy is rescaled to zero as it ~~[illegible]~~ does not change the probability.

$$q = \sum_{i=1}^{t} e^{-\beta\epsilon_i} = e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3} + \cdots + e^{-\beta\epsilon_t}$$

After rescaling of ground state energy to zero, $E_1 = 0$, partition function becom

$$q = e^{0} + e^{-\beta(E_2-\epsilon_1)} + e^{-\beta(\epsilon_3-\epsilon_1)} + e^{-\beta(\epsilon_4-\epsilon_1)} + \cdots e^{-\beta(\epsilon_t-E_1)}$$

$$= 1 + e^{-\beta\epsilon_2'} + e^{-\beta\epsilon_3'} + \cdots + e^{-\beta\epsilon_t'}$$

Partition function for degenerate states/energy levels.

$$q = \sum_{i=1}^{t} g(\epsilon_i)\, e^{-\beta\epsilon_i}$$ where $g(\epsilon_i)$ is the degeneracy of ith energy level.

Thus the probability becomes,

$$P(\epsilon_i) = \frac{g(\epsilon_i)\cdot e^{-\beta\epsilon_i}}{\sum_i g(\epsilon_i)\, e^{-\beta\epsilon_i}}$$

The number $g(\epsilon_i)$ is known as density of states, ~~[illegible]~~

Partition function for independent and distinguishable particles.

Say, there are two particles and they ~~can~~ be distinguished, particle A and particle B. They are non-interacting thus independent with one another

Energy levels of particle A, : ϵ_i^A $i = 1, 2, \cdots a$

〃 〃 〃 B : ϵ_j^B $j = 1, 2, \cdots b$.

The total energy $E_K = \epsilon_i^A + \epsilon_j^B$

Partition function for ~~a~~ particle A : $q_A = \sum_{i=1}^{a} e^{-\beta\epsilon_i^A}$

〃 〃 〃 B : $q_B = \sum_{j=1}^{b} e^{-\beta\epsilon_j^B}$

Partition function for the joint system i.e. particle A and B together

$$Q = \sum_{K=1}^{t} e^{-\beta E_K} = \sum_{i=1}^{a}\sum_{j=1}^{b} e^{-\beta(\epsilon_i^A+\epsilon_j^B)} = \sum_{i=1}^{a} e^{-\beta\epsilon_i^A}\cdot\sum_{j=1}^{b} e^{-\beta\epsilon_j^B} = q_A q_B$$

- Thus if ~~there are~~ for independent and distinguishable states/particle the ~~total~~ partition function for the entire system

$$\boxed{Q = q_A q_B q_C \cdots}$$

- For N no. of identical noninteracting and distinguishable particles

$$\boxed{Q = q^N}$$

- ~~I~~ For N no. of identical noninteracting and indistinguishable parti

$$\boxed{Q = \frac{1}{N!} q^N}$$

N! is the correction factor for the no. of permutation among N particles.

If energy takes continuous value the partition function becomes

$$q = \int g(\epsilon)\, e^{-\beta\epsilon}\, d\epsilon$$

& probability density $p(\epsilon) = \dfrac{g(\epsilon)\, e^{-\beta\epsilon}\, d\epsilon}{\int g(\epsilon)\, e^{-\beta(\epsilon)}\, d\epsilon}$

- <u>Partition function and thermodynamic variables</u>

<u>Average energy</u>; Or Internal energy (U)

$$\bar{E} = \sum_{i=1}^{t} \epsilon_i\, p(\epsilon_i) \qquad \text{at const, } N \,\&\, V$$

$$= \sum_{i=1}^{t} \epsilon_i \left(e^{-\beta\epsilon_i} \Big/ \sum_{i=1}^{t} e^{-\beta\epsilon_i} \right)$$

$$= \frac{\sum_{i=1}^{t} \epsilon_i\, e^{-\beta\epsilon_i}}{\sum_{i=1}^{t} e^{-\beta\epsilon_i}}$$

$$= \frac{1}{q} \cdot \sum_{i=1}^{t} \epsilon_i\, e^{-\beta\epsilon_i}$$

$$= -\frac{1}{q} \cdot \sum_{i=1}^{t} \frac{d}{d\beta}\left(e^{-\beta\epsilon_i}\right)$$

$$= -\frac{1}{q} \cdot \frac{d}{d\beta} \cdot \sum_{i=1}^{t} e^{-\beta\epsilon_i}$$

$$= -\frac{1}{q} \cdot \frac{dq}{d\beta}$$

$$= -\left(\frac{d\ln q}{\partial\beta}\right)_{N,V}$$

Average energy $\boxed{\bar{\epsilon} = -\left(\frac{d\ln q}{d\beta}\right)_{N,V}}$

Now, $\dfrac{d\beta}{dT} = \dfrac{d}{dT}\left(\dfrac{1}{KT}\right) = -\dfrac{1}{KT^2}, \quad \dfrac{dT}{d\beta} = -KT^2$

$$\therefore \quad \bar{\epsilon} = -\left(\frac{d\ln q}{d\beta}\right)_{N,V}$$

$$= -\left(\frac{d\ln q}{dT}\right)_{N,V} \cdot \left(\frac{dT}{d\beta}\right)$$

$$\bar{\epsilon} = KT^2 \cdot \left(\frac{d\ln q}{}\right.$$

For N distinguishable, independent particles.

$$\bar{\epsilon} = -\left(\frac{\partial \ln q^N}{\partial \beta}\right)_{N,V} = -N\cdot\left(\frac{\partial \ln q}{\partial \beta}\right)_{N,V} \equiv U \equiv -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

q = one particle partifimfu

Q = N particle P.F.

If the particles are indistinguishable then.

$$\bar{\epsilon} = -\frac{d}{d\beta}\left(\ln\left(\frac{q^N}{N!}\right)\right) = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_{N,V} \equiv U$$

* Thus the av. energy doesn't depend on ~~whether~~ the particles are distinguishable or not!

A bit of thermodynamics : review

Helmholtz free energy, $A = U - TS$

$$dA = dU - TdS - SdT$$
$$= TdS - PdV + \mu dN - TdS - SdT$$
$$\boxed{dA = -SdT - PdV + \mu dN}$$

Thus $S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$; $P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$; $\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$

Therefore by calculating these partial derivatives many macroscopic quantities can be estimated.

By definition of Helmholtz free energy, ~~$A = U + TS$~~ $A = U - TS$

$$U = A + TS = A - T\cdot\left(\frac{\partial A}{\partial T}\right)_{N,V}$$
$$= -T^2\left[-\frac{A}{T^2} + \frac{1}{T}\cdot\left(\frac{\partial A}{\partial T}\right)_{N,V}\right]$$
$$= -T^2\cdot\frac{\partial}{\partial T}\left(A/T\right)$$
$$= -T^2\cdot\frac{\partial}{\partial \beta}\left(A/T\right)\cdot\left(\frac{\partial \beta}{\partial T}\right) \qquad \text{Const. N,V}$$
$$= -T^2\frac{\partial}{\partial \beta}\left(A/T\right)\cdot\left(-\frac{1}{kT^2}\right)$$

$$U = \frac{\partial}{\partial \beta}\left(\frac{A}{kT}\right)$$

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

$$\beta A = -\ln Q$$

$$\therefore \boxed{A = -kT \cdot \ln Q}$$

~~For N particles, A = −NkT ln q~~

~~= RTq~~

Thus Helmholtz free energy.

$$\boxed{A = -RT \ln Q}$$

Entropy:

Method 1:

$$S = -k \sum_i p_i \ln p_i$$

$$\therefore \left(\frac{S}{k}\right) = -\sum_i p_i \ln p_i = -\sum_i \left[\left\{\frac{e^{-\beta\epsilon_i}}{Q}\right\} \ln\left\{\frac{e^{-\beta\epsilon_i}}{Q}\right\}\right]$$

$$= -\sum_i \left[\left\{\frac{e^{-\beta\epsilon_i}}{Q}\right\}\left\{\ln(e^{-\beta\epsilon_i}) - \ln Q\right\}\right]$$

$$= -\sum_i \left[\left\{\frac{e^{-\beta\epsilon_i}}{Q}\right\} \cdot \left\{-\beta\epsilon_i - \ln Q\right\}\right]$$

$$= \frac{\beta}{Q}\sum_i \epsilon_i e^{-\beta\epsilon_i} + \ln Q \sum_i \frac{e^{-\beta\epsilon_i}}{Q}$$

$$= \beta \cdot U + \ln Q$$

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

$$= \beta \cdot RT^2 \cdot \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + \ln Q$$

$$= T\,(\partial \ln Q$$

$$U = \frac{\sum_i \epsilon_i e^{-\beta\epsilon_i}}{Q}$$

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

$$= RT^2 \cdot \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

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

Method 2

ⓐ Calculate A, from $A = -KT\ln Q$

ⓑ Calculate S, from $S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$

$$= +K\left[\frac{\partial}{\partial T}\left(T\ln Q\right)\right]_{N,V}$$

$$= K\left[\ln Q + T\cdot\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}\right]$$

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

Enthalpy

$$H = U + PV$$

$$= KT^2\cdot\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} - V\cdot\left(\frac{\partial A}{\partial V}\right)_{T,N}$$

$$= KT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + VKT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

Gibbs Free energy

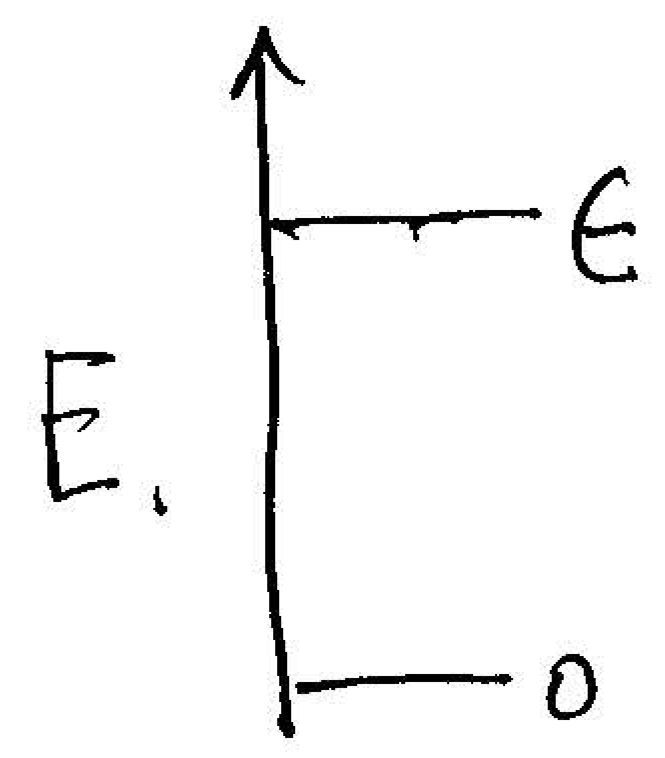
$$G = A + PV$$

$$= -KT\ln Q - V\cdot\left(\frac{\partial A}{\partial V}\right)_{T,N}$$

$$= -KT\ln Q + VKT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

Application #1 : Two level system.

A system for with only two possible values of energy.

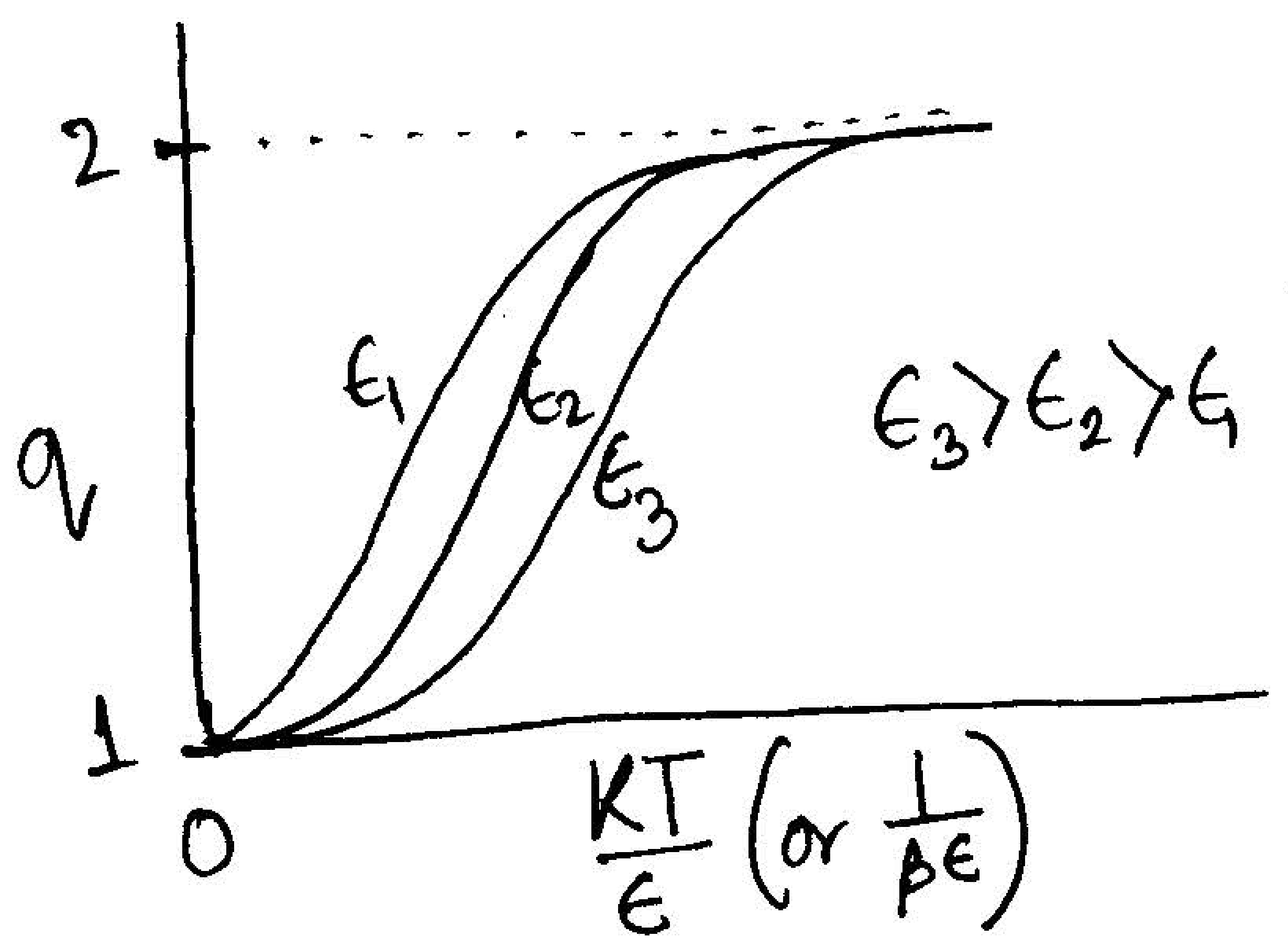


The partition function.

$$q = \sum_i e^{-\beta\epsilon_i} = e^0 + e^{-\beta\epsilon} = 1 + e^{-\beta\epsilon}$$

$$\text{At } T \to 0, \quad q = 1 + e^{-\epsilon/KT} = 1$$

$$\text{At } T \to \infty, \quad q = 2$$



With larger value of energy at the upper state the curve shifts to the right.

Probability that the system remains at lower energy state: P_0

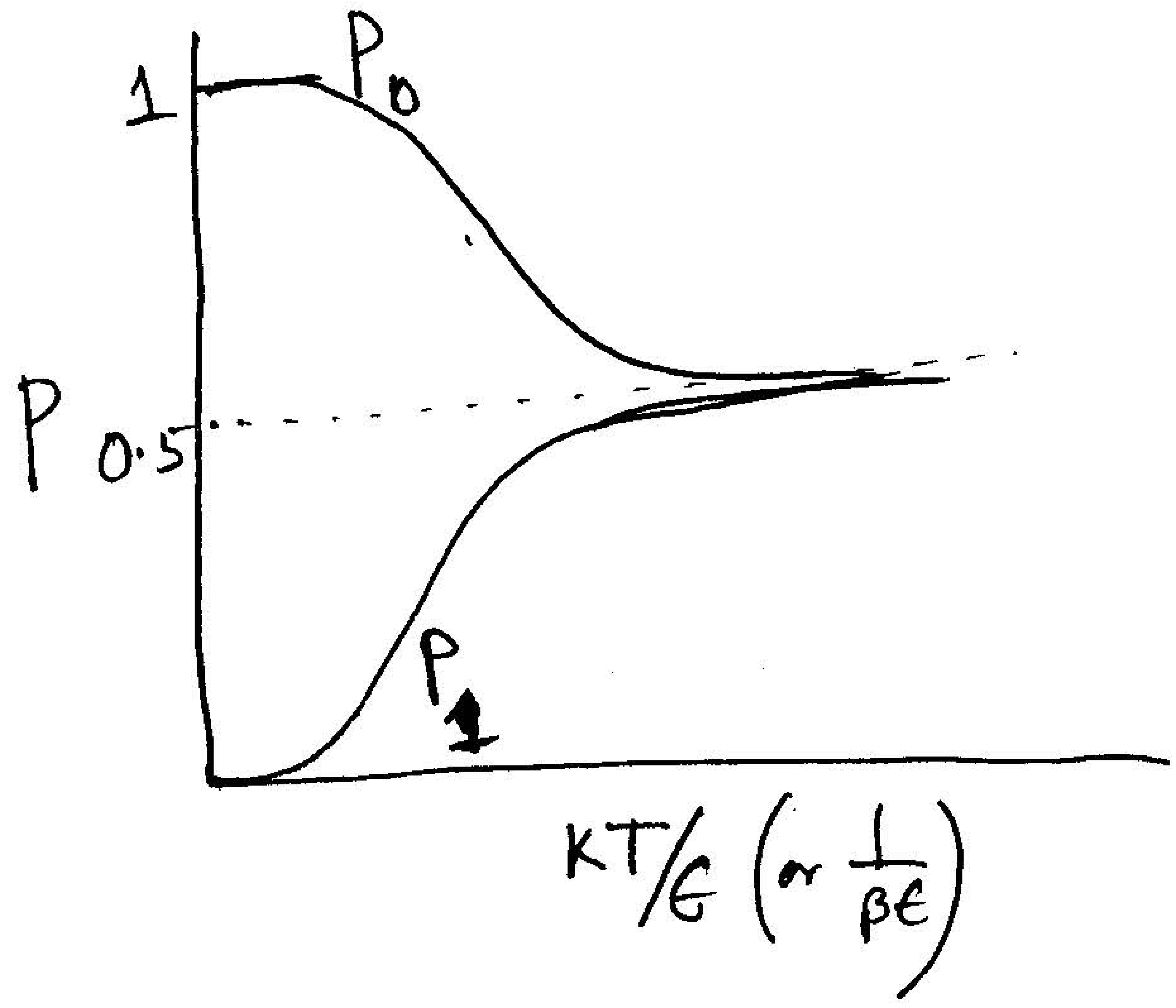
$$P_0 = \frac{e^{-\beta\epsilon_0}}{\sum_i e^{-\beta\epsilon_i}} = \frac{e^{-\beta\cdot 0}}{1+e^{-\beta\epsilon}} = \frac{1}{1+e^{\beta\epsilon}}$$

Similarly the probability corresponding to the upper energy state, P_1

$$P_1 = \frac{e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}}$$

Limiting cases.

	$T \to 0$	$T \to \infty$
P_0	1	0.5
P_1	0	0.5



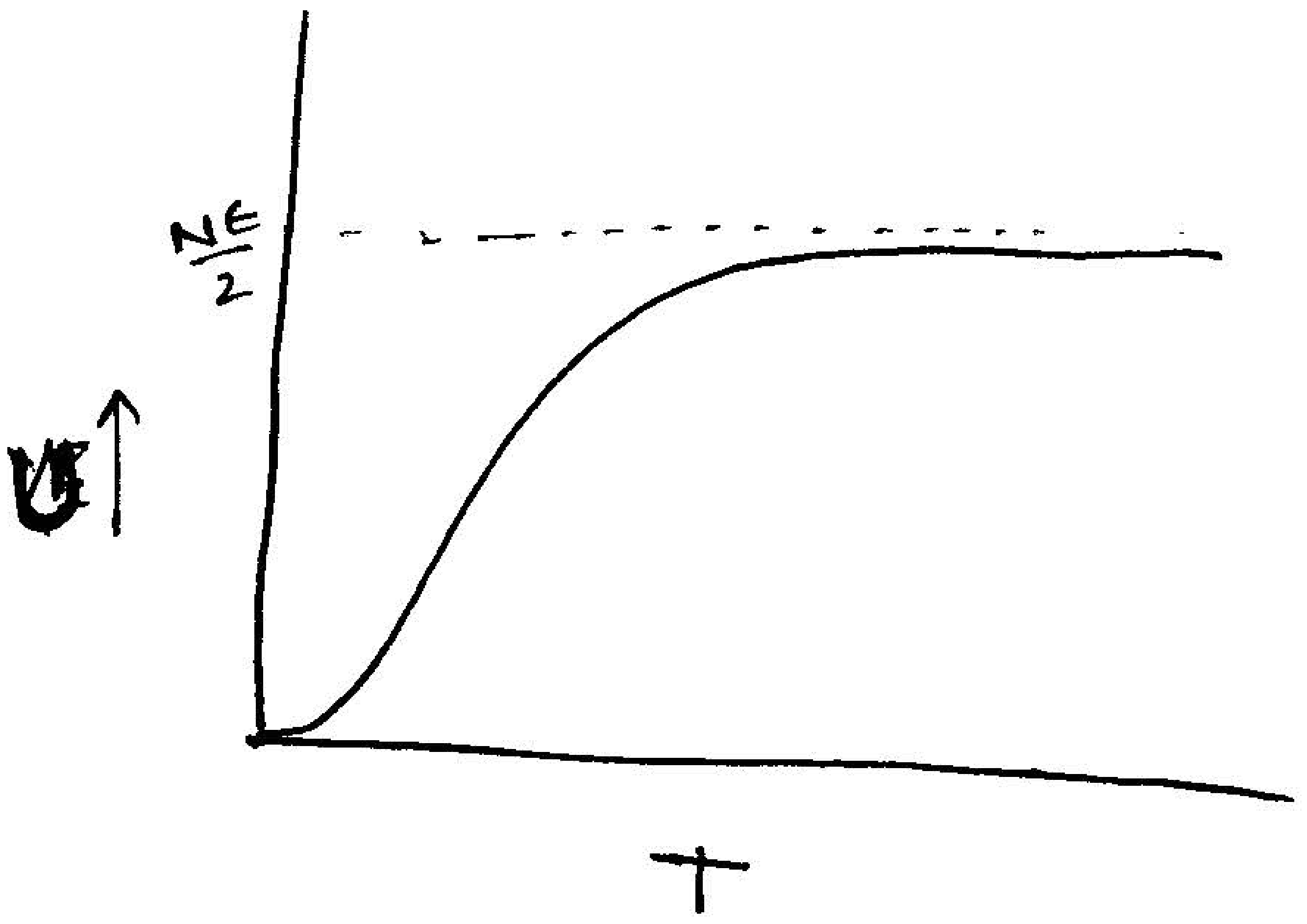
Average energy

$$U = \langle \epsilon \rangle = -\left(\frac{\partial \ln q^N}{\partial \beta}\right)_{N,V}$$

$$= -N\frac{\partial}{\partial \beta}\left[\ln\left(1+e^{-\beta\epsilon}\right)\right]$$

$$= -\frac{-\epsilon \cdot e^{-\beta\epsilon} \cdot N}{\left(1+e^{-\beta\epsilon}\right)}$$

$$= \frac{N\epsilon \cdot e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}}$$



$$\boxed{\langle\epsilon\rangle = U = \frac{N\epsilon}{1+e^{\beta\epsilon}}}$$

$T \to 0$, $\langle \epsilon \rangle = 0$ $\quad \beta\epsilon \to \infty$

$T \to \infty$, $\langle \epsilon \rangle = \frac{1}{2}\epsilon N$ $\quad \beta\epsilon \to 0$

Heat Capacity:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial \langle\epsilon\rangle}{\partial T}\right)_V$$

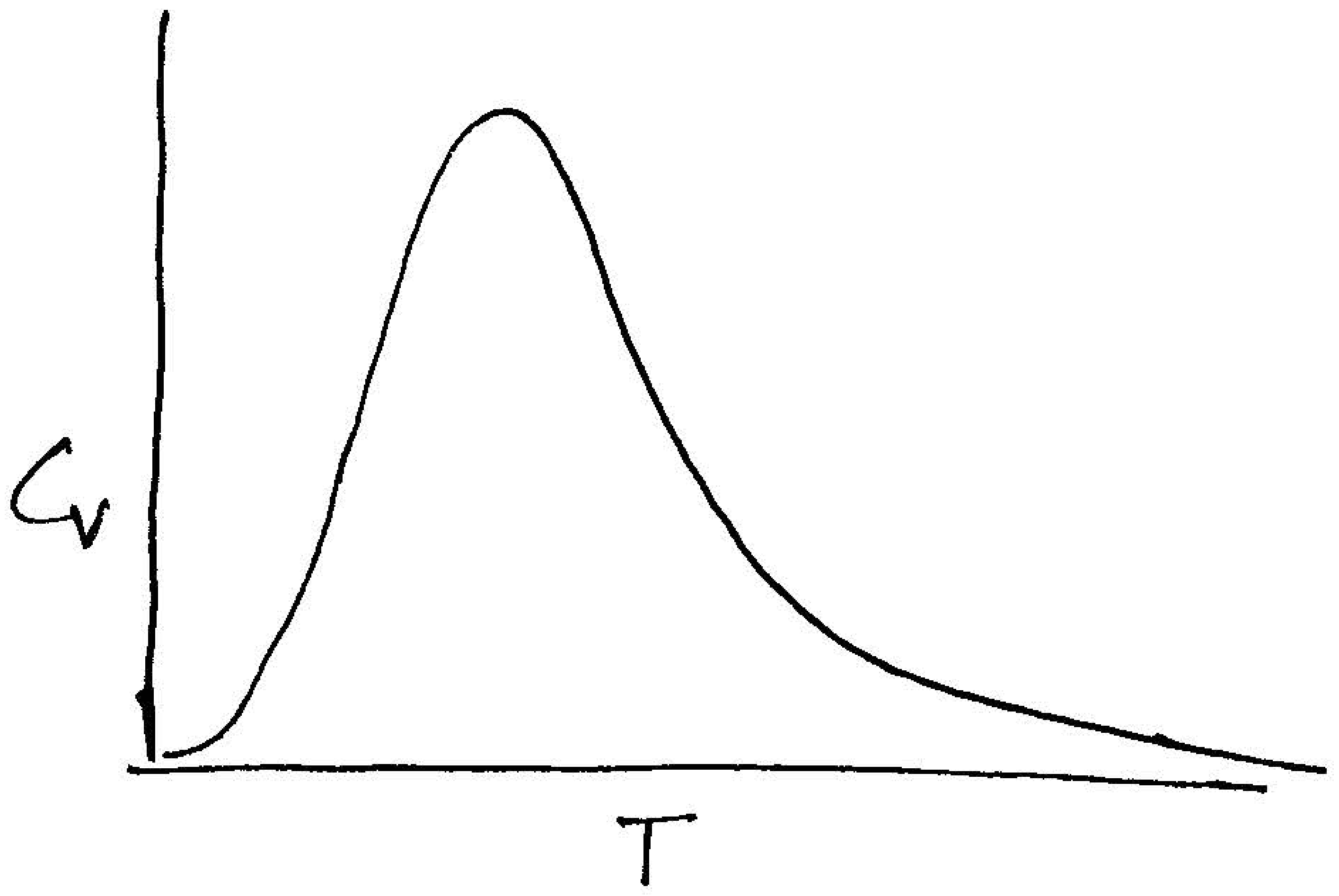
$$\frac{\partial \beta}{\partial T} = -\frac{1}{KT^2} \quad \frac{\partial T}{\partial \beta} = -KT^2$$

$$= -\frac{1}{KT^2}\frac{\partial}{\partial \beta}\left(\langle\epsilon\rangle\right)$$

$$= -\frac{1}{KT^2}\cdot\frac{\partial}{\partial \beta}\left[\frac{N\epsilon}{1+e^{\beta\epsilon}}\right]$$

$$= -\frac{N\epsilon}{KT^2}\cdot -\frac{\epsilon e^{\beta\epsilon}}{\left(1+e^{\beta\epsilon}\right)^2}$$

$$\boxed{C_V = \frac{N\epsilon^2}{KT^2}\cdot\frac{e^{\beta\epsilon}}{\left(1+e^{\beta\epsilon}\right)^2}}$$

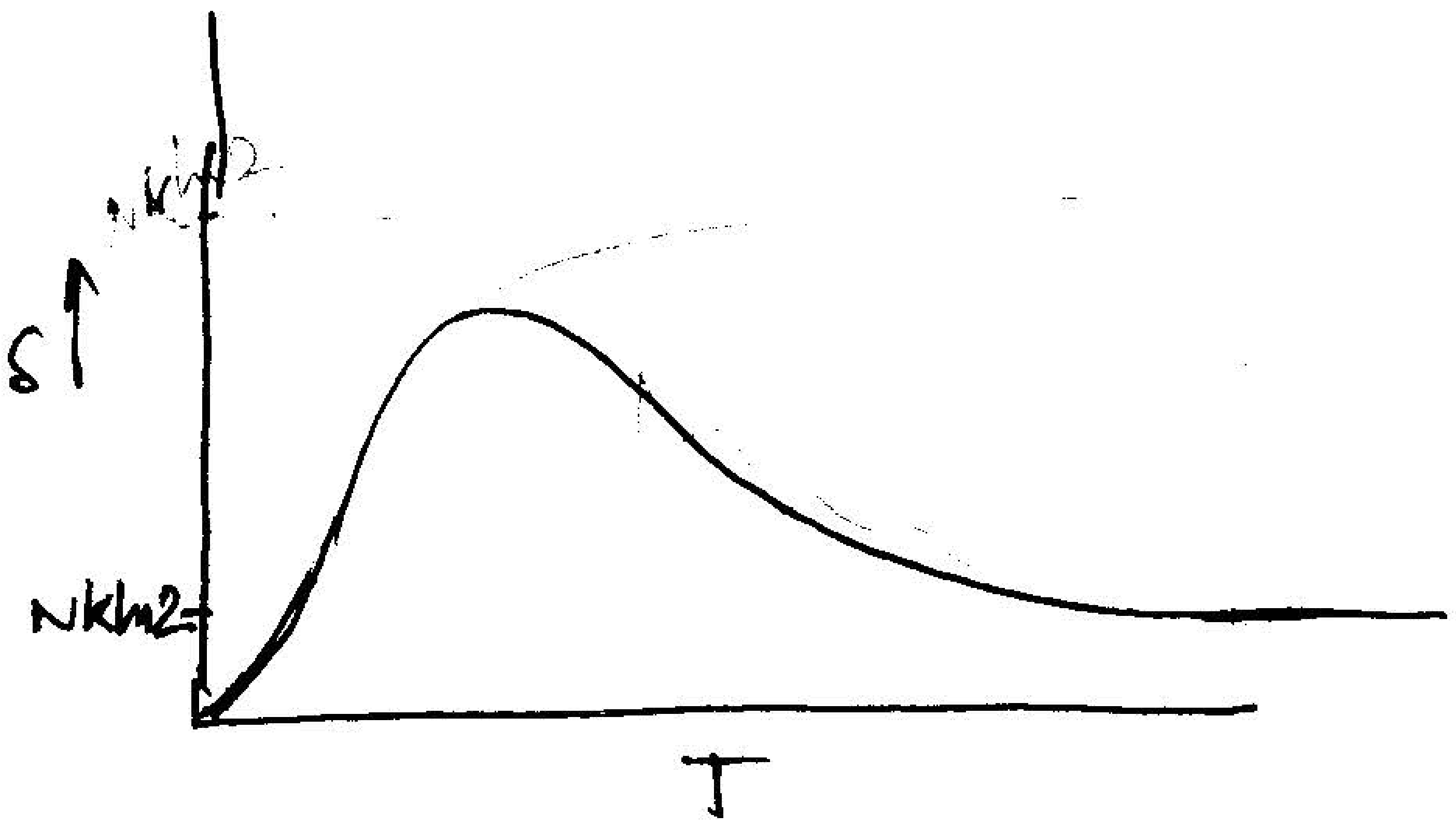


Entropy

$$S = K\ln Q + \frac{U}{T}$$

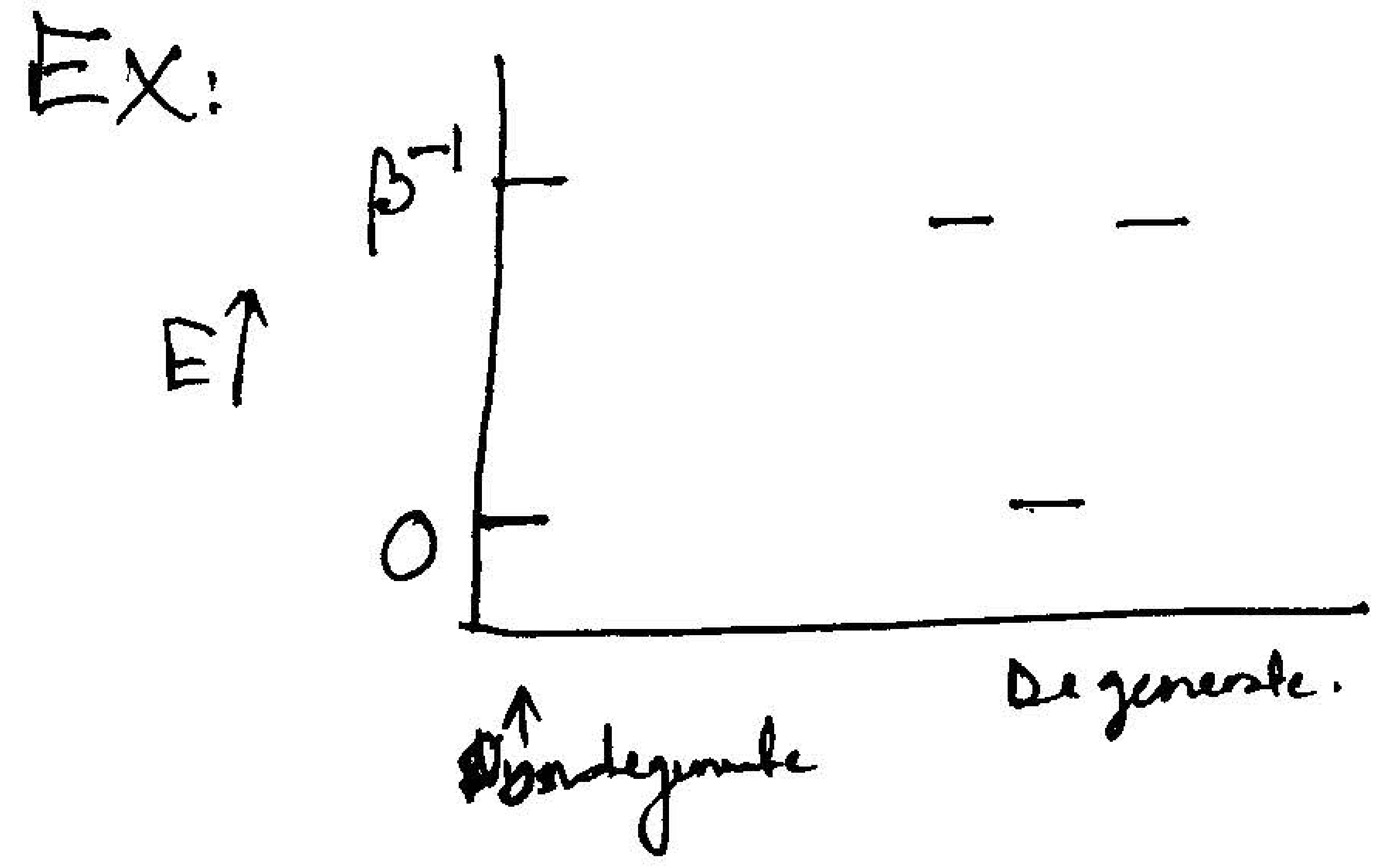
$$= K\cdot\ln\left(1+e^{-\beta\epsilon}\right)^N + \frac{N\epsilon}{T\left(1+e^{\beta\epsilon}\right)}$$

$$= NK\cdot\ln\left(1+e^{-\beta\epsilon}\right) + \frac{N\epsilon}{T\left(1+e^{\beta\epsilon}\right)}$$



* Degenerate energy states are more probable than nondegenerate energy states having same energy!

EX:



$$Z_{nd} = 1+e^{-1} = 1+0.37 = 1.37$$

$$Z_{d} = 1+2\cdot e^{-1} = 1.74$$

$$p_{g,nd} = \frac{1}{1.37} = 0.73;\; p_{e,nd} = \frac{e^{-1}}{1.37} = 0.27$$

$$p_{e,d} = \frac{1}{1.74} = 0.57,\; p_{e,d} = \frac{2e^{-1}}{1.74} = 0.43$$

Application 2: Free particles → Ideal gas.

N no. of particles in volume, V, at temperature T. Particles are noninteracting & they all have same mass, m. We also assume that the particles are ~~noninteracting and~~ distinguishable.

The partition function for the entire system ⇒ $Q = q^N$

↳ partition function for one partic

One particle function, $q = \frac{1}{h^3}\int_p\int_q e^{-\beta H(\{p,q\})}\, dq^3 dp^3$

The h^3 term is introduced to make the partition function dimensionle

h has the dimension of $(q \times p)$.

$$q = \frac{1}{h^3}\int_p\int_q e^{-\beta\left(\sum_{i=1}^{3} p_i^2/2m\right)} \cdot dq^3 dp^3$$

$$= \frac{1}{h^3}\int_{p_x}\int_{p_y}\int_{p_z}\int_{q_x}\int_{q_y}\int_{q_z} \cdot e^{-\beta\left(\sum_i p_i^2/2m\right)} \cdot dq_x\, dq_y\, dq_z \cdot dp_x\, dp_y\, dp_z$$

$$= \frac{1}{h^3}\int^{+\infty}\int^{+\infty}\int^{+\infty}\int^{L_x}\int^{L_y}\int^{L_z} e^{-\beta p_x^2/2m} \cdot e^{-\beta p_y^2/2m} \cdot e^{-\beta p_z^2/2m} \cdot dq_x\, dq_y\, dq_z \cdot dp_x\, dp_y\, dp_z$$

$$= \frac{L_x L_y L_z}{h^3} \int_{-\alpha}^{+\alpha} e^{-\frac{p_x^2}{2mKT}} \cdot dp_x \int_{-\alpha}^{+\alpha} e^{-\frac{p_y^2}{2mKT}} dp_y \int_{-\alpha}^{+\alpha} e^{-\frac{p_z^2}{2mKT}} dp_z$$

$$= \frac{V}{h^3} \cdot (2\pi mKT)^{1/2} (2\pi mKT)^{1/2} (2\pi mKT)^{1/2}$$

$$q = \frac{V}{h^3} \cdot (2\pi mK_iT)^{3/2}$$

For N particles. $\boxed{Q = \frac{V^N}{h^{3N}} \cdot (2\pi mKT)^{3N/2}} \boxed{= V^N \left(\frac{2\pi mKT}{h^2}\right)^{3N/2}}$

Helmholtz free energy. $A = -KT \ln Q$

$$= -NKT \left[\ln V + \frac{3}{2} \ln\left(\frac{2\pi mKT}{h^2}\right)\right]$$

$$= -NKT \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{2\pi mK}{h^2}\right)\right]$$

Pressure

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$$

$$= NKT \frac{\partial}{\partial V} (\ln V) = \frac{NKT}{V} \rightarrow \quad PV = NKT \text{ or } \boxed{PV = nRT}$$

ideal gas law!

Average energy

$$U = \langle \epsilon \rangle = KT^2 \cdot \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

$$= KT^2 \cdot N \cdot \frac{\partial}{\partial T} \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{2\pi mK}{h^2}\right)\right]$$

$$= NKT^2 \cdot \frac{3}{2} \cdot \frac{1}{T}$$

$\boxed{\langle \epsilon \rangle = \frac{3}{2} NKT} = \boxed{\frac{3}{2} nRT}$ n = no. of moles of gas.
R = gas constant.

Heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{\partial}{\partial T}\left(\frac{3}{2} NKT\right) = \frac{3}{2} NK = \frac{3}{2} nR,$$

molar heat capacity at constant volume.

Entropy:

Enthalpy, $H = U + PV = \frac{3}{2}NKT + NKT = \frac{5}{2}NKT$

Heat Capacity at constant Pressure $C_p = \left(\frac{\partial H}{\partial T}\right)_P = \frac{5}{2}NK = \frac{5}{2}nR$

molar $\bar{C}_p = \frac{5}{2}R$

$\bar{C}_p - \bar{C}_v = R$

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

$$= NKT \cdot \frac{3}{2T} + NK\left[\ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln\left(\frac{2\pi mk}{h^2}\right)\right]$$

$$= NK\left[\ln V + \frac{3}{2}\left\{\ln T + \ln\left(\frac{2\pi mk}{h^2}\right) + 1\right\}\right]$$

$$= NK\left[\ln V + \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2} + \frac{3}{2}\right]$$

$$S = NK\left[\ln\left\{V \cdot \left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{3}{2}\right]$$

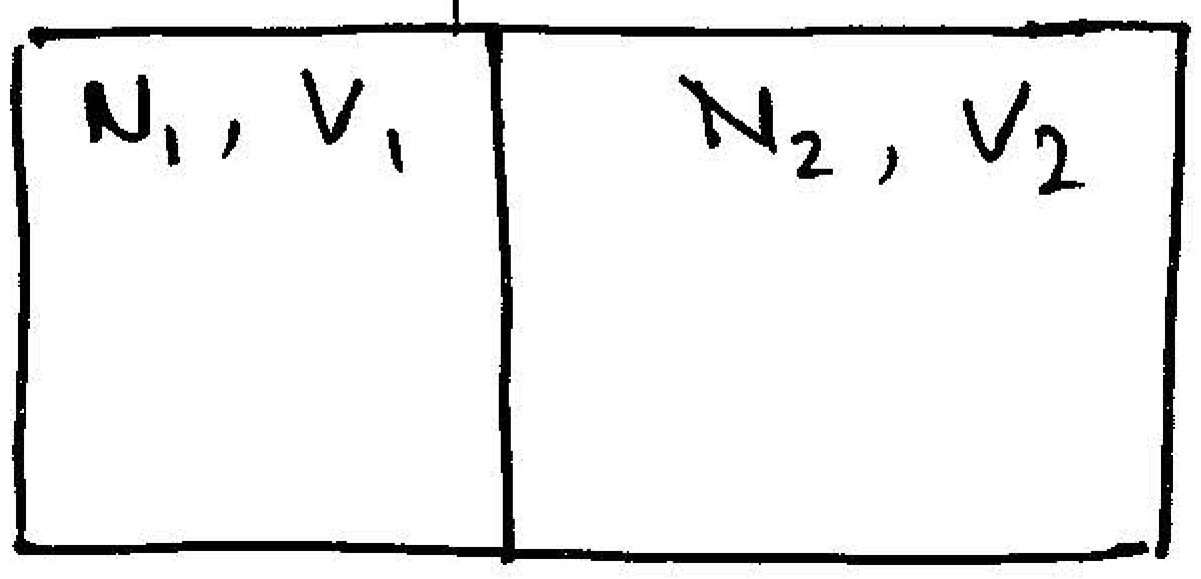
By definition entropy must be extensive quantity. Thus When ~~by~~ the no. of molecules (N) and Volume (V) are changed by a common factor, entropy must scale accordingly.

$N' \to aN$, $V' \to aV$ then entropy $S' \to aS$.

$S' = aNK\left[\ln\left\{aV\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right\} + \frac{3}{2}\right]$ thus entropy doesn't scale!

Gibbs Paradox:

Entropy of mixing ~~two~~ of a gas kept in two diffent containers at same temperature. The density of gas in two containers are same but the no. of molecules and volume of containers are different.



T. kept const.

density of gas. $\rho = \frac{N_1}{V_1} = \frac{N_2}{V_2}$ is same in both Containers.

Now if the partition is lifted then the molecules of the gas swap their position (mixing):

Now since the density is same and the same gas is mixed, the entropy change $\Delta S = 0$.

entropy before mixing, $S_{bf} = S_1 + S_2$

$$= \left[N_1 k \ln V_1 + \frac{3}{2} N_1 k + N_1 k \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$
$$+ \left[N_2 k \ln V_2 + \frac{3}{2} N_2 k + N_2 k \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$

After mixing,

$$N = N_1 + N_2, \quad V = V_1 + V_2.$$

The entropy

$$S_m = (N_1+N_2)k \ln(V_1+V_2) + \frac{3}{2}(N_1+N_2)k + (N_1+N_2)\ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

Change of entropy, $\Delta S = S_m - S_{bf}$

$$= (N_1+N_2)k \ln(V_1+V_2) - N_1 k \ln V_1 - N_2 k \ln V_2$$
$$= N_1 k \ln\left(\frac{V_1+V_2}{V_1}\right) + N_2 k \ln\left(\frac{V_1+V_2}{V_2}\right)$$
$$= N_1 k \ln\left(\frac{V}{V_1}\right) + N_2 k \ln\left(\frac{V}{V_2}\right) > 0 \quad \text{as } V > V_1 \text{ \& } V > V_2$$

Thus this is paradoxical to the knowledge about the system. and it is known as Gibbs paradox.

We assumed that the particles are distinguishable thus exchange of particles during mixing leads to a new microstates. Therefore the entropy of mixing ~~is~~ nonzero. If we assume that the particles are indistinguishable then the partition function,

$$Q = \frac{q^N}{N!}$$

$$Q = \frac{V^N}{N!\,h^{3N}} \cdot (2\pi mkT)^{3N/2} = \frac{V^N}{N!} \cdot \left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

Modified ~~entropy~~, Helmholtz free energy.

$$A = -kT \ln Q$$
$$= -NkT\left\{\ln V + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right)\right\} + kT \ln N!$$
$$= -NkT\left\{\ln V + \frac{3}{2}\ln\left(\frac{2\pi mkT}{}\right)\right\} + NkT \ln N - NkT$$

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

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

$$\boxed{S = NK\left[\ln\left(\frac{V}{N}\right) + \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2} + \frac{5}{2}\right]}$$

Sackur-Tetrode relation

① Now if $N' = aN$, $V' = aV$,

$$S' = aNk\left[\ln\left(\frac{aV}{aN}\right) + \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2} + \frac{5}{2}\right]$$

$\boxed{S' = aS}$ Thus entropy scales with system's size!

② Entropy of mixing.

$$\Delta S = S_m - S_{bm}$$

$$= (N_1+N_2)k\left[\ln\left(\frac{V_1+V_2}{N_1+N_2}\right) + \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2} + 5/2\right]$$

$$- \sum_{i=1}^{2} N_i k\left[\ln\left(\frac{V_i}{N_i}\right) + \ln\left(\frac{2\pi mkT}{h^2}\right)^{3/2} + 5/2\right]$$

$$= N_1 k\ln\left(\frac{V}{N}\right) - N_1 k\ln\left(\frac{V_1}{N_1}\right) + N_2 k\ln\left(\frac{V}{N}\right) - N_2 k\ln\left(\frac{V_2}{N_2}\right)$$

$$= N_1 k\ln\left(\frac{V}{N}\cdot\frac{N_1}{V_1}\right) + N_2 k\ln\left(\frac{V}{N}\cdot\frac{N_2}{V_2}\right)$$

$$= 0$$

Since, $\rho = \frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V}$

& $\ln(1) = 0$

Molecular partition function:

For poly-atomic molecules there are four energetic degrees of freedom

- Translation
- Rotation
- Vibration &
- Electronic

Assuming that the energetic degrees of freedom are not coupled The total energy can be written as the sum of all the energies.

$$\epsilon_T = \epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e$$

For a molecule.

$$q_{Total} = \sum g_{total} e^{-\beta\epsilon_T}$$

$$= \sum g_t \cdot g_r \cdot g_v \cdot g_e \, e^{-\beta\epsilon_t} \cdot e^{-\beta\epsilon_r} \cdot e^{-\beta\epsilon_v} \cdot e^{-\beta\epsilon_e}$$

$$= q_t \cdot q_r \cdot q_v \cdot q_e .$$

Therefore molecular partition function can be written as product of partition function of each molecular energetic degree of freedom.

For N number of distinguishable molecules.

$$Q_{total} = q_t^N \quad \text{(distinguishable)}$$

$$= \frac{1}{N!} q_t^N \quad \text{(for indistinguishable).}$$

$$Q_{total}(N,V,T) = q(V,T)^N$$

$$= q_t(V,T) \cdot q_r(T) \cdot q_v(T) \cdot q_e(T)$$

The probability that the molecule is in ith translational, jth rotational, kth vibrational and lth electronic state:

$$P_{ijkl} = \frac{e^{-\beta\epsilon_i^{tran}} \cdot e^{-\beta\epsilon_j^{rot}} \cdot e^{-\beta\epsilon_k^{vib}} \cdot e^{-\beta\epsilon_l^{ele}}}{q_t \cdot q_r \cdot q_v \cdot q_e}$$

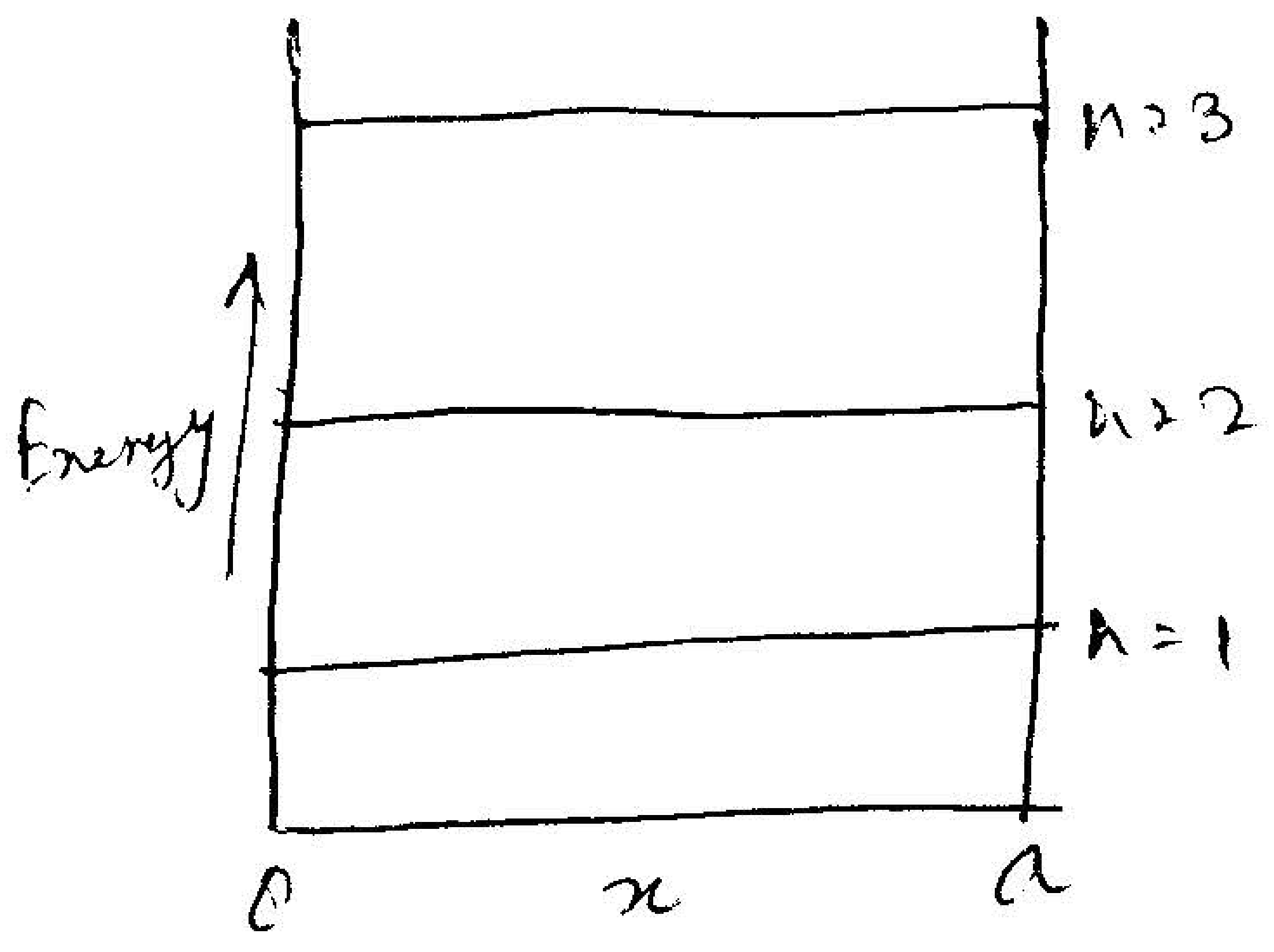
Note. prob. that the molecule is in kth vibrational state.

$$P_k^{vib} = \sum P_{ijkl} = \frac{q_t \cdot q_r \cdot e^{-\beta\epsilon_k^{vib}} \cdot q_e}{q_t \, q_r \, q_v \, q_e} = \frac{e^{-\beta\epsilon_k^{vib}}}{q_v}$$

Translational Partition Function:

Translational partition function of an atom or molecule in a container of volume V.

Particle in a one-dimensional box of length a



$$E_n = \frac{n^2h^2}{8ma^2}$$

$$q_{t,1D} = \sum_{n=1}^{\infty} e^{-\beta\frac{n^2h^2}{8ma^2}}$$

$0 \leq x \leq a$

Calculating this series sum is a difficult. But for a finite dimensional box (~cm), The energy spacing between the energy levels are very small compared to thermal energy at room temperature. ~~In that situation~~ There-fore a large number of translational energy states will be accessible ~~by the~~ at room temperature. Then the sum can be replaced by an integration. (energy is now a continuous variable). so is 'n'

$$q_{t,1D} = \int_0^{\infty} e^{-\beta\frac{n^2h^2}{8ma^2}}\,dn$$

$$= \int_0^{\infty} e^{-cn^2}\,dn$$

$$= \frac{1}{2}\sqrt{\frac{\pi}{c}}$$

$$= \frac{1}{2}\sqrt{\frac{\pi\cdot 8ma^2}{h^2\beta}} = \sqrt{\frac{2\pi mkT\,a^2}{h^2}} = \sqrt{\frac{2\pi mkT}{h^2}}\;a$$

Thermal de Broglie wavelength, $\Lambda = \sqrt{\frac{h^2}{2\pi mkT}}$,

$$q_{t,1D} = \frac{a}{\Lambda}$$

In three dimension. $q_{t,3D} = q_t = \frac{a_x}{\Lambda}\cdot\frac{a_y}{\Lambda}\cdot\frac{a_z}{\Lambda}$

$$\boxed{q_t = \frac{V}{\Lambda^3} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V}$$

As volume increases energy spacing decreases

Eg. What is the translational partition function for molecular O_2 confined in a volume 1 L at 298K ?

$$\Lambda = \sqrt{\frac{h^2}{2\pi mKT}} = \frac{6.62 \times 10^{-34}\,Js}{\sqrt{2 \times 3.14 \times 5.31 \times 10^{-25}\,kg \times 1.34 \times 10^{-23}\,JK^{-1} \times 298K}}$$

$$= \frac{6.62 \times 10^{-34}\ kg\ m^2/s^2 . s}{\left(6.26 \times 5.31 \times 1.34 \times 2.98 \times 10^{-46} \times Kg \times kg\,m^2/s^2\right)^{1/2}}$$

$$= \frac{6.62 \times 10^{-34}}{(1.32)^{1/2} \times 10^{-22}}$$

$$= 5.75 \times 10^{-12}\ m$$

$$q = \frac{V}{\Lambda^3} = \frac{1L}{\Lambda^3} = \frac{1000\ cm^3}{(5.75 \times 10^{-12})^3 \times m^3} = \frac{1000 \times cm^3 \times \left(\frac{1\,m}{100\,cm}\right)^3}{(5.75 \times 10^{-12})^3 \times m^3} = \frac{\cancel{0.001}\,1 \times 10^{-3}\,m^3}{1.9 \times 10^2 \times 10^{-36}\,m^3}$$

$$\boxed{q = 5 \times 10^{30}}$$

$$\frac{d}{dT} = -K\beta^2 \frac{d}{d\beta}$$

$$\langle \epsilon_T \rangle = -\frac{\partial \ln q}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\ln\left(\frac{2\pi mKT}{h^2}\right)^{3/2} V\right]$$

$$= -\frac{\partial}{\partial \beta}\left[\ln\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} . V\right]$$

$$= -\frac{\partial}{\partial \beta}\left[\ln\left\{\frac{1}{\beta}\right\}^{3/2} + \ln C\right]$$

$$= \frac{3}{2}N . \frac{d}{d\beta}(\ln \beta)$$

$$= \frac{3}{2}N\frac{1}{\beta} = \frac{3}{2}NKT = \frac{3}{2}RT$$

$$\overline{C}_{V,T} = \frac{d}{dT}\left(\langle E_T \rangle\right) = \frac{3}{2}R$$

Rotational partition function:

- Diatomic molecule · asymmetrical (A – B)
- Rigid rotor approximation: bond length assumed to remain const during rotational motion.
- Centrifugal distortion is neglected.

Quantum mechanical energy:

$$E_J = \cancel{B}\, J(J+1)\frac{\hbar^2}{2I}; \quad J: \text{rotational quantum number}, \ J = 0, 1, 2, 3 \cdots$$

$$= BhcJ(J+1) \qquad B: \text{rotational constant.}$$

$$\frac{\hbar^2}{2I} = Bhc \Rightarrow \frac{h}{8\pi^2 cI}$$

$$B = \frac{\hbar}{4\pi cI}$$

h; Planck's constant.

c, ~~velocity~~ speed of light

I; moment of inertia.

$$I = \mu r^2 \ ; \quad \mu: \text{reduced mass}, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

r: distance betn two atoms.

$$\boxed{q_R = \sum_J (2J+1)\, e^{-\beta hcBJ(J+1)}}$$

Because rotational energy level spacing are small compared to thermal energy at r.t.

$$q_R = \int_0^\infty (2J+1)\, e^{-\beta hcBJ(J+1)} dJ$$

kT = 205 cm⁻¹ at 298K

B values are less than kT ~~value~~ for most of the diatomic linear molecules except H_2. For H_2 large B because of small mass so small I.

$$\frac{d}{dJ} e^{-\beta hcBJ(J+1)} = -\beta hcB\left[(J+1) + J\right] \cdot e^{-\beta hcBJ(J+1)}$$

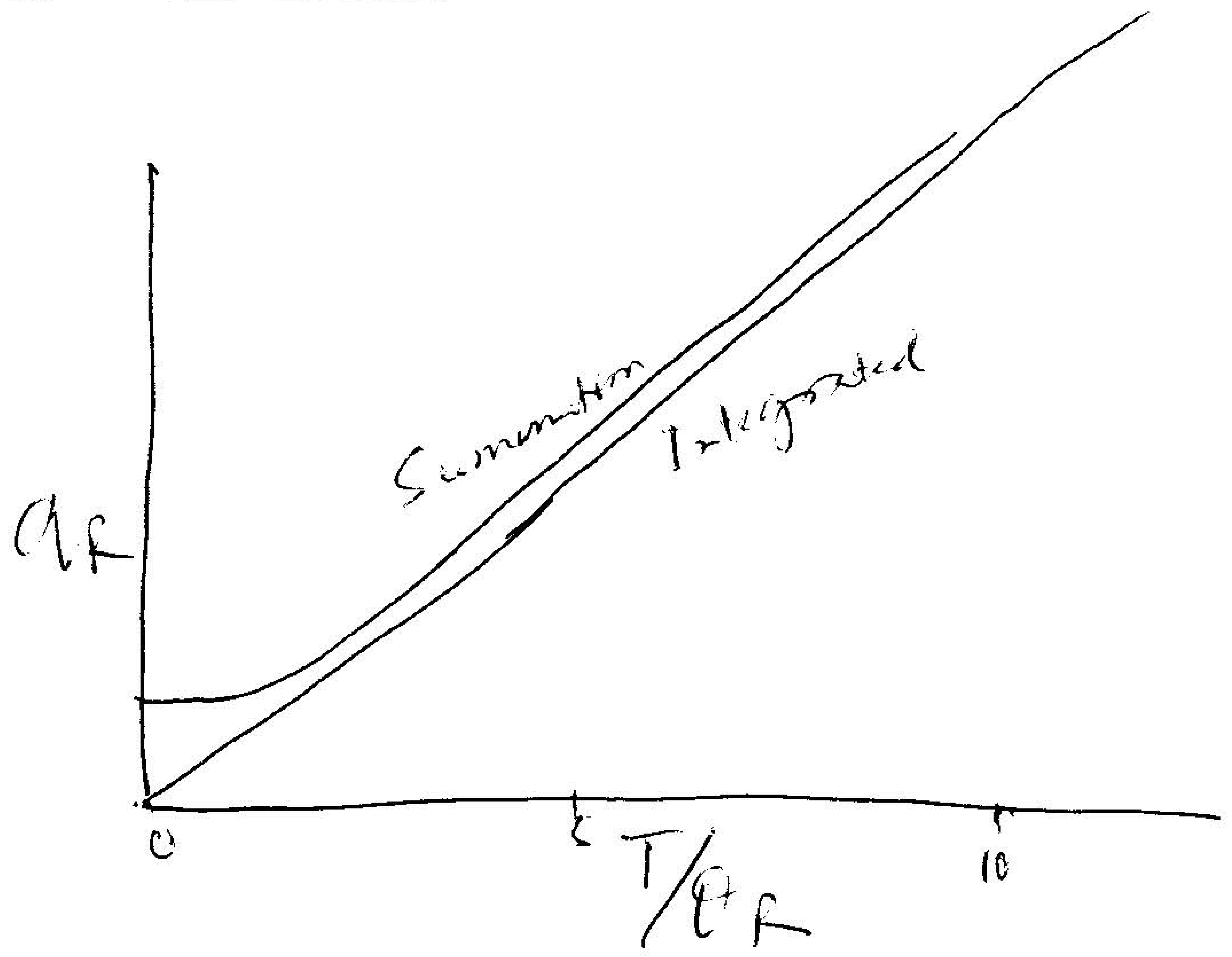
$$= -\beta hcB\,(2J+1)\, e^{-\beta hcBJ(J+1)}$$

$$q_R = -\frac{1}{\beta hcB}\int_0^\infty \frac{d}{dJ} e^{-\beta hcBJ(J+1)} dJ$$

$$= -\frac{1}{\beta hcB}\left[e^{-\beta hcBJ(J+1)}\right]_0^\infty = \frac{1}{\beta hcB} = \frac{kT}{hcB} \quad \boxed{q_R = \frac{1}{\beta hcB} = \frac{kT}{\cancel{\beta}hcB}}$$

Rotational temp. $\boxed{\theta_R = \frac{hcB}{K}}$ → high temp limit.

$\boxed{q_r = \frac{T}{\theta_R}}$



high temp : Summation = Integrated. because ~~[illegible]~~ because thermal energy > rotational energy gap. ~~[illegible]~~

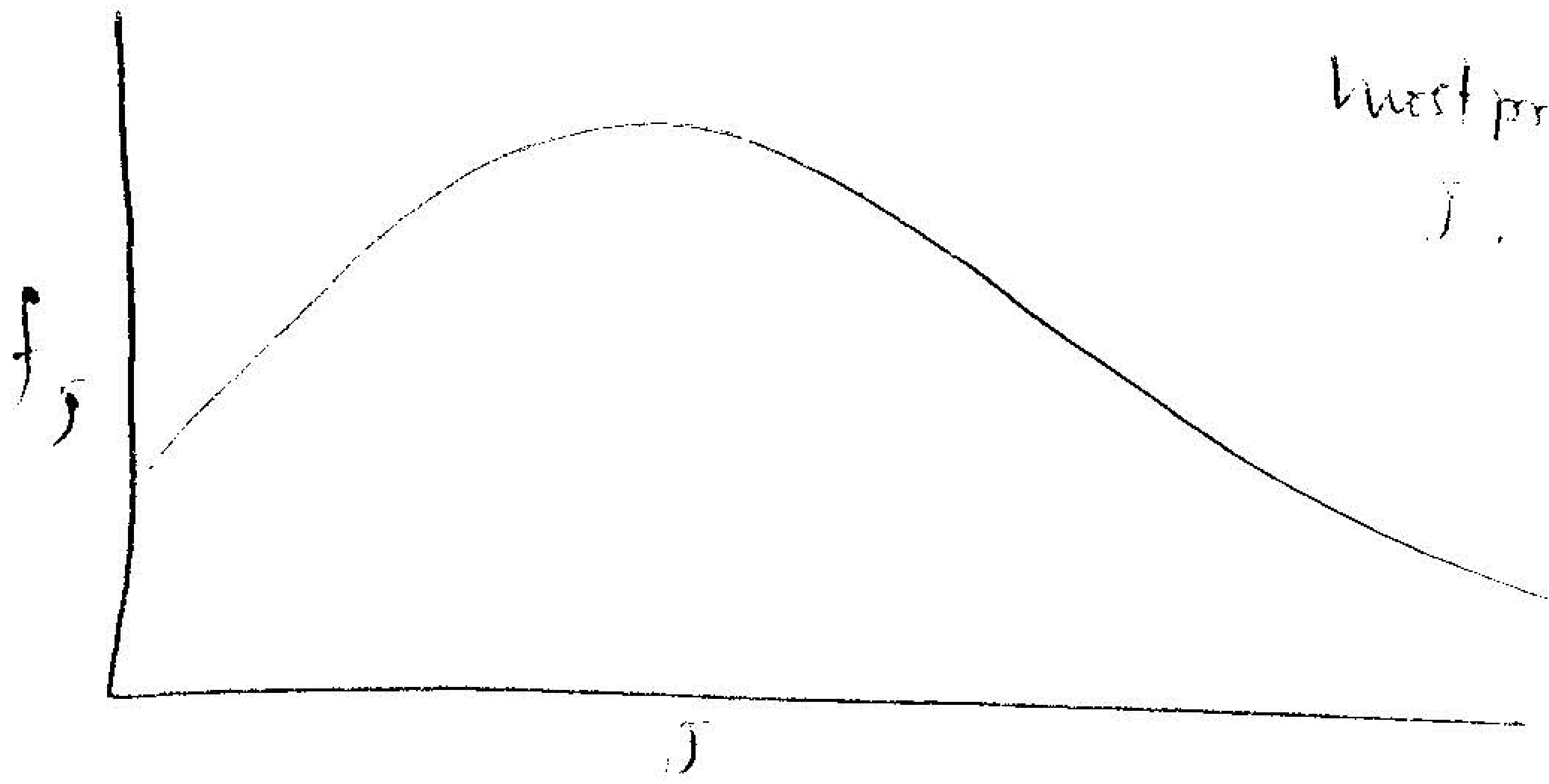
$\boxed{T > \theta_R \times 10}$ → Sum ≃ Integration.

H_2 $\theta_R = 85.3$ K, large. thus it is better to use summation series but for most other diatomics high temp limit gives good result because low θ_R.

$$\langle E_R \rangle = -\frac{\partial \ln q_r^N}{\partial \beta} = -N \frac{\partial \ln q_r}{\partial \beta} = -N \frac{\partial}{\partial \beta}\left(\frac{1}{\beta hcB}\right) = -N \frac{1}{Bhc}\cdot\left(-\frac{1}{\beta^2}\right)$$

$$= \frac{N}{Bhc}\cdot(KT)^2 = \frac{N(KT)^2}{\frac{h}{8\pi^2 I}hc} = \frac{N(KT)^2 \cdot 8\pi^2 I}{h^2}$$

$$f_J = \frac{(2J+1)\cdot e^{-\beta hcJ(J+1)/kT}}{q_{rot}} = \frac{(2J+1)\,e^{\theta_R J(J+1)/T}}{q_{rot}}$$



most probable J. } J_{mp} : $\frac{\partial f_J}{\partial J} = 0 = \gamma \cdot e^{-\theta_R J(J+1)/T}$

$\simeq \left(\frac{T}{2\theta_R}\right)^{1/2} - \frac{1}{2}$

Most probable J or J_{max}:

$\theta_R = \frac{Bhc}{K}$

$$f_J = \frac{g_J \cdot e^{-\beta G_J}}{q_{rot}} = \frac{(2J+1)\cdot e^{-\beta hcBJ(J+1)}}{(T/\sigma\theta_R)}$$

J_{max}: The value of J where f_J has maxima.

$$\frac{df_J}{dJ} = 0 = \frac{d}{dJ}\left[\frac{(2J+1)\cdot e^{-\beta hcBJ(J+1)}}{(T/\sigma\theta_R)}\right]$$

$$= \frac{d}{dJ}\left[(2J+1)\cdot e^{-\beta hcBJ(J+1)}\right] = 0.$$

$$\Rightarrow \left[2\cdot e^{-\beta hcBJ(J+1)} - (2J+1)\cdot\beta hcB\cdot(2J+1)\cdot e^{-\beta hcBJ(J+1)}\right] = 0$$

$$2 - \beta hcB(2J+1)^2 = 0$$

$$(2J+1)^2 = \frac{2}{\beta hcB}$$

$\Rightarrow$ At what temp f_J maximized?

$$J_{max} = \frac{1}{2}\sqrt{\frac{2}{\beta hcB}} - \frac{1}{2}$$

$$= \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

$$\boxed{J_{max} = \sqrt{\frac{T}{2\theta_R}} - \frac{1}{2}}$$

$$\frac{2}{\beta hcB} = (2J+1)^2$$

$$2\frac{kT}{hcB} = (2J+1)^2$$

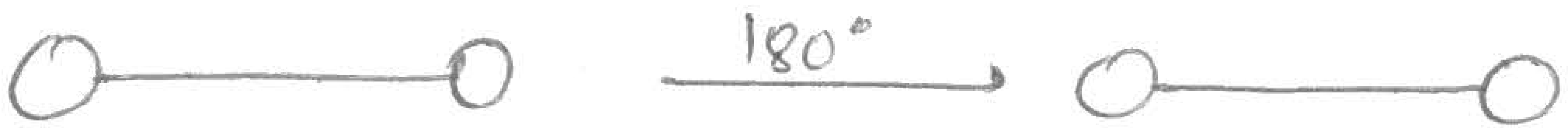
$$\frac{2T}{\theta_R} = (2J+1)^2$$

$$\boxed{T = \frac{1}{2}\cdot\theta_R(2J_{max}+1)^2}$$

Symmetry no.

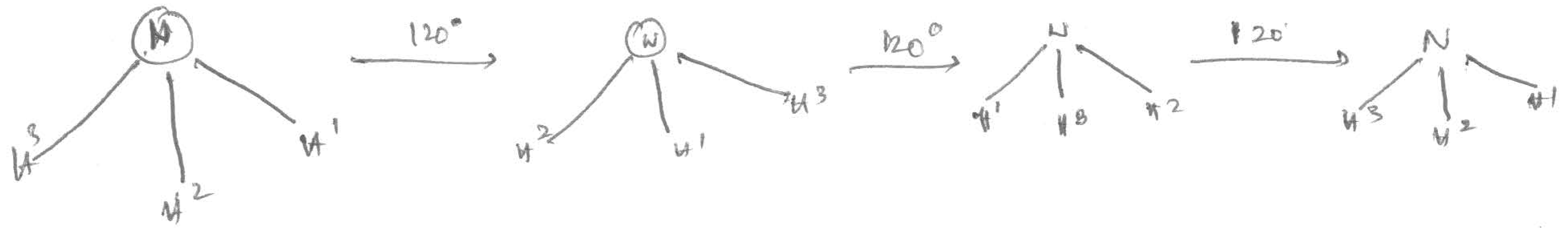
two distinct states.

but for ~~homo~~ homonuclear.



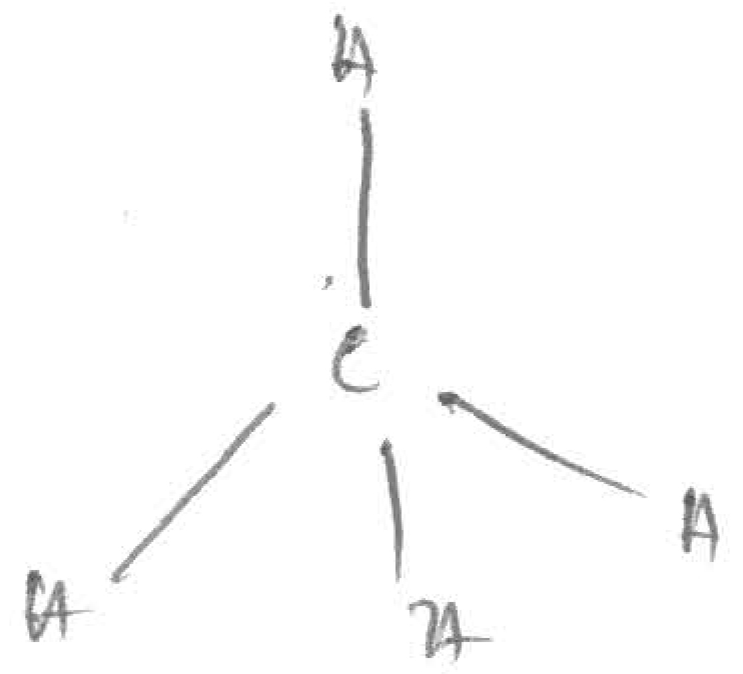
indistinguishable.

$q_r = \frac{T}{\sigma\theta_r} = \frac{kT}{\sigma Bhc}$, σ = symmetry no. ⇒ no. of equivalent representations occur due to rotation.



$\sigma = 3$

CH$_4$.



$\sigma = 4 \times 3$.

σ = Order of rotational subgroup.
= i.e. total no. of elements in the rotational subgroup including identity.

e.g. H_2O, $\{E, C_2\}$, $\sigma = 2$

NH_3 $\{E, 2C_3\}$ $\sigma = 3$

CH_4, $\{E, 8C_3, 2C_2\} = \sigma = 12$

C_6H_6, $\sigma = 2$

Nonlinear molecule.

Linear rotor: $I_A = I_B,\ I_C = 0,\quad E_J = \frac{\hbar^2}{2I}J(J+1) = hcBJ(J+1),\quad q_r = \frac{1}{\sigma}\sum_J (2J+1)\cdot e^{-\beta hcBJ(J+1)}$

$g_J = (2J+1)$

$$= \frac{1}{\sigma}\sum_J (2J+1)\cdot e^{-\frac{\theta_R}{T}J(J+1)}$$

if $T > \theta_R$
$$\simeq \frac{1}{\sigma}\cdot\left(\frac{T}{\theta_R}\right) = \frac{1}{\sigma}\cdot\left(\frac{1}{\beta hcB}\right)$$

$$= \frac{1}{\sigma}\cdot\left(\frac{1}{\beta hcB}\right)^{1/2}\left(\frac{1}{\beta hcB}\right)^{1/2}$$

$$= \frac{1}{\sigma}\cdot\left(\frac{T}{\theta_R}\right)^{1/2}\cdot\left(T/\theta_R\right)^{1/2}$$

- Sherical ~~rotor~~:

$I_A = I_B = I_C,\quad E_J = \frac{\hbar^2}{2I}J(J+1),\quad g_J = (2J+1)^2 \qquad J = 0, 1, 2, 3 \ldots$

$$q_r = \frac{1}{\sigma}\sum_{J=0}^{\infty}(2J+1)^2 e^{-\frac{\hbar^2}{2I}J(J+1)} = \frac{1}{\sigma}\sum_{J=0}^{\infty}(2J+1)^2\cdot e^{-\frac{\cancel{I}\theta_R}{\cancel{\theta_R}T}J(J+1)}$$

; For all Spherical top molecule.
- $\theta_R \ll T$, large J will be populated
- J treated as continuous variable. so $J \gg 1$

$$\simeq \frac{1}{\sigma}\int_0^{\infty}(2J)^2\cdot e^{-\frac{\cancel{\theta}\theta_R}{\cancel{\theta_R}}J^2}dJ = \frac{4}{\sigma}\cdot\int_0^{\infty}J^2\cdot e^{-\frac{\theta_R}{\cancel{\theta_R}T}J^2}dJ$$

$$= \frac{4}{\sigma}\cdot\frac{1}{4(\theta_R/T)}\left(\frac{\pi}{\theta_R/T}\right)^{1/2} = \frac{\pi^{1/2}}{\sigma}\cdot\left(\frac{T}{\theta_R}\right)^{3/2} = \frac{\sqrt{\pi}}{\sigma}\cdot\left(\frac{T}{\theta_R}\right)^{1/2}\cdot\left(T/\theta_R\right)^{1/2}\cdot\left(T/\theta_R\right)^{1/2}$$

- Symmetric rotor/top:

$I_A = I_B \neq I_C,\quad \theta_A = \theta_B \neq \theta_C$

$$q_r = \frac{\sqrt{\pi}}{\sigma}\cdot\left(\frac{T}{\theta_A}\right)\cdot\left(\frac{T}{\theta_C}\right)^{1/2}$$

- Asymmetric top : $I_A \neq I_B \neq I_C$,

$$q_r = \frac{\sqrt{\pi}}{\sigma}\cdot\left(\frac{T}{\theta_A}\right)^{1/2}\cdot\left(\frac{T}{\theta_B}\right)^{1/2}\cdot\left(\frac{T}{\theta_C}\right)^{1/2}$$

$$\langle E_r\rangle = -\frac{\partial \ln q_r^N}{\partial\beta} = kT^2\frac{\partial \ln q_r^N}{\partial T} = N\cdot kT^2\cdot\frac{\partial \ln q_r}{\partial T} = NkT^2\cdot\frac{\partial}{\partial T}\left[\ln(T^{3/2}) + \ln C\right]$$

$$= \frac{3}{2}NkT^2\cdot\frac{1}{T} = \frac{3}{2}NkT,\qquad \langle E_{r,m}\rangle = \frac{3}{2}N_A\cdot kT = \frac{3}{2}RT$$

$$C_V^r = \left(\frac{\partial\langle E_r\rangle}{\partial T}\right)_V = \frac{3}{2}Nk,\quad C_{V,m}^r = \frac{3}{2}R.$$

Vibrational Partition function

A diatomic molecule is having a single vibrational degrees of freedom: the vibration of chemical bond about its equilibrium bond distance. The energy of vibration given by quantum mechanical calculations is, (assuming harmonic oscillator model of vibrat

$$\epsilon_n = \left(n+\tfrac{1}{2}\right)\hbar\omega \quad \text{with } n = 0, 1, 2 \ldots\ldots$$

n: vibrational quantum number.

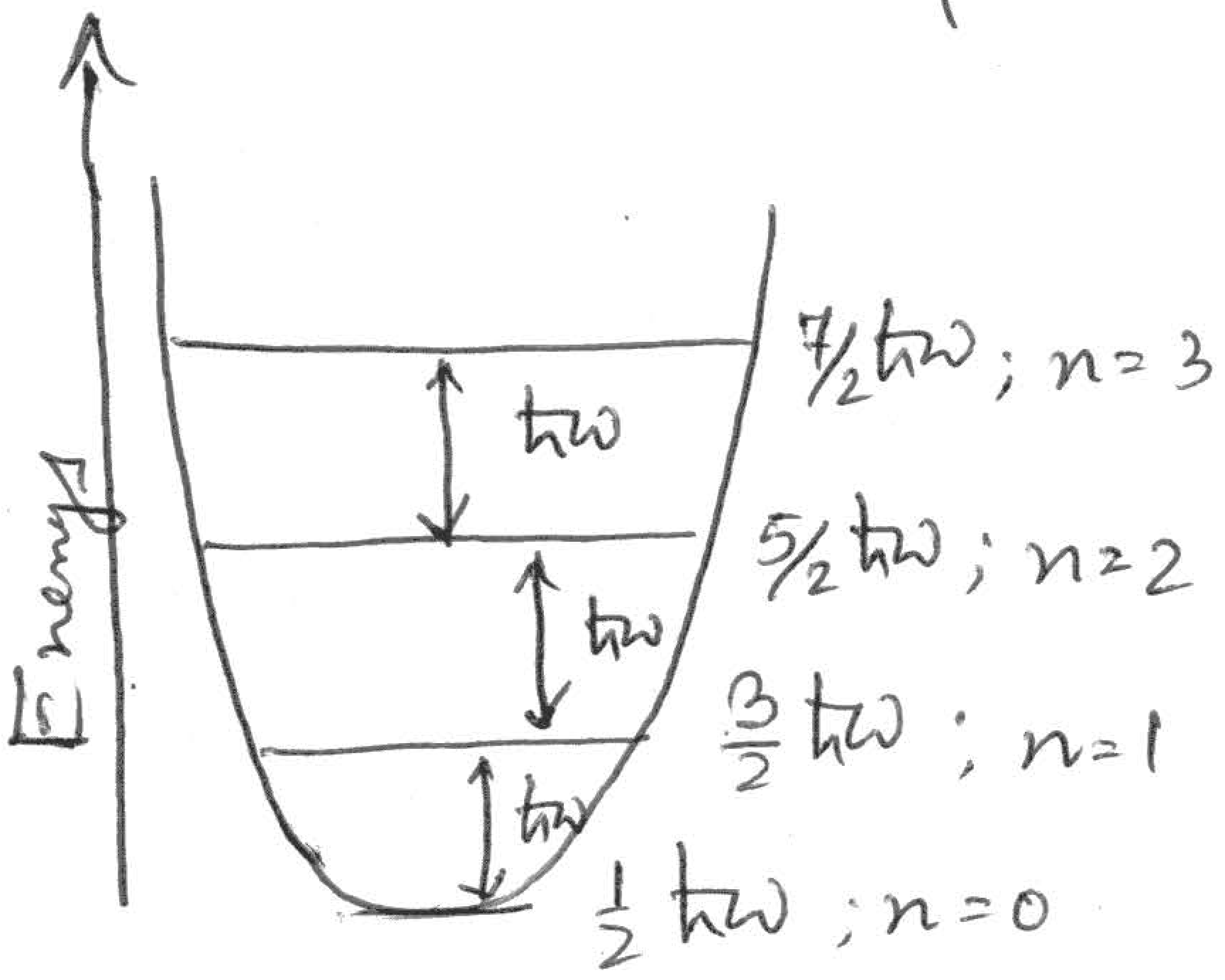
ω: angular frequency of vibration.

Alternative expressions of $\epsilon_n = \left(n+\frac{1}{2}\right)h\nu$, ν = linear frequency

$\omega = 2\pi\nu$

$= \left(n+\frac{1}{2}\right)hc\bar{\nu}$

$\bar{\nu}$ = wave number.



The energy associated with $n=0$ is $\frac{1}{2}\hbar\omega$ and it is called "zero point energy" of the quantized harmonic oscillator.

Using this expression of energy the vibrational partition function ~~for the~~ becomes.

$$q_v = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega}$$

, as vibrational energy levels are nondegenerat

$$= e^{-\frac{1}{2}\beta\hbar\omega}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}$$

$$= e^{-\frac{1}{2}\beta\hbar\omega}\sum_{n=0}^{\infty} a^n$$

assuming $a = e^{-\beta\hbar\omega}$

$$= \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-a}$$

, $\left[\ \sum_{n=0}^{\infty} a^n = \frac{1}{1-a}\right.$

$$= \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

Thus vibrational partition function q_v, ~~with~~

$$q_v = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \quad \text{with zero point energy.}$$

$$= \frac{1}{1-e^{-\beta\hbar\omega}} \quad \text{without the zero point energ}$$

Quantum harmonic oscillator:

$E_n = (n+\frac{1}{2})\hbar\omega$ energy eigen values.

Mutually independent (non interacting) distinguishable

$Z_N = Z_1^N$

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\cdot(n+\frac{1}{2})\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega}\cdot\sum_{n=0}^{\infty} e^{-n\cdot\beta\hbar\omega}$$

$$= e^{-\frac{1}{2}\beta\hbar\omega}\cdot\sum_{n=0}^{\infty}\left(e^{-\beta\hbar\omega}\right)^n$$

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

$$= e^{-\frac{1}{2}\beta\hbar\omega}\cdot\frac{1}{1-e^{-\beta\hbar\omega}}$$

$$\boxed{Z_1 = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}}$$

$$\boxed{Z_N = \frac{e^{-\frac{1}{2}N\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^N}}$$

The probability that an oscillator to be in state ψ_n with energy E_n

$$P(n) = \frac{e^{-\beta E_n}}{Z_1} = \frac{e^{-\beta(n+\frac{1}{2})\hbar\omega}\cdot(1-e^{-\beta\hbar\omega})}{e^{-\frac{1}{2}\beta\hbar\omega}}$$

$$= \frac{e^{-\frac{1}{2}\beta\hbar\omega}\cdot e^{-n\beta\hbar\omega}\cdot(1-e^{-\beta\hbar\omega})}{e^{-\frac{1}{2}\beta\hbar\omega}}$$

$$= e^{-n\beta\hbar\omega}(1-e^{-\beta\hbar\omega})$$

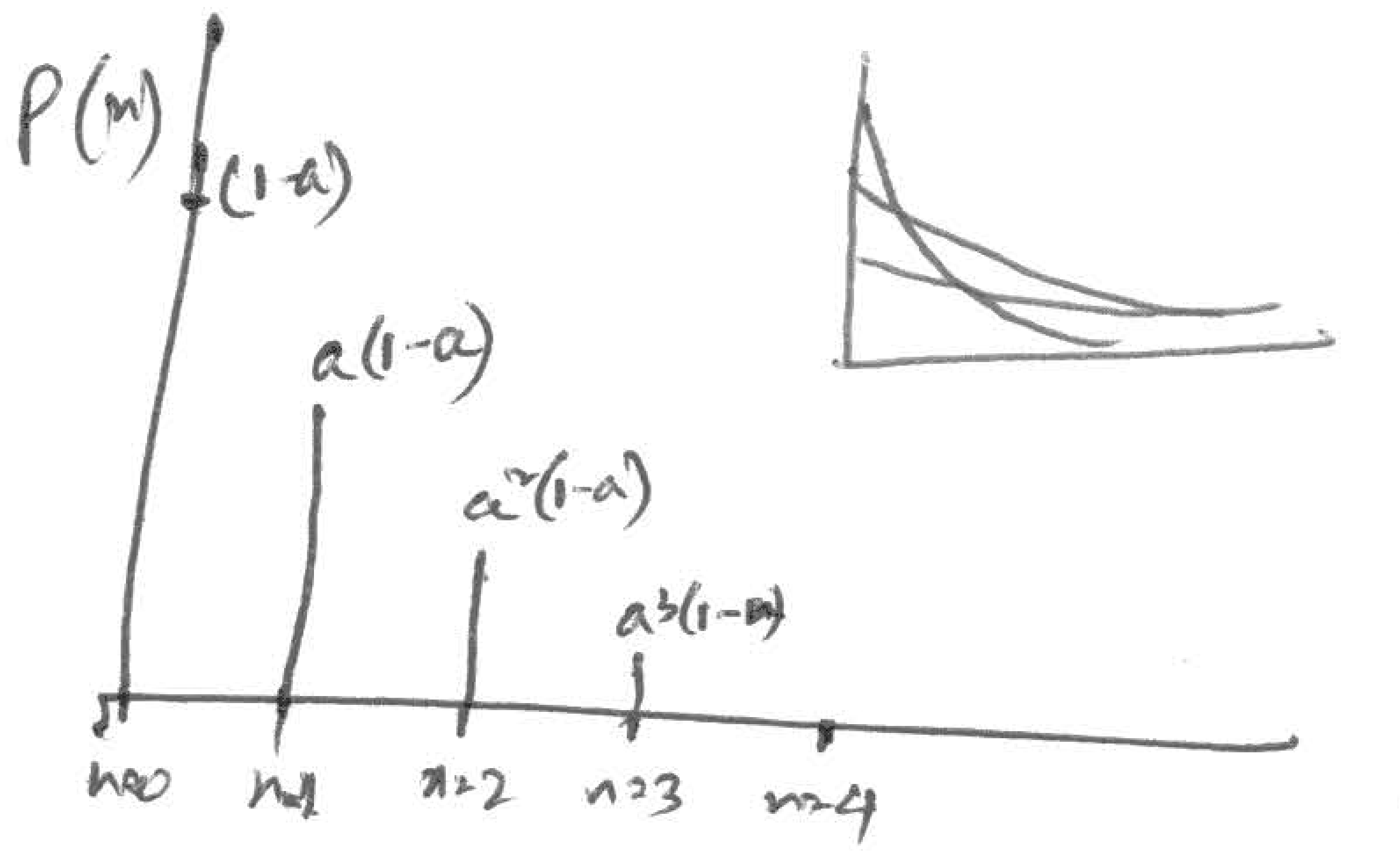
say $a = e^{-\beta\hbar\omega}$

$$\boxed{P(n) = a^n(1-a)}$$

$0 \le a \le 1$

$T\to\infty$ $\beta\to 0$ $a\to 1$

$T\to 0$ $\beta\to\infty$ $a\to 0$



average occupancy:

$$\langle n\rangle = \sum_{n=0}^{\infty} n\,P(n)$$

$$= \sum_{n=0}^{\infty} n\cdot a^n(1-a)$$

$$= (1-a)\cdot\sum_{n=0}^{\infty} n a^n = (1-a)\cdot\sum_{n=0}^{\infty} a\cdot\frac{d(a^n)}{da} = (1-a)a\cdot\frac{d}{da}\left(\sum_{n=0}^{\infty} a^n\right)$$

$$= (1-a)\cdot a\cdot \frac{d}{da}\left(\frac{1}{1-a}\right)$$

$$= \frac{a(1-a)}{(1-a)^2} = \frac{a}{1-a} = \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{1}{e^{\beta\hbar\omega}-1}$$

mean energy.

$$\langle E_n\rangle = \left\langle\left(n+\frac{1}{2}\right)\hbar\omega\right\rangle = \left(\langle n\rangle+\frac{1}{2}\right)\hbar\omega$$

$$\boxed{\langle E_n\rangle = \left(\frac{1}{e^{\beta\hbar\omega}-1}+\frac{1}{2}\right)\hbar\omega}$$

$$q = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$= \frac{1}{e^{\frac{1}{2}\beta\hbar\omega}-e^{-\frac{1}{2}\beta\hbar\omega}}$$

$$-\left(\frac{\partial \ln q}{\partial\beta}\right) = \frac{\partial}{\partial\beta}\left(\ln\left(e^{\frac{1}{2}\beta\hbar\omega}-e^{-\frac{1}{2}\beta\hbar\omega}\right)\right)$$

$$= \frac{1}{e^{\frac{1}{2}\beta\hbar\omega}-e^{-\frac{1}{2}\beta\hbar\omega}}\cdot\frac{1}{2}\hbar\omega\left(e^{\frac{1}{2}\beta\hbar\omega}+e^{-\frac{1}{2}\beta\hbar\omega}\right.$$

$$q = \left(\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right) \quad \ln q = -\frac{1}{2}\beta\hbar\omega - \ln(1-e^{-\beta\hbar\omega}$$

$$-\left(\frac{\partial \ln q}{\partial\beta}\right) = \frac{1}{2}\hbar\omega + \frac{e^{-\beta\hbar\omega}\hbar\omega}{1-e^{-\beta\hbar\omega}}$$

$$= \hbar\omega\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}\right)$$

Partition function at high temp.
$KT \gg \hbar\omega$.

$$Z_1 = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{\left(1-e^{-\beta\hbar\omega}\right)}$$

; the denominator term comes because of zero point energy.

At high temp. $(KT \gg \hbar\omega)$ there will be no meaning of zero point energy.

$$Z_1 = \frac{1}{\left(1-e^{-\beta\hbar\omega}\right)}$$

$$= \frac{1}{1-\left\{1-\beta\hbar\omega+\frac{1}{2!}(\beta\hbar\omega)^2+\cdots\right\}}$$

$$= \frac{1}{1-\left\{1-\beta\hbar\omega+O(\beta\hbar\omega^2)\right\}}$$

$$= \frac{1}{1-1+\beta\hbar\omega}$$

$$= \frac{1}{\beta\hbar\omega} = \boxed{\frac{KT}{\hbar\omega}} \longrightarrow$$ Classical oscillator partition function.

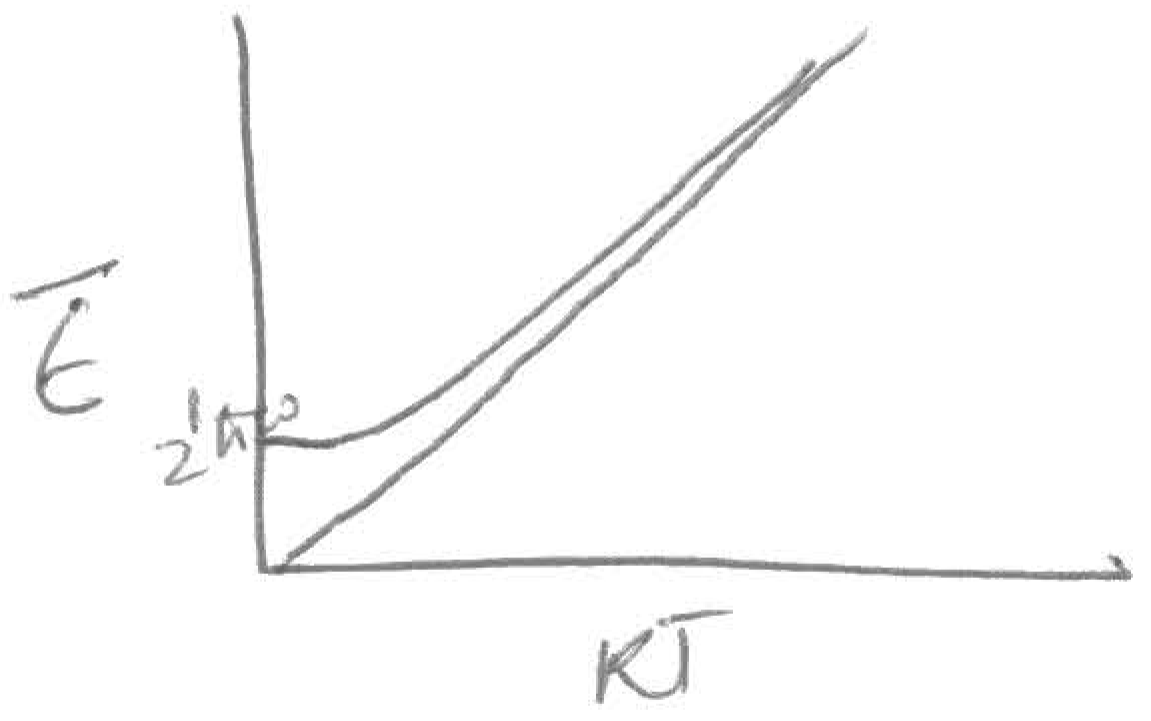
$$Z = \frac{1}{\beta\hbar\omega}, \quad \langle E\rangle = -\frac{\partial}{\partial\beta}\left(\ln\frac{1}{\beta\hbar\omega}\right) = \frac{1}{\beta\hbar\omega}\cdot\hbar\omega = KT.$$

low temp., $KT \ll \hbar\omega$, $\beta\hbar\omega \gg 1$

$$\bar{E}_n = \left(\frac{1}{e^{\beta\hbar\omega}}+\frac{1}{2}\right)\hbar\omega$$

$$= \left(e^{-\beta\hbar\omega}+\frac{1}{2}\right)\hbar\omega$$

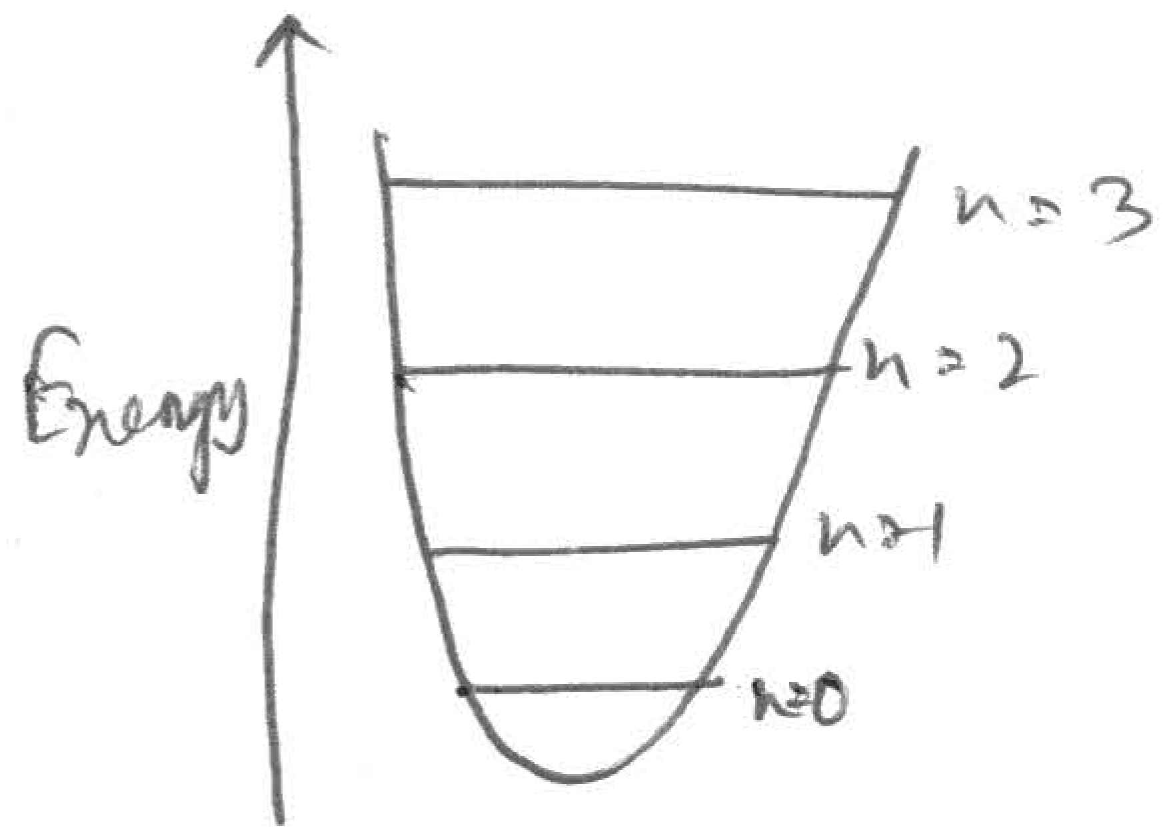
$$\approx \frac{1}{2}\hbar\omega$$



Vibrational Partition Function :

$$E_n = \left(n+\tfrac{1}{2}\right)\hbar\omega = \left(n+\tfrac{1}{2}\right)hc\tilde{\nu}$$

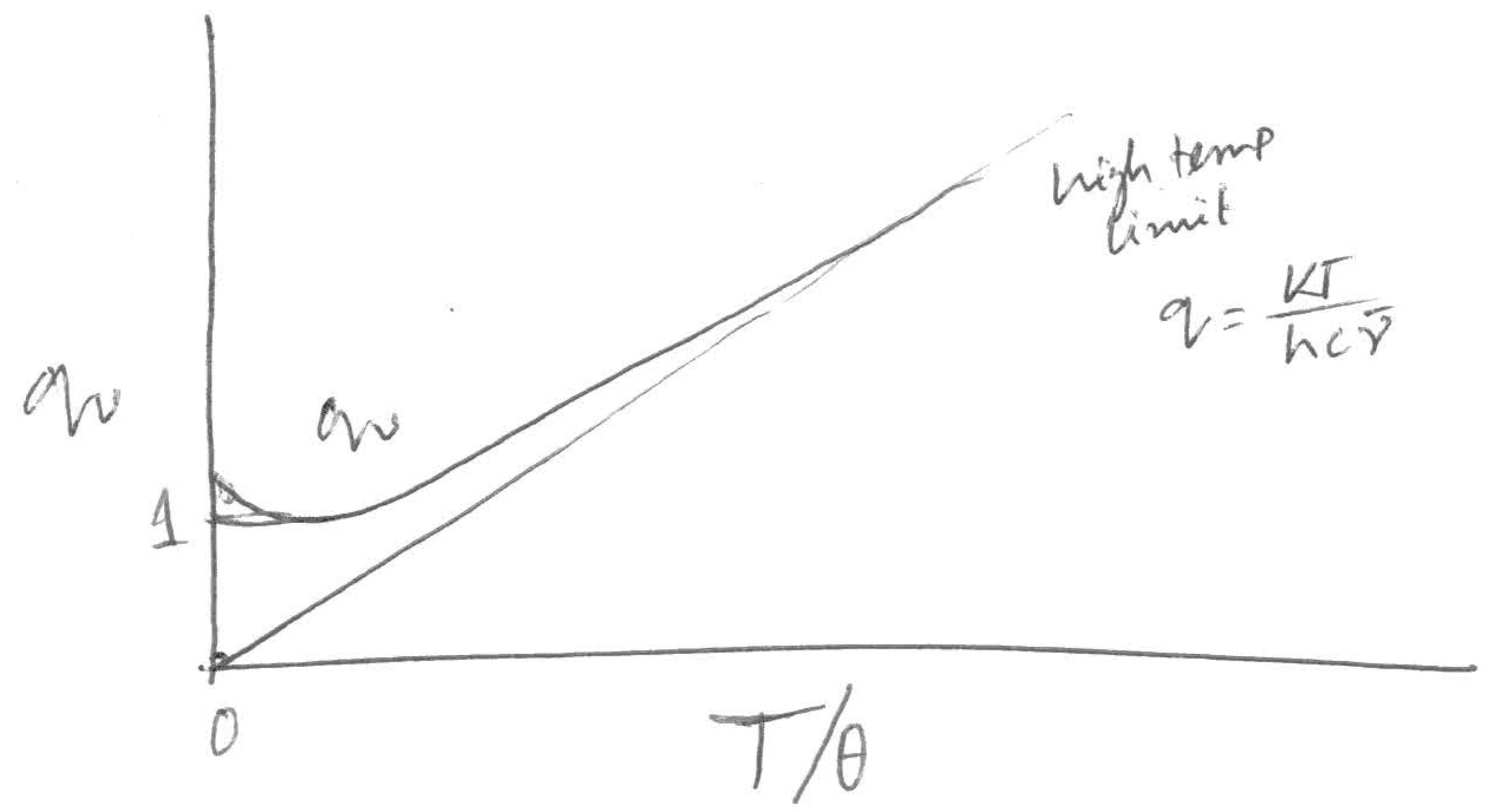
$\omega = 2\pi\nu$, $\nu = c\tilde{\nu}$
$= 2\pi c\tilde{\nu}$



$$q_v = \sum_{n=0}^{\infty} e^{-\beta E_n}$$

$$= \frac{e^{-\frac{1}{2}\beta hc\tilde{\nu}}}{1-e^{-\beta hc\tilde{\nu}}}$$

$$q_v = \frac{1}{1-e^{-\beta hc\tilde{\nu}}}$$ w/o zero point energy.



vibrational temp: $\theta_v = \frac{hc\tilde{\nu}}{k}$, $q_v = \frac{1}{1-e^{-\theta_v/T}}$

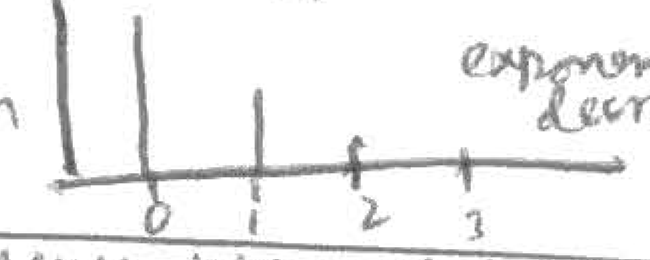
Classical limit: $T \gg \theta_v$, or $kT \gg \hbar\omega$
$kT \gg hc\tilde{\nu}$

$$\boxed{q_v = \frac{T}{\theta_v}}$$

fraction of molecules in a given vibrational states

p_n: $f_n = \frac{e^{-(n+\frac{1}{2})\theta_v/T}}{q} = \frac{e^{-(n+\frac{1}{2})\theta_v/T}}{\left(e^{-\frac{1}{2}\theta_v/T}\big/1-e^{-\theta/T}\right)}$

* $= \left(1-e^{-\theta/T}\right)\cdot e^{-n\theta/T}$



For Br_2, higher vib level is more populated because of low θ_v, hence, high mass & low k

For polyatomic molecules. (N atom)

Total no. of degree of freedom : 3N , corresponding to three cartesian degrees of freedom/coordinate for each atom

Rotational degree of freedom : 3 (nonlinear molecules,)
2 (linear molecules)

Vibrational degrees of freedom : 3N−6 (for nonlinear molecules)
: 3N−5 (for linear molecules)

Translational degrees of freedom = 3

Normal mode representation : (harmonic Vibrations)

$$\boxed{q_v = \prod_{i=1}^{3N-6 \text{ or } 3N-5} q_{v,i}}$$

Vibrational temperature : $\theta_v = \frac{hc\tilde{\nu}}{k}$. $q_v = \frac{1}{1-e^{-\theta_v/T}}$

* Br_2 : low spring constant & large mass

θ_v is low.

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$,

$\theta = \frac{hc\tilde{\nu}}{k}$

* most diatomic molecules are in ground vibrational state in room temp.

Average vibrational energy for diatomic molecules

$$\bar{U} = \langle E_{vib} \rangle = -\frac{\partial \ln q_{vib}^N}{\partial \beta} = -N \cdot \frac{\partial \ln q_{vib}}{\partial \beta} = N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)$$

$$q_{vib} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$\hbar\omega = h\nu = hc\bar{\nu} \qquad = N\cancel{h}hc\bar{\nu}\left(\frac{1}{2} + \frac{1}{e^{\beta hc\bar{\nu}} - 1}\right)$$

$$= N.K.\theta_v\left(\frac{1}{2} + \frac{\cancel{\theta_v}1}{e^{\theta/T} - 1}\right)$$

$$= NK\left(\frac{\theta_v}{2} + \frac{\theta_v}{e^{\theta_v/T} - 1}\right)$$

$$= N \cdot \langle \epsilon \rangle$$

$$\bar{C}_{V,vib} = \frac{\partial \langle E_{vib} \rangle}{\partial T} = \frac{\partial}{\partial T}\left[NK\left(\frac{\theta_v}{2} + \frac{\theta_v}{e^{\theta_v/T} - 1}\right)\right]$$

(molar)

$$= NK \cdot \frac{(-) \cdot \theta_v \cdot \theta_v \cdot (-1)\frac{1}{T^2} e^{\theta/T}}{(e^{\theta_v/T} - 1)^2}$$

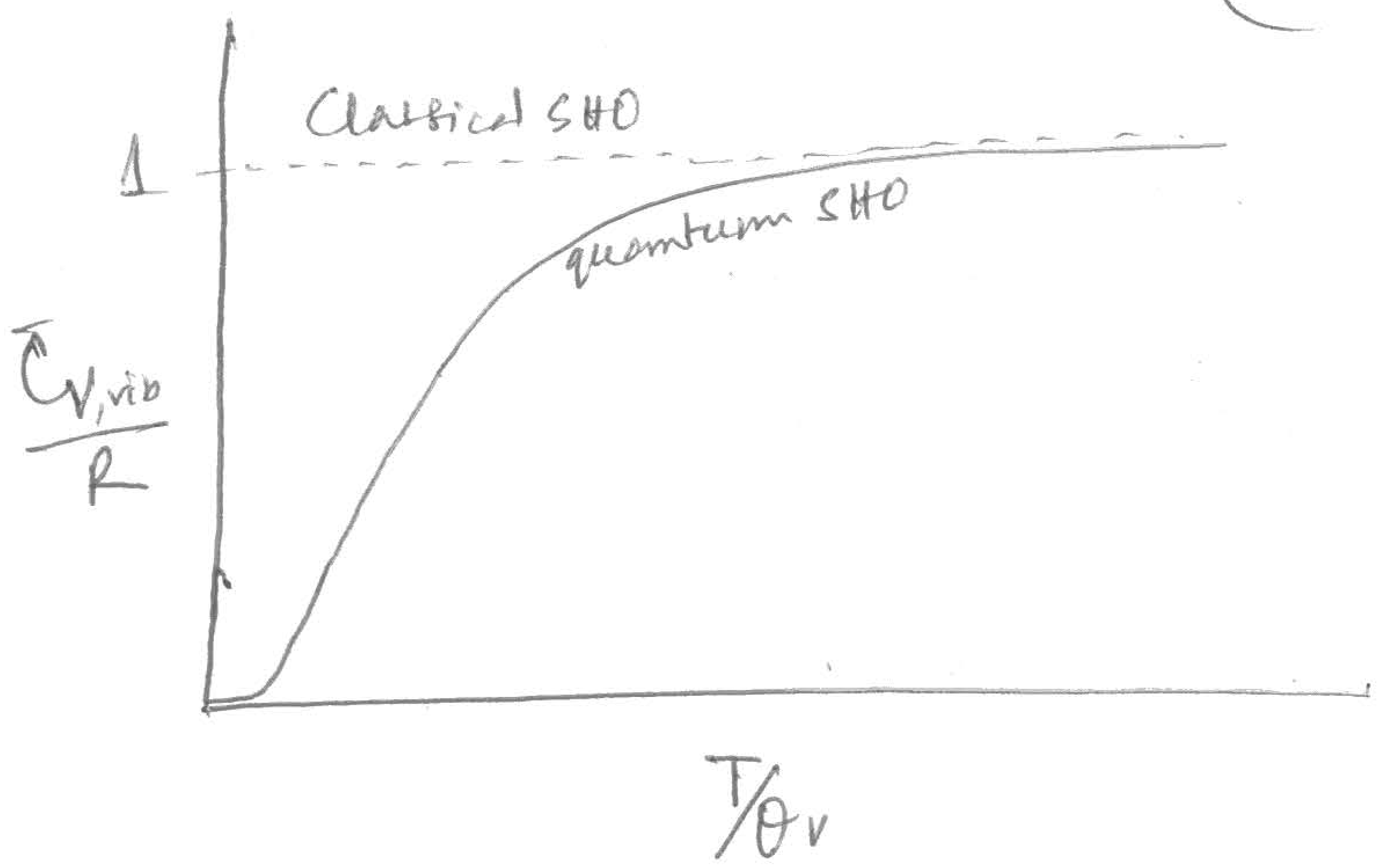
$$= NK \cdot \frac{(\theta_v/T)^2 \cdot e^{\theta/T}}{(e^{\theta_v/T} - 1)^2}$$

$$= R \cdot \left(\theta/T\right)^2 \cdot \frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2} \qquad \text{(quantum)}$$

Classical.

$\langle E \rangle = NKT = RT$

$\bar{C}_{V,vib} = R$



* high temp limit; $T \gg \theta_v$; i.e. $\theta/T \ll 1$

$$\frac{\bar{C}_{V,vib}}{R} = \left(\frac{\theta_v}{T}\right)^2 \frac{1 + \theta/T + O((\theta/T)^2)}{\left(1 + \theta/T + O((\theta/T)^2) - 1\right)^2}$$

$$= \left(\frac{\theta_v}{T}\right)^2 \cdot \frac{1}{(\theta/T)^2}$$

$$= 1$$

* low temp. limit. $T \ll \theta_v$; $\theta/T \gg 1$

$$\bar{C}_{V}/R = \left(\theta/T\right)^2 \cdot e^{-\theta/T}$$

Vibrational partition function for polyatomic molecules:

- Vibrational motion of polyatomic molecules are represented in terms of normal coordinates.
- In normal mode representation all the vibrational motions can be expressed as a set of independent harmonic ossillators.
- Total Vibrational energy of a polyatomic molecule:

$$E_V = \sum_i \epsilon_{v,i} \qquad (\text{'i' represents individual normal modes})$$

$$= \sum_i^{m} \left(n_i + \tfrac{1}{2}\right)\hbar\omega_i \qquad (n_i = 0, 1, 2, \ldots)$$

m = no. of vibrational degrees of freedom.

$m = 3N-6$; non linear polyatomic molecule.

$= 3N-5$; linear polyatomic molecule.

$$q_{vib} = \sum_i e^{-\beta\epsilon_{v,i}} = \sum e^{-\beta(n_i+\frac{1}{2})\hbar\omega_i}$$

$$= \sum_{n_1=0}^{\infty} e^{-\beta(n_1+\frac{1}{2})\hbar\omega_1} \cdot \sum_{n_2=0}^{\infty} e^{-\beta(n_2+\frac{1}{2})\hbar\omega_2} \cdots\cdots \sum_{n_m=0}^{\infty} e^{-\beta(n_m+\frac{1}{2})}$$

$$= \frac{e^{-\theta_{v,1}/2T}}{1-e^{-\theta_{v,1}/T}} \cdot \frac{e^{-\theta_{v,2}/2T}}{1-e^{-\theta_{v,2}/T}} \cdots\cdots \frac{e^{-\theta_{v,m}/2T}}{1-e^{-\theta_v/T}}$$

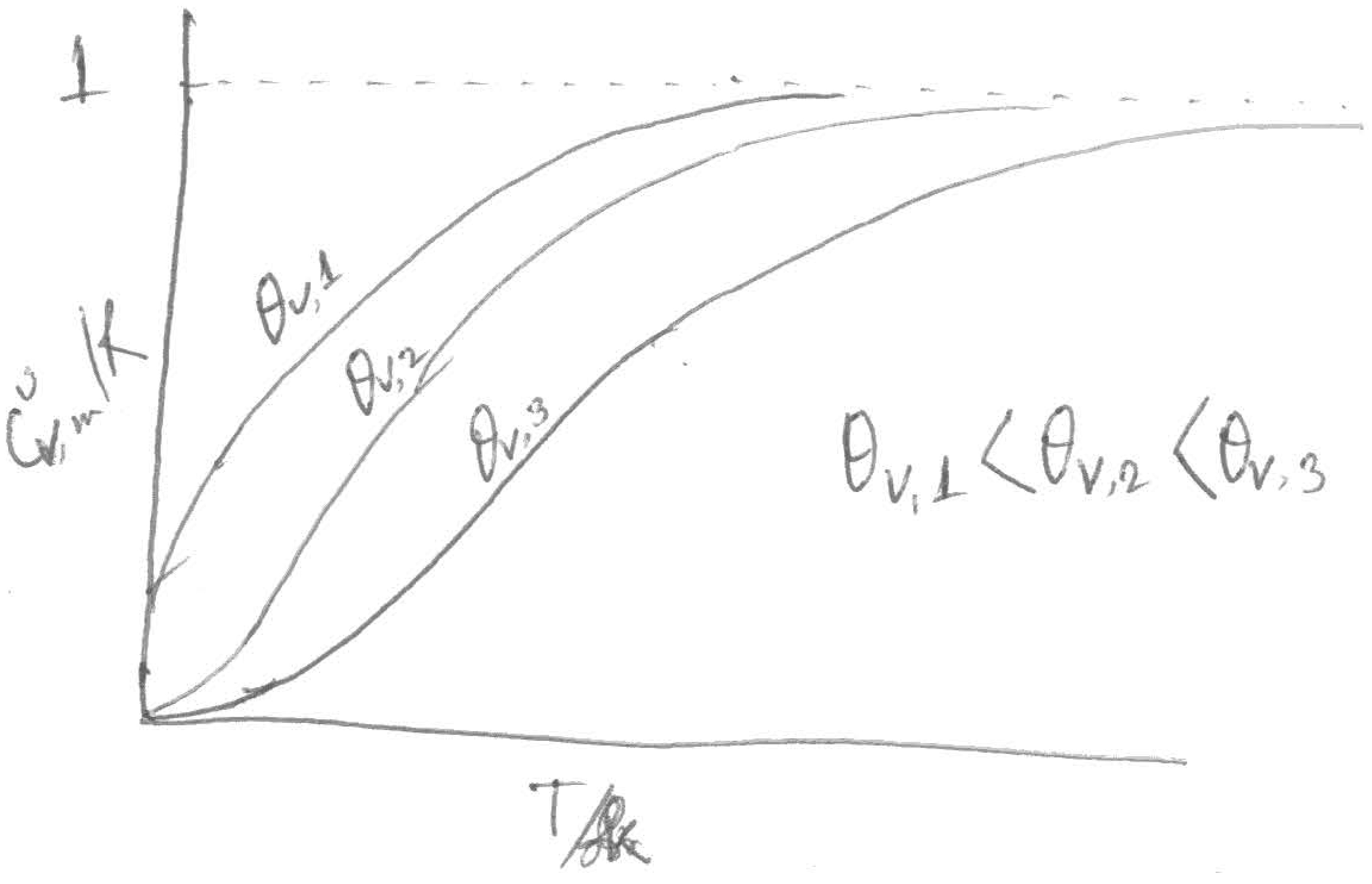
$$\boxed{q_{vib} = \prod_{i=1}^{m} \frac{e^{-\theta_{v,i}/2T}}{1-e^{-\theta_{v,i}/T}}} \quad \boxed{q_{vib} = \prod_{i=1}^{m} q_i}$$

$$\langle E_v \rangle = -\frac{\partial \ln q_{vib}^N}{\partial \beta} = -N\frac{\partial}{\partial \beta}\left[\ln\left(\prod_{i=1}^{m} q_i\right)\right] = -\frac{\partial}{\partial \beta}\left[\ln q_1 + \ln q_2 + \cdots + \ln q_m\right]$$

$$= -N\sum_{i=1}^{m} \frac{\partial \ln q_i}{\partial \beta} = NK\sum_{i=1}^{m}\left[\frac{\theta_{v,i}}{2} + \frac{\theta_{v,i}}{e^{\theta_{v,i}/T}-1}\right]$$

$$C_V^v = \left(\frac{\partial \langle E_v \rangle}{\partial T}\right)_V = NK \sum_{i=1}^{m} \left(\frac{\theta_{v,i}}{T}\right)^2 \cdot \frac{e^{\theta_{v,i}/T}}{\left(e^{\theta_{v,i}/T} - 1\right)^2}$$

$$C_{V,m}^v = \sum_{i=1}^{m} \left(\frac{\theta_{v,i}}{T}\right)^2 \cdot \frac{e^{\theta_{v,i}/T}}{\left(e^{\theta_{v,i}/T} - 1\right)^2}$$



- higher the value of θ_V, ~~lower~~ is the probability for the population to be in the higher ~~other~~ vibrational energy levels at a given temp.

$$p_n = \frac{e^{-n\theta_v/T}}{q} = e^{-n\theta_v/T}\left(1 - e^{-\theta_v/T}\right)$$

- The relative magnitudes of θ_V and T determines the probability.
- For most diatomic molecule (except Br_2) $\theta_V \sim T$ ~~at~~ room temp. because of small mass and high spring constant (i.e. high fundamental frequency)
- for Br_2, mass is high and spring constant is ~~to~~ small. Thus higher levels are populated at r.t.
- $10\theta_V > T$ then $e^{-\theta_V/T} \approx 0$. thus $q_V = 1$.
- Thus higher is the $\tilde{\nu}$, q_V value decreases at a given ~~temp~~.

Electronic partition function.

- Electronic energy associated with various ~~energy levels~~ arrangement of electron in atoms or molecules.

- Hydrogen atom: orbital energy

$$E_n = -\frac{m_e \cdot e^4}{8\varepsilon_0^2 h^2 n^2} = -109737 \frac{1}{n^2} \text{cm}^{-1} \quad (n=1,2,3$$

$$g_n = 2n^2$$

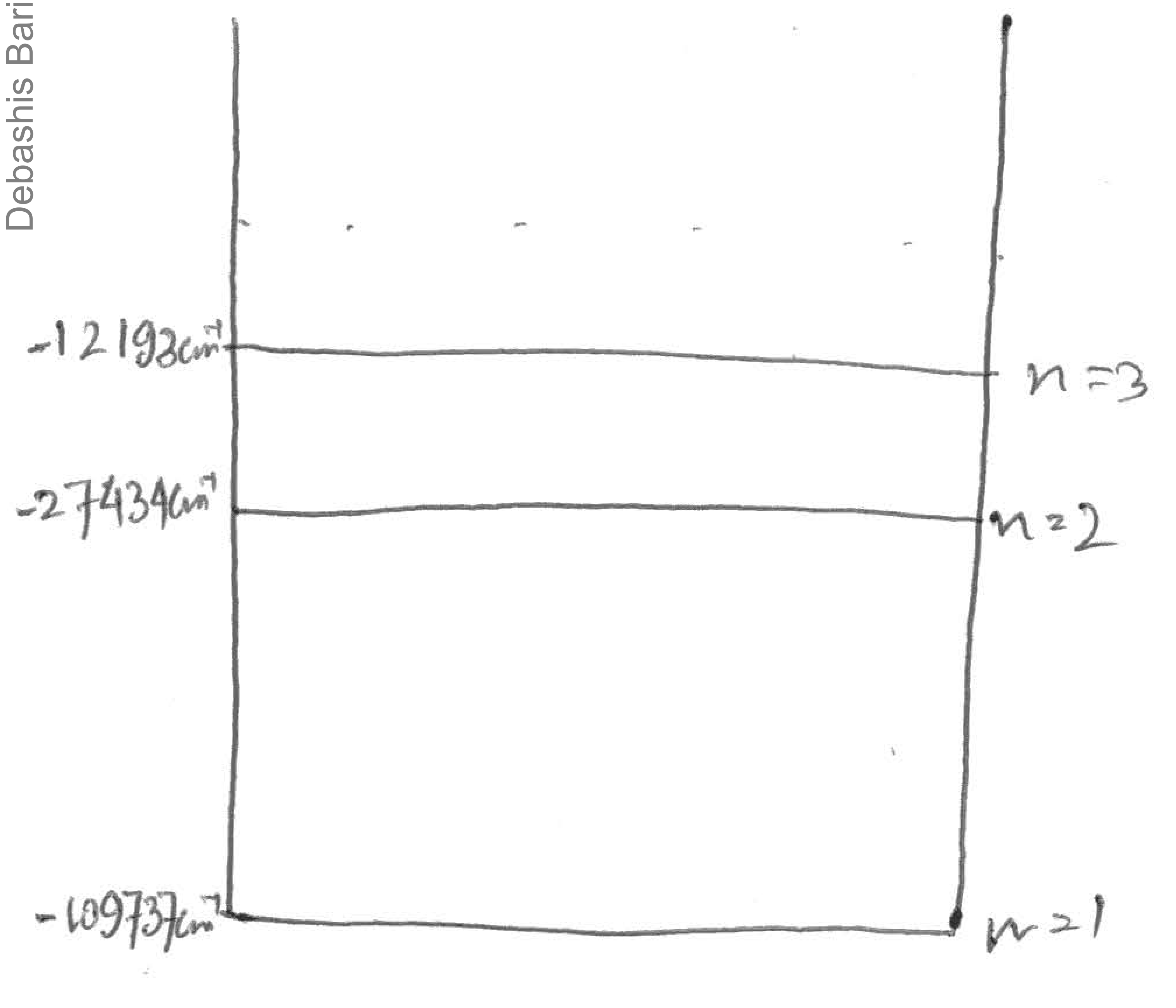
~~Reg~~ $$q_e = \sum_n g_n e^{-\beta E_n}$$

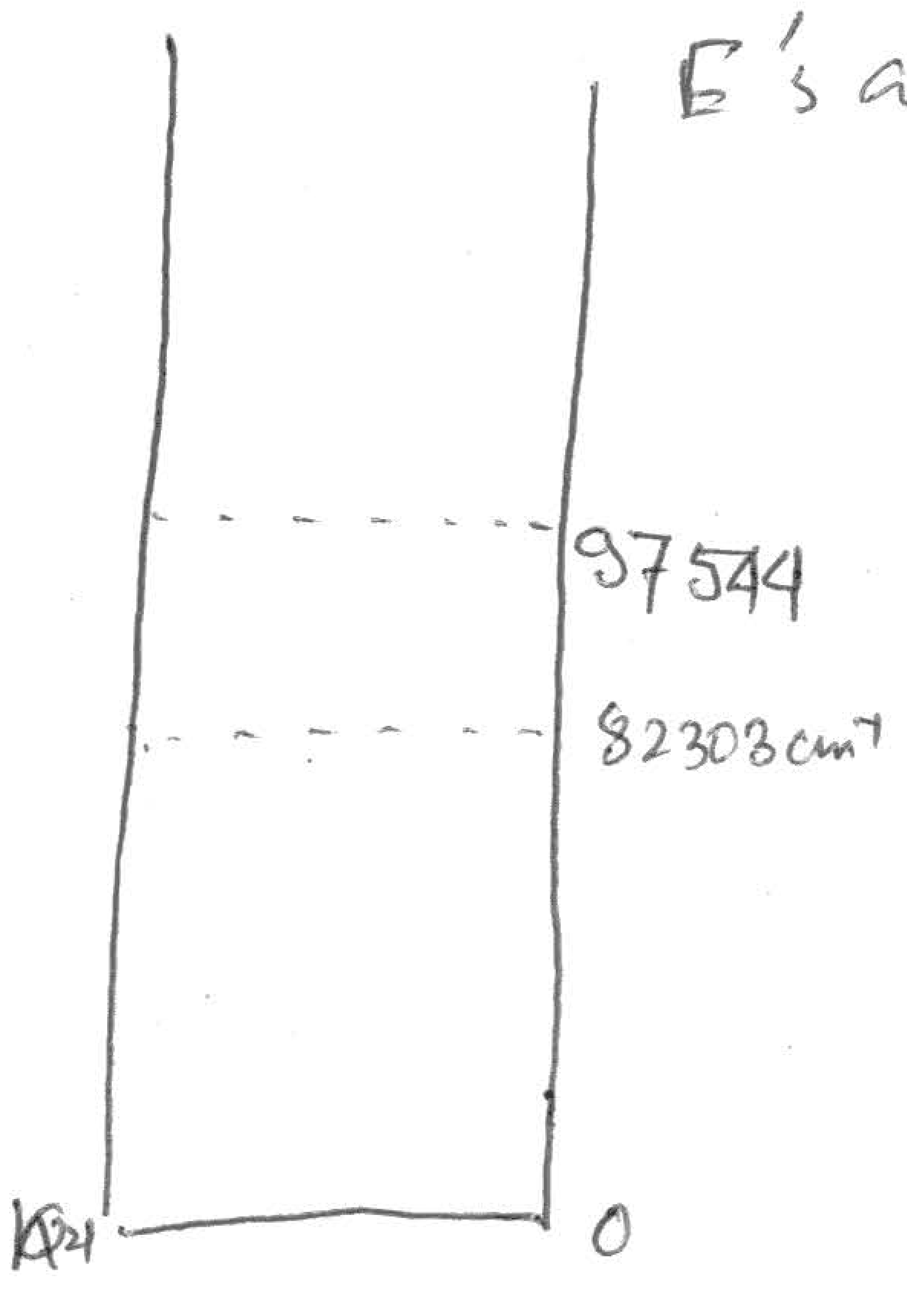
$$= \sum g_n e^{-\beta hc E_n} = \cancel{\sum}\left(g_0 e^{-\beta hc E_0} + g_1 e^{-\beta hc E_1} + g_2 e^{-\beta hc E_2} + \cdots\right)$$

$$= g_0 \cdot e^{-\beta hc(E_0 - E_0)} + g_1 e^{-\beta hc(E_1 - E_0)} + g_2 e^{-\beta hc(E_2 - E}$$
$+$

$$= g_0 + g_1 e^{-\beta hc E_1'} + g_2 e^{-\beta hc E_2'} + \cdots$$

E's are rescaled energies.





Lets define electronic temp: $\theta_E = \frac{hcE_n}{k} = \frac{6.626\times10^{-34}\,\text{Js} \times 3\times10^{10}\,\text{cm/s}}{1.38\times10^{-23}\,\text{JK}^{-1}} \cdot E_n$

$$= 1.5\ \text{cm K} \cdot E_n$$

$$\theta_E(n=2) = 1.5\ \text{cm K} \times 82303\ \text{cm}^{-1}$$
$$= 120000\ \text{K}\ !$$

Electronic partition function:

Lets startwith hydrogen atom.

Electronic orbital energy, $E_n = -\dfrac{m_e \cdot e^4}{8\epsilon_0^2 h^2 n^2} = -109737\,\text{cm}^{-1}\dfrac{1}{n^2}$ $n = 1, 2, 3, 4 \cdots$

m_e = mass of electron
e = charge of electron
ϵ_0 = permittivity of free space or vacuum.

for H atom: $g_n = 2n^2$

As $n\uparrow$ the difference between the subsequent energy levels decreases.

For hydrogen atom, the electronic partition function,

$$q_e = \sum_{n=1}^{\infty} g_n \cdot e^{-\beta E_n} = \sum_{n=1} g_n e^{-\beta hc E_n}$$

Now, if we ~~change~~ set the ground electronic energy scale from zero, Then
meaning electronic energys to measured relative to ground state.

$$\rightarrow q_e = 2\cdot e^{-\beta hc E_1} + 8 e^{-\beta hc E_2} + 18 e^{-\beta hc E_3} + \cdots$$

$$= 2\cdot e^{-\beta hc 0} + 8\cdot e^{-\beta hc E_2'} + 18 e^{-\beta hc E_3'} + \cdots$$

$$E_2' = E_2 + (109737) = -\frac{109737}{4} + 109737$$

$$\simeq 82303\,\text{cm}^{-1}$$

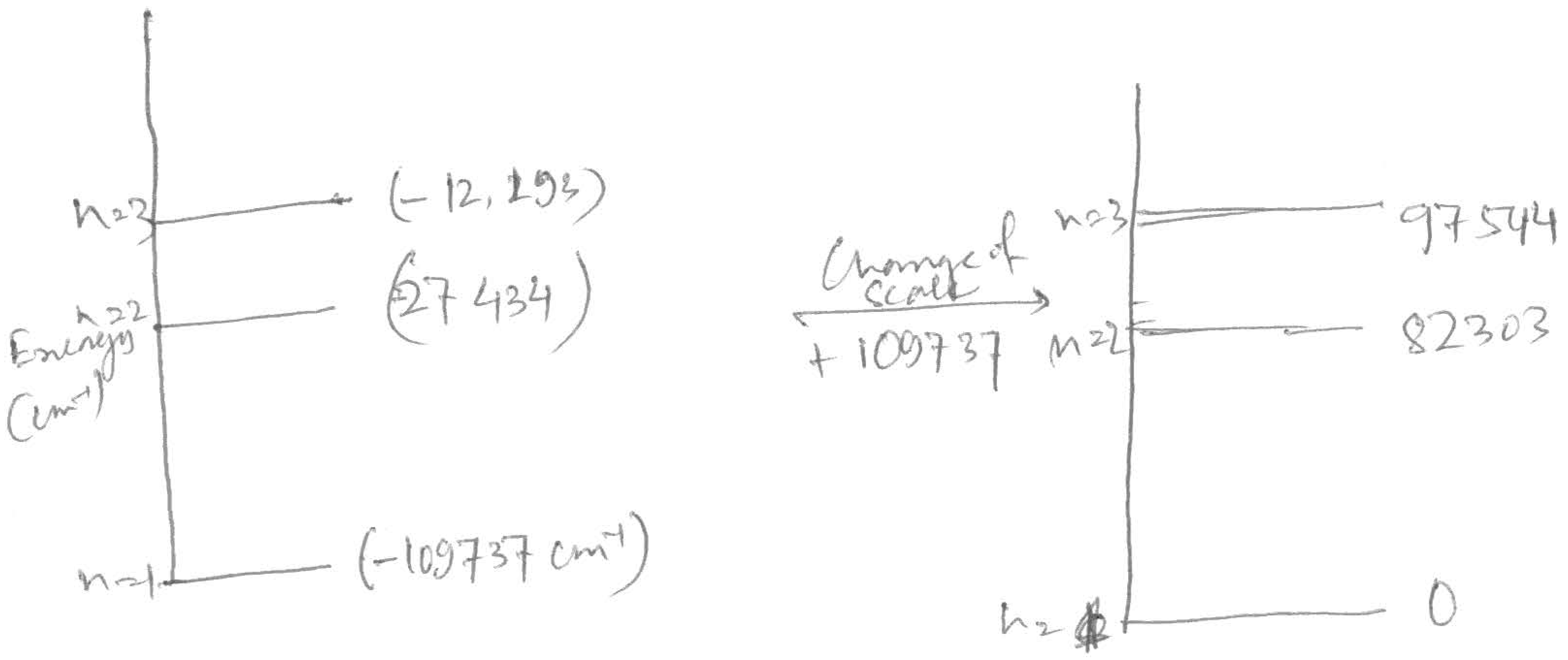
$$E_3' = E_3 + 109737$$

$$= -\frac{109737}{9} + 109737 = 97544\,\text{cm}^{-1}$$

$$= 2 + 8\cdot e^{-\beta hc\cdot(82303)} + 18\cdot e^{-\beta hc\,(97544)}$$

$$\simeq 2$$

$\Rightarrow$ ~~For $n\geq 2$~~ At r.t. $n \geq 2$ donot contribute to electronic partition function at r.t. as the energy gap beetween the subsequent levels are large compared to kT ($200\,\text{cm}^{-1}$)



One can define electronic temp.

$$\Theta_E = \frac{hcE_n}{K} = \frac{E_n}{0.695\ cm^{-1}K^{-1}}$$. for n=2, $\Theta_E = \frac{82303\ cm^{-1}}{0.695\ cm^{-1}K^{-1}}$

$\approx 118421\ K \gg 298K$

<u>Conclusion</u>: At room temp. the electronic partition function is given by the ground state degeneracy of the atom.

$$\boxed{q_E = g_0}$$

* Exception is vanadium(V).

n	energy(cm^{-1})	degeneracy
0	0	4
1	137.38	6
2	323.46	8
3	552.96	10
-	-	-

For molecule. due to large energy diff between ground and first excited state i.e. HOMO and LUMO: typically the energy gap ranges, 5000-50000

$$\boxed{q_E = g_0}$$

• Equilibrium Constant of a Chemical Reaction

A chemical reaction, represented by a general reaction scheme

$$aA + bB \rightleftharpoons cC + dD$$

- We consider the chemical species involved are all ideal in nature.
- lower case letters represent no. of moles of chemical species and upper case letters represent chemical species.
- The Gibbs free energy change in the reaction.

$$\Delta G_{rxn} = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

, μ_i's are chemical potential of ith species

Chemical potential, (assuming gas phase reaction)

$$\mu_i = \mu_i^0(T) + RT\ln\left(\frac{P_i}{P_i^0}\right)$$

; P_i = partial pressure of ith chemical species.

$\uparrow$ Standard state Chemical potential

P_i^0 = standard state Chemic potential.

$$\Delta G_{rxn} = \left(c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0\right) + RT\ln\frac{\left(P_C/P_C^0\right)^c\left(P_D/P_D^0\right)^d}{\left(P_A/P_A^0\right)^a\left(P_B/P_B^0\right)^b}$$

$$\Delta G_{rxn} = \Delta G^0_{rxn} + RT\ln Q$$

ΔG^0_{rxn}: standard state free energy change f the rxn.

where $$Q = \frac{\left(P_C/P_C^0\right)^c\left(P_D/P_D^0\right)^d}{\left(P_A/P_A^0\right)^a\left(P_B/P_B^0\right)^b}$$, is called reaction quotient.

~~if $Q > 1$~~ The shift of equilibrium in chemical reaction can be predicted by the value of Q.

A equilibrium, $\Delta G_{rxn} = 0$, thus.

$$\boxed{\Delta G^\circ_{rxn} = -RT \ln K_p} \quad \ldots \text{①}$$

$$K_p = \frac{\left(P_C/P_C^\circ\right)^c \left(P_D/P_D^\circ\right)^d}{\left(P_A/P_A^\circ\right)^a \left(P_B/P_B\right)^b}$$; equilibrium constant of the chemical reaction in gas phase.

If the reaction occurs ~~at~~ in condensed phase, then.

$$\mu_i = \mu_i^\circ(T) + RT \ln\left(C_i/C_i^\circ\right)$$

C_i: concentration of ith chemical species.

C_i°: standard state concentration.

following similar procedure.

$$K_c = \frac{\left(C_C/C_C^\circ\right)^c \left(C_D/C_D^\circ\right)^d}{\left(C_A/C_A^\circ\right)^a \left(C_B/C_B^\circ\right)^b}$$

Since we assumed that species are ideal in nature, thus ideal gas law holds for every species.

$$P_i V = n_i RT.$$

$$P_i = \left(\frac{n_i}{V}\right) \cdot RT$$

$$P_i = C_i RT$$

$$K_p = (RT)^{(c+d)-(a+b)} \cdot K_c$$

$$\boxed{K_p = (RT)^{\nu} \cdot K_c} \qquad \nu = (c+d)-(a+b).$$

Chemical potential

$$\mu_i = N_a \left(\frac{\partial A}{\partial N_i}\right)_{T,V}$$

A : Helmholtz free energy

N_A = Avogadro's No.

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V}$$

$$n_i = \frac{N_i}{N_a}$$

$$A = -kT \ln Q = -kT \ln \left(q_i^{N_i}/N_i!\right)$$

$$= \cancel{-N_i kT \ln q_i + kT \ln N_i!}$$

$$= \cancel{-N_i kT \ln q_i + kT}$$

$$A = -kT \left[N_i \ln q_i - \ln N_i!\right]$$

$$= -kT \left[N_i \ln q_i - N_i \ln N_i + N_i\right]$$

using Sterling's approximation.

$$\mu_i = -N_a kT \cdot \frac{\partial}{\partial N_i} \left\{ N_i \ln q_i - N_i \ln N_i + N_i \right\} \Big|_{T,V}$$

$$= -RT \left[\frac{\cancel{\partial} \ln q_i}{\cancel{\partial N_i}} - \ln N_i - \frac{N_i}{N_i} + 1 \right]_{T,V}$$

$$\boxed{\mu_i = -RT \ln \left(q_i/N_i\right)}$$

$$\Delta G^\circ_{rxn} = c\mu^\circ_C + d\mu^\circ_D - a\mu^\circ_A - b\mu^\circ_B$$

$$= -RT \ln \frac{(q_C/N_C)^c \, (q_D/N_D)^d}{(q_A/N_A)^a \, (q_B/N_B)^b} \quad \ldots\ldots ②$$

Comparing ① and ②

$$K_p = \frac{(q_C/N_C)^c \, (q_D/N_D)^d}{(q_A/N_A)^a \, (q_B/N_B)^b}$$

Defining molar partition function, $\bar{q}_i = \frac{q_i}{n_i}$, n_i = no. of moles of ith species.

$$\frac{q_i}{N_i} = \frac{q_i}{n_i \cdot N_A} = \frac{\bar{q}_i}{N_A}$$

; N_A : Avogadro's No.

$$K_p = \frac{\left(\frac{\bar{q}_C}{N_A}\right)^c \left(\frac{\bar{q}_D}{N_A}\right)^d}{\left(\frac{\bar{q}_A}{N_A}\right)^a \left(\frac{\bar{q}_B}{N_A}\right)^b}.$$

Since different species will have different electronic ground state energy, in the molar partition function, $\bar{q}_i$, the ground state energy has to be included explicitly.

$$\bar{q}_i = \frac{1}{n_i} q_t q_r q_v q_e$$

$$= \underbrace{\frac{1}{n_i} q_t q_r q_v g_0}_{} \cdot e^{-\epsilon_i/KT}$$

$$= q_i' e^{-\epsilon_i/KT}$$

$$q_i' = \frac{1}{n_i} q_t q_r q_v g_0$$

$$K_p = \frac{(q_C'/N_A)^c (q_D'/N_A)^d}{(q_A'/N_A)^a (q_B'/N_A)^b} \cdot e^{({}^c\epsilon_C + {}^d\epsilon_D - {}^a\epsilon_A - {}^b\epsilon_B)/KT}$$

$$= \frac{(q_C'/N_A)^c (q_D'/N_A)^d}{(q_A'/N_A)^a (q_B'/N_A)^b} \cdot e^{-\Delta\epsilon/KT}$$

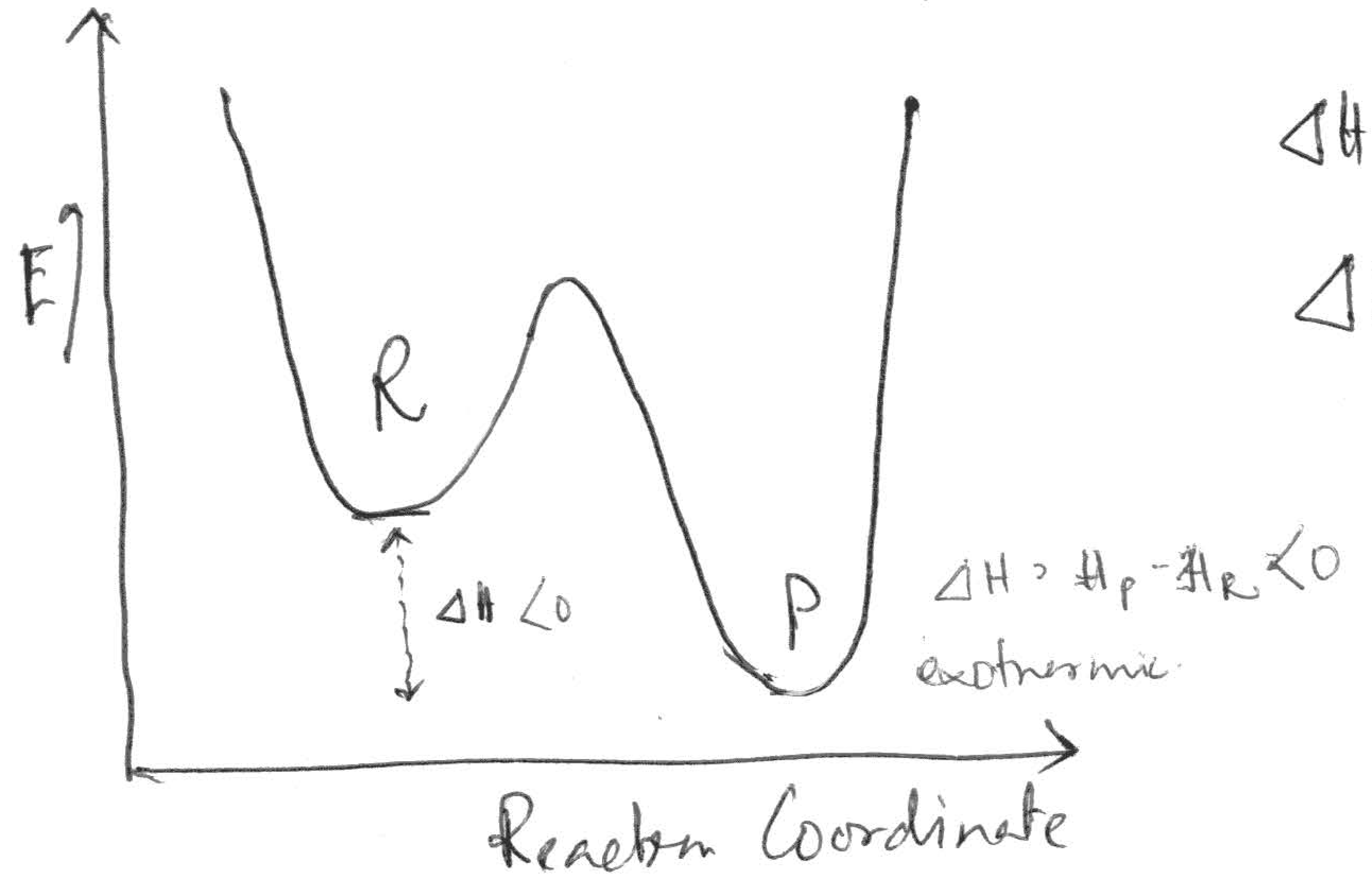
, $\Delta\epsilon = ({}^c\epsilon_C + {}^d\epsilon_D) - ({}^a\epsilon_A + {}^b\epsilon_B)$

$= \epsilon_r - \epsilon_p$

ϵ_r : Total ground state electronic energy of all reactant

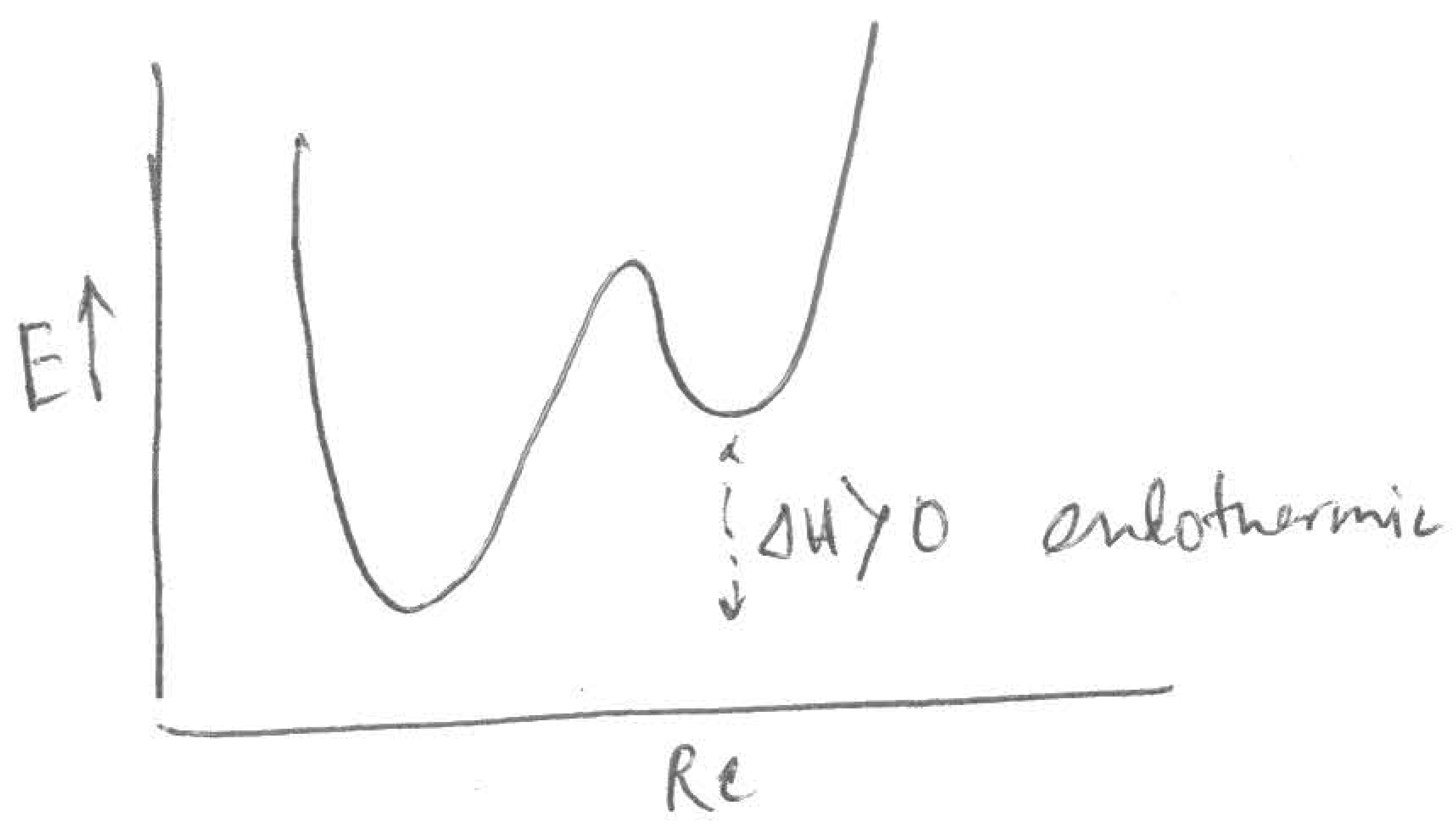
ϵ_p : Total ground state electronic

ΔE = enthalpy change in the reaction = ΔH.



$\Delta H < 0$ exothermic reaction

$\Delta H > 0$ endothermic reaction.



A general expression of equilibrium const.

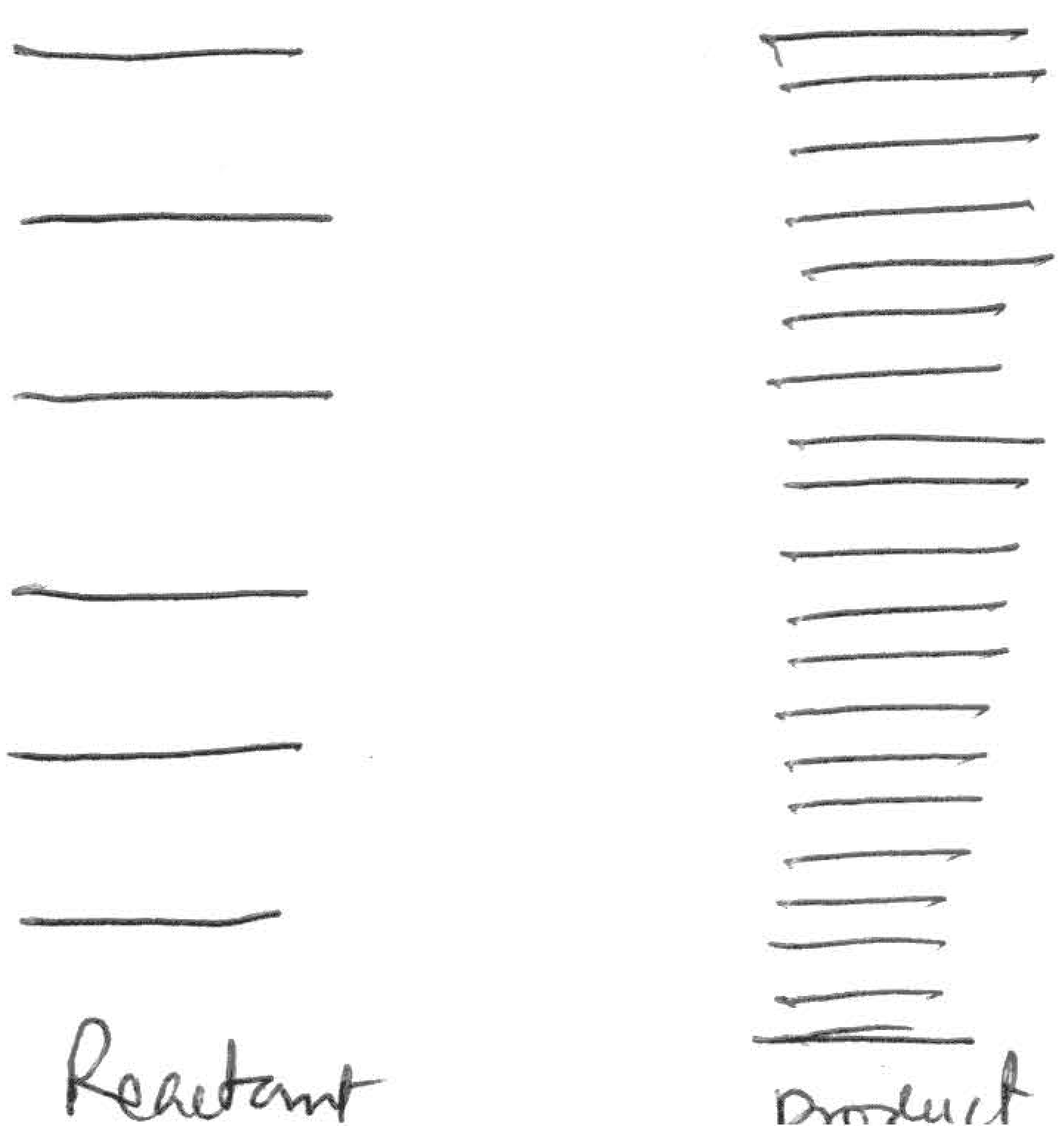
$$K_p = \frac{\prod_p \left(\frac{q'_p}{N_A}\right)^p}{\prod_r \left(\frac{q'_r}{N_A}\right)^r} e^{-\Delta H/kT}$$

Statistical mechanical interpretation of eqm Const.

Case I: $\Delta H = 0$, $e^{-\Delta H/kT} = 1$, $K_p = \frac{\prod_p \left(\frac{q'_p}{N_A}\right)^p}{\prod_r \left(\frac{q'_r}{N_A}\right)^r}$

if $\prod_p \left(\frac{q'_p}{N_A}\right)^p > \prod_r \left(\frac{q_p}{N_A}\right)^r$, the reaction proceeds towards product states.

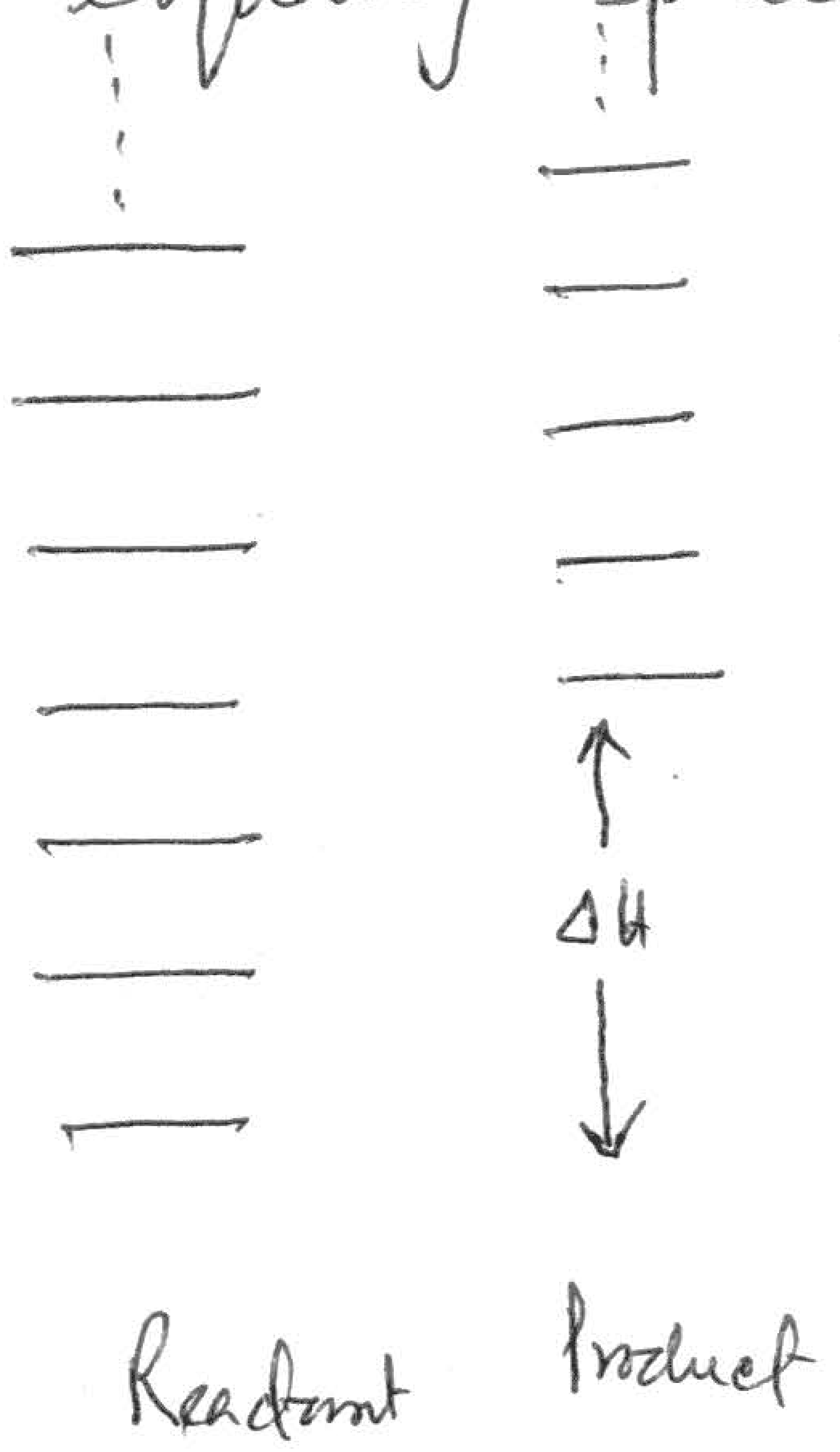
This is possible only if the product states have more accessible energy states than the reactant states.



- When $\Delta H = 0$, equilibrium will proceed towards a state where more number of accessible states can be occupied by the system.

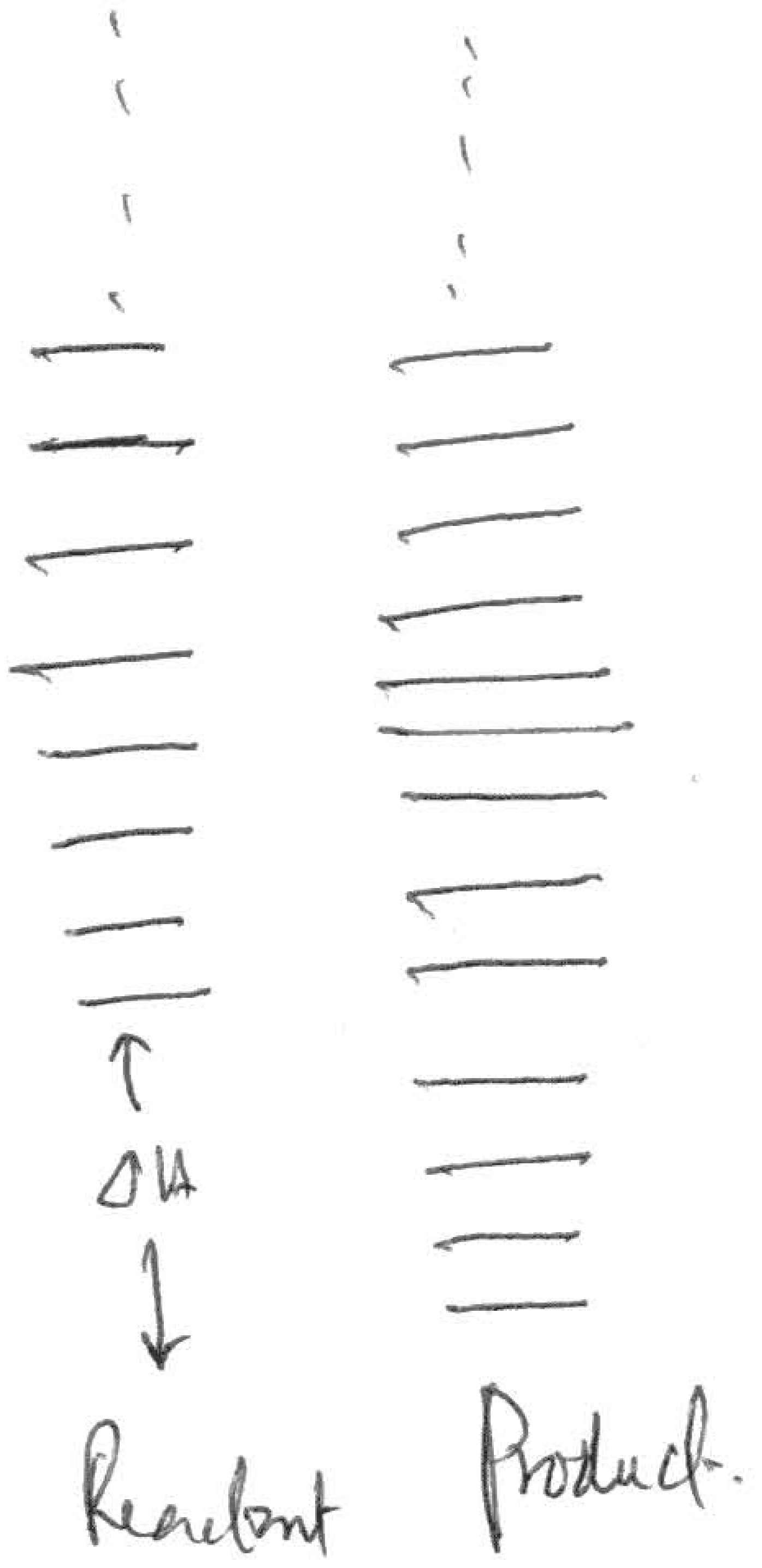
Case II : $\Delta H > 0$, endothermic reaction.

We assume that energy gaps for both reactant and product are equally spaced.



Since at any given temperature reactant would occupy more number of accessible states (as the ground electronic state energy for reactant is lower than that of product). the equilibrium constant would be < 1. Thus reactant state is favoured.

Case III : $\Delta H < 0$ exothermic reaction, with similar energy gaps for reactants as products.



Here $K > 1$ for the similar reason as described above.

A Simple way : For $A \rightleftharpoons B$ type reaction

N : Total no. of molecules of A and B.

N_A : no. of molecules of A ; N_B : no. of molecules of B.

$N_A = \sum_i N_i$, N_i : no of molecules in ith energy level
'i' runs over all energy states for A.

$= \sum_i (N P_i)$ P_i : probability that the system to at ith state.

$= \sum_i N \cdot \frac{e^{-\beta\epsilon_{i,A}}}{q}$ $\epsilon_{i,A}$: energy levels for A.

q : partition function for the total system. A & B.

$= \frac{N}{q} \cdot \sum_i e^{-\beta\epsilon_{i,A}}$

$= \frac{N}{q} \cdot q_A$ q_A : Partition function for A.

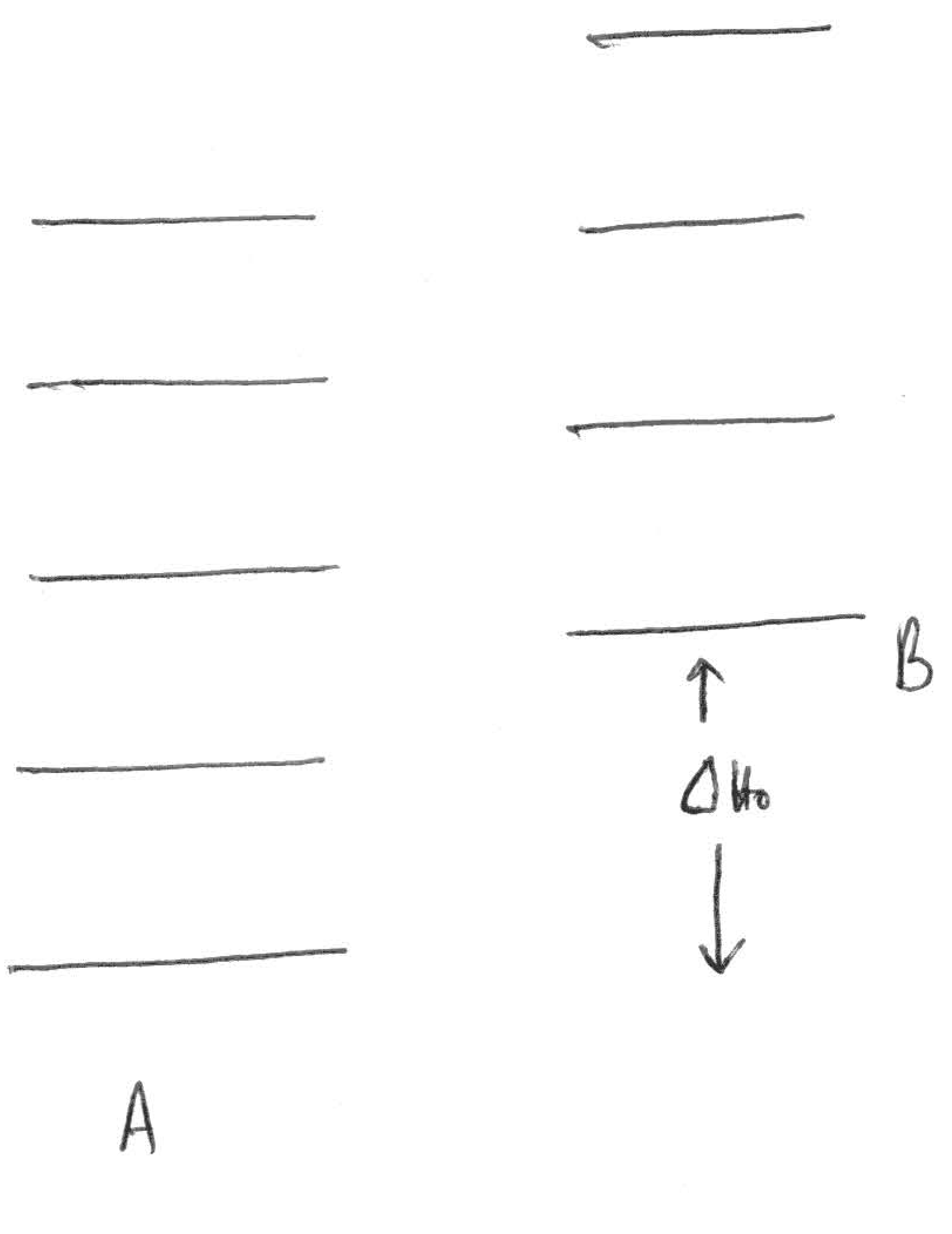
Similarly, $N_B = \frac{N}{q} \cdot \sum_j e^{-\beta[\epsilon_{j,B} + \Delta H_0]} = \frac{N}{q} \cdot \left(\sum_j e^{-\beta\epsilon_{j,B}}\right) \cdot e^{-\beta\Delta H_0}$

$N_B = \frac{N}{q} \cdot q_B \cdot e^{-\beta\Delta H_0}$

At eqm, $K = \frac{N_B}{N_A}$

$$\boxed{K = \frac{q_B}{q_A} \cdot e^{-\beta\Delta H_0}}$$

↑
Same expression !



Heat Capacity at constant volume (C_V)

Measures the ability of a substance to take up heat as the substance is heated.

When heated a substance, thermal energy is dissipated into various energetic degrees of freedom; namely, translational, rotational, vibrational & electronic. Therefore overall heat capacity of a substance is due to contributions from all the energetic degrees of freedom. For gaseous substance all the energetic degrees of freedom contribute to heat Capacity. On the other hand for solid substance ~~translational~~ translational & rotational energetic degrees of freedom do not contribute, as rotational & translational motions are not possibl in case of solid.

$$C = \frac{Q}{\Delta T} = \left(\frac{\partial Q}{\partial T}\right). \quad C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

Translational heat capacity:

Average energy $\langle \epsilon \rangle_t = U_t = \frac{3}{2} NKT$

$$C_{V,t} = \left(\frac{\partial U_t}{\partial T}\right)_{N,V} = \frac{3}{2} NK$$

Rotational heat capacity:

$\langle \epsilon \rangle_t = U_r = NKT$ for linear molecule

$= \frac{3}{2} NKT$ for nonlinear molecu

$C_{V,r} = NK$ for linear molecule

$= \frac{3}{2} NK$ for nonlinear molecule.

Vibrational heat Capacity:

$$\langle \epsilon \rangle_v = U_v = NK \sum_{i=1}^{m} \left(\frac{\theta_{v,i}}{2} + \frac{\theta_{v,i}}{e^{\theta_{v,i}/T} - 1} \right)$$

$m = 3N-5$ for linear molecul

$= 3N-6$ for nonlinear molec

②

$$C_{V,v} = NK \sum_{i=1}^{m} \left(\frac{\theta_{v,i}}{T}\right)^2 \frac{e^{\theta_{v,i}/T}}{\left(e^{\theta_{v,i}/T}-1\right)^2}$$

~~Tha~~

~~$C_{V,e}=$~~ Electronic heat capacity,

$$\langle E \rangle_e = U_e = 0$$

~~degeneracy~~ f ~~ground~~ electronic ~~state~~.

$$C_{V,e} = 0.$$

Thus for the entire system.

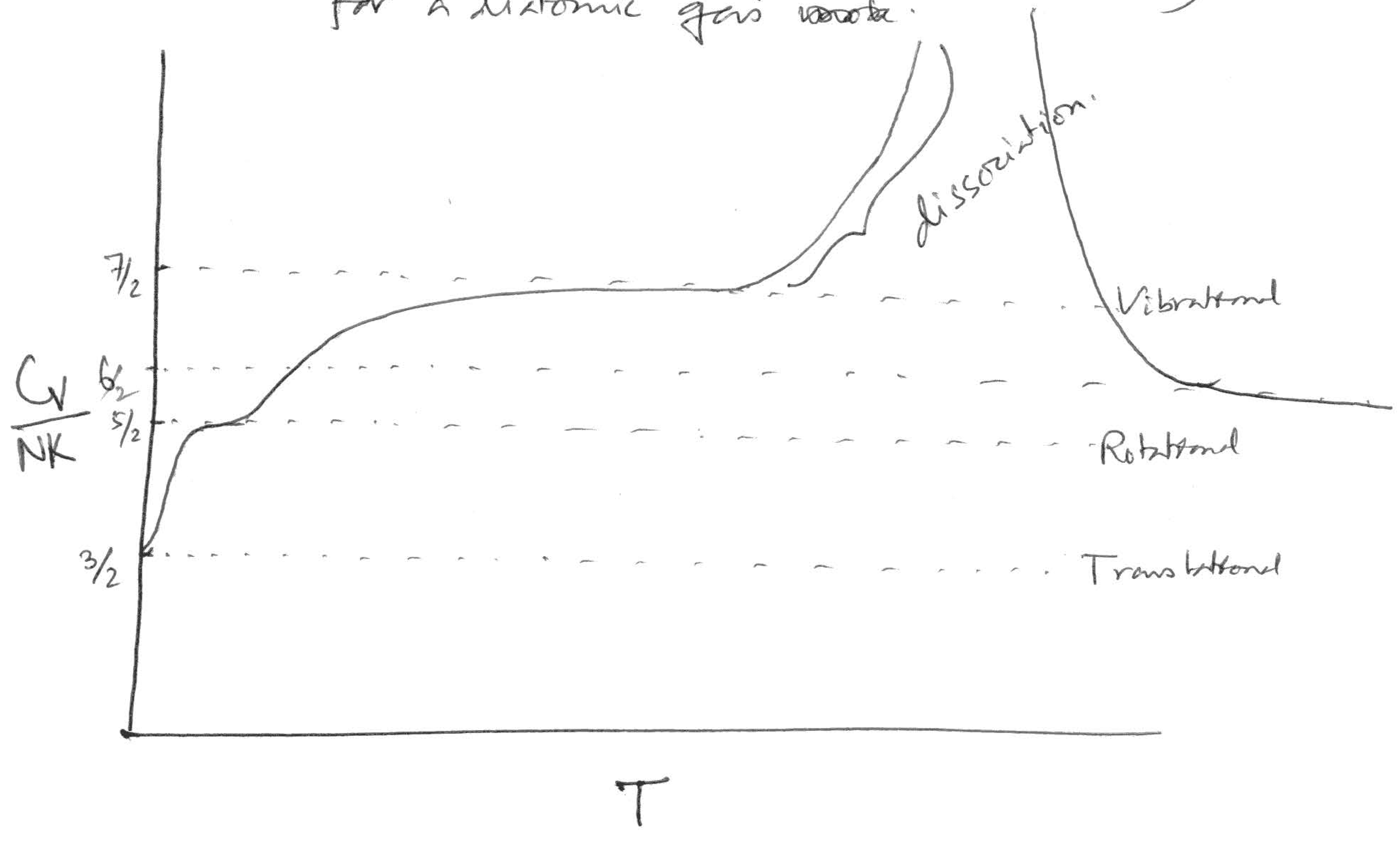
$$C_V = C_{V,t} + C_{V,r} + C_{V,v} + C_{V,e}$$

$$= \frac{3}{2}NK + f \cdot NK + NK \sum_{i=1}^{m} \left(\frac{\theta_{v,i}}{T}\right)^2 \frac{e^{\theta_{v,i}/T}}{\left(e^{\theta_{v,i}/T}-1\right)^2}$$

$f = 1$ & $m = 3N-5$
for linear

$f = \frac{3}{2}$ and $m = 3N-6$
for nonlinear

- Temperature dependence of C_V (for gaseous substance) for a diatomic gas ~~mole~~.



Heat capacity of solids.

- Dulong - Petit: Heat capacity at constant volume of [redacted] solids do not depend on temperature. and the value of it is ~25 $JK^{-1}mol^{-1}$

$C_V = 25\,JK^{-1}mol^{-1}$ and it nearly equals to

$3NK\left(= 3\times 6.023\times10^{23}mol^{-1}\times1.38\times10^{-23}JK^{-1}\right)$

[redacted].

- However C_V was found to depend on temperature at very low temperature it is very small and it increases with temperature finally to saturate at ~ 25 $JK^{-1}mol^{-1}$.

Einstein's model:

Model

- Atoms on lattice vibrate independently with a common frequency (ω_E)

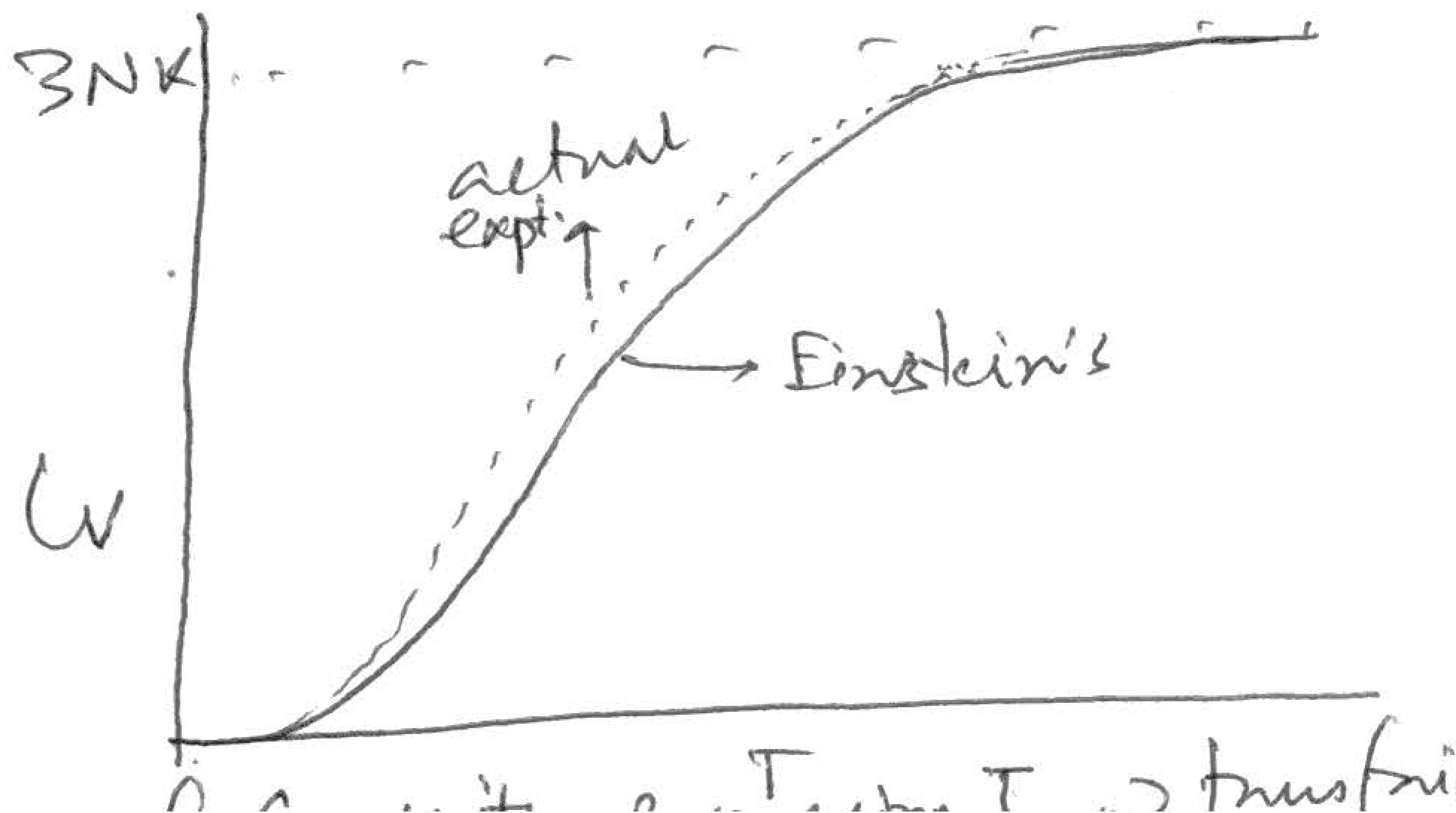
Following the procedure done before in the class for harmonic oscillator:

$$E = 3NK\left[\frac{\theta_E}{2} + \frac{\theta_E}{e^{\theta_E/T}-1}\right] \qquad \theta_E = \frac{\hbar\omega_E}{K}$$

$$C_V = 3NK\left(\frac{\theta_E}{T}\right)^2 \cdot \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}$$

High temperature limit; $T\to\infty$, $\theta_E/T \ll 1$ $\left\{\begin{array}{l} e^{\theta_E/T}\approx 1 \\ e^{\theta_E/T}-1 \approx \theta_E/T \end{array}\right.$

$$C_V = 3NK$$



Low temp. limit

$T\to 0$, $\theta_E/T \gg 1$,

$$C_V = 3NK\left(\frac{\theta_E}{T}\right)^2 \cdot e^{-\theta_E/T}$$

thus fails at low T.

Debye-model of heat capacity of solids.

- Atoms/particles in the lattice cannot vibrate independenty.
- Vibrations inside lattice can be considered as vibration of stings on which atoms are silting (beads on string).
- Lattice vibrations are qualatized just like photons, and these quantized vibrations are called phonons.
- The vibrating lattice can take only certain maximum and minimum frequencies.

$\lambda_{max} = 2L$ L: length of lattice

$\lambda_{min} = 2d$ d: lattice spacing.

$\lambda = \frac{2L}{n}$, $n = 0, 1, 2, 3 \ldots$

- The ~~average~~ total energy of lattice with N atoms.

$$= \int (\text{Energy of a phonon}) \times \left(\text{No. of phonons with a given frequency}\right) d\omega$$

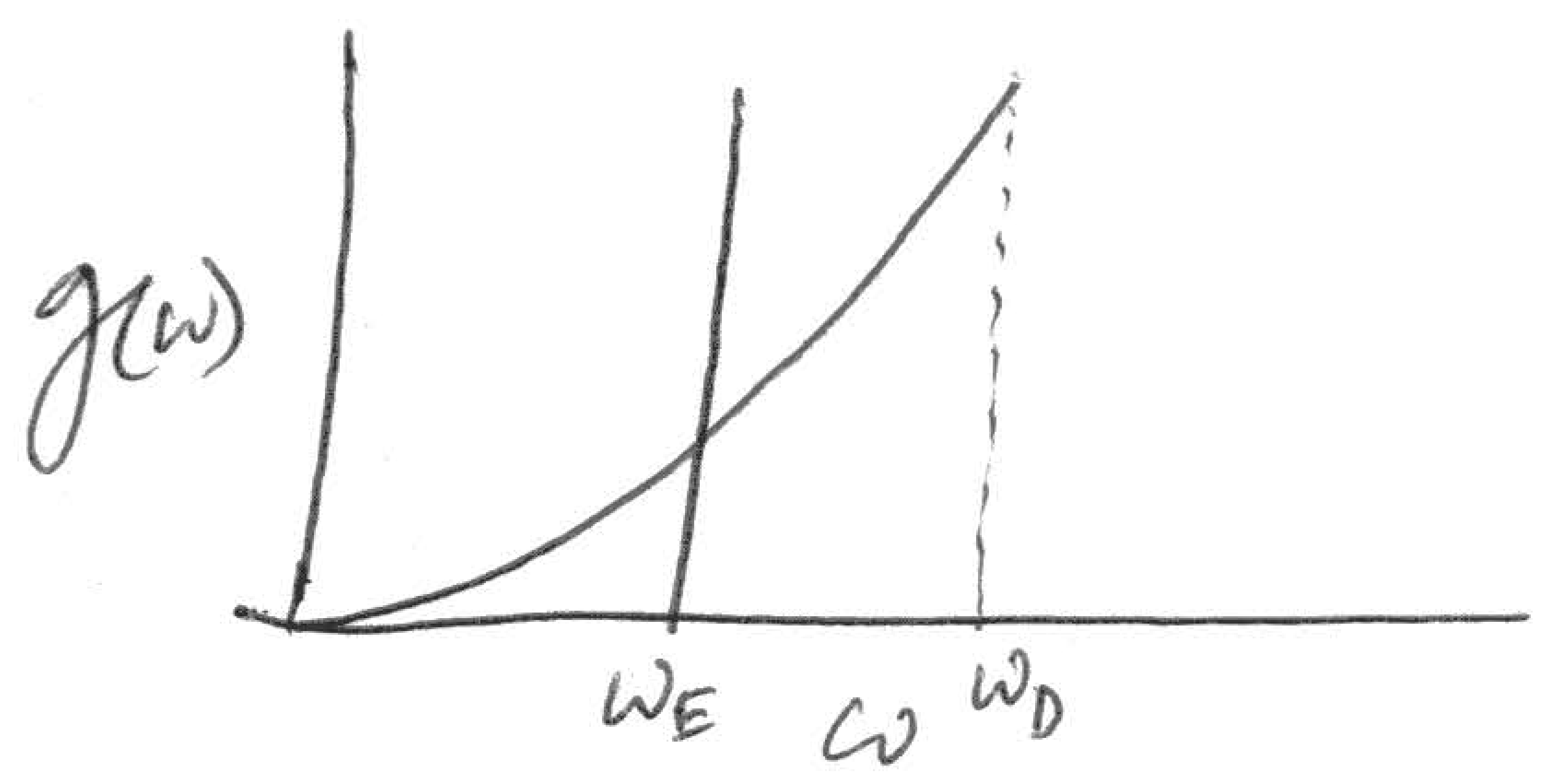
$$= \int E(\omega) \underbrace{g(\omega)}_{\text{density of states.}} d\omega$$

$$E = \cancel{3} \int E(\omega) g(\omega)\, d\omega$$

for three dimension.

$$= 3 \int \underbrace{\left[\frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}\right]}_{\text{energy of a phonon with frequency } \omega} g(\omega)\, d\omega$$

Debye's assumption was $g(\omega) \propto \omega^2$ with a cut-off frequency ω_D



- The main difference with Einstein's model is that, in Einstein's model, all the atoms were assumed to vibrate with a same frequency ω_E,

$$g(\omega) = \delta(\omega - \omega_E) \text{ if } \omega = \omega_E$$
$$= 0 \quad \text{elsewhere.}$$

After some mathematics!

$$E = 9NKT\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^3}{e^x - 1}\, dx \,, \qquad x_D = \frac{\theta_D}{T} = \frac{\hbar\omega_D}{kT}$$

ω_D

$$x = \frac{\hbar\omega}{kT}$$

$$C_V = 9NK\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2}\, dx$$

$$g(\omega) = \frac{9N}{\omega_D^3}\omega^2$$

We are interested in ~~two~~ very high and very low temperature limits of C_V.

High temperature limit (Classical limit!):

$$T \to \alpha, \quad x \left(= \frac{\hbar\omega}{kT}\right) \ll 1$$

$$e^x - 1 = (1 + x + x^2 + \cdots) - 1 \approx x$$

$$E = 9NKT\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^3}{x}\, dx$$

$$= 9NKT\left(\frac{T}{\theta_D}\right)^3 \left[\frac{1}{3}x^3\right]_0^{x_D}$$

$$= 9NKT\left(\frac{T}{\theta_D}\right)^3 \cdot \frac{1}{3} \cdot \left(\frac{\theta_D}{T}\right)^3$$

$$= 3NKT$$

$$\boxed{C_V = 3NK}$$

Low temperature limit.

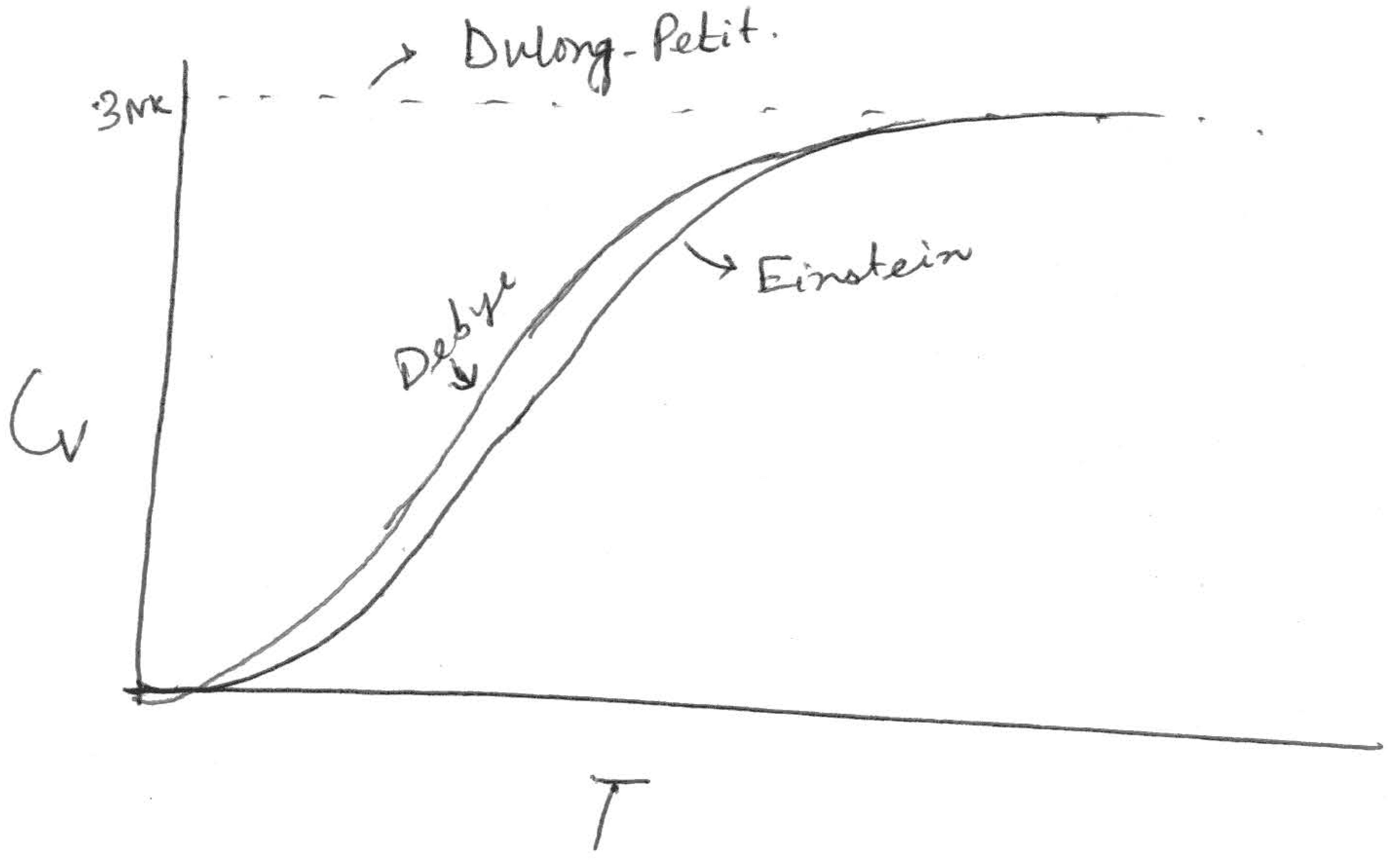
$T \to 0, \quad x \gg 1, \quad x_D \to \infty$

$$E = 9NKT\left(\frac{T}{\theta_D}\right)^3 \int_0^\infty \frac{x^3}{e^x - 1}\,dx$$

$$= 9NKT\left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15}$$

$$C_V = 9NK\cdot 4\cdot\left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15}$$

$$\boxed{C_V = \frac{12}{5}\cdot\pi^4 NK\left(\frac{T}{\theta_D}\right)^3} \to \text{Debye } T^3 \text{ law.}$$



Details of calculation

①

$$\bar{E} = \int g(\omega)\, E(\omega)\, d\omega \qquad g(\omega) = \frac{9N}{\omega_D^3}\cdot\omega^2$$

$$E(\omega) = \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}$$

$$= \int_0^{\omega_D} \frac{9N}{\omega_D^3}\cdot\omega^2\cdot \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\, d\omega$$

$$= \frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\hbar\omega/kT}-1}\, d\omega.$$

$$x = \frac{\hbar\omega}{kT} \qquad \omega^3 = \left(\frac{kT}{\hbar}\right)^3\cdot x^3$$

$$dx = \frac{\hbar}{kT}\cdot d\omega$$

$$d\omega = \frac{kT}{\hbar}\, dx$$

$$= \frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\cdot\left(\frac{kT}{\hbar}\right)^3\cdot x^3}{e^x-1}\, \left(\frac{kT}{\hbar}\right)\cdot dx$$

$$\theta_D = \frac{\hbar\omega_D}{k}$$

$$= \frac{9kTN}{\omega_D^3}\cdot\left(\frac{kT}{\hbar}\right)^3\cdot\int_0^{\omega_D} \frac{x^3}{e^x-1}\, dx$$

$$\cancel{\omega_D^3 = \theta_D^3\cdot\left(\frac{k}{\hbar}\right)^3}$$

$$\theta_D^3\left(\frac{k}{\hbar}\right)^3 = \omega_D^3$$

$$= \frac{9NkT}{\theta_D^3\cdot\left(\frac{k}{\hbar}\right)^3}\cdot\left(\frac{k}{\hbar}\right)^3\cdot T^3\cdot\int_0^{\omega_D} \frac{x^3}{e^x-1}\, dx$$

defining.

$$x_D = \frac{\hbar\omega_D}{kT} = \frac{\theta_D}{T}$$

$$\boxed{\bar{E} = 9NkT\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x-1}\, dx}$$

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

$$\cancel{= \frac{d}{dT}\left[9NkT\left(\frac{T}{\theta_D}\right)^3\cdot\int_0^{\theta_D/T}\frac{x^3}{e^x-1}\, dx\right]}$$

$$\cancel{= \frac{9Nk}{\theta_D^3}\left[\frac{d}{dT}\left(T^4\right)\cdot\int_0^{\theta_D/T}\right.}$$

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

$$= \frac{d}{dT}\left[\frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\hbar\omega/kT}-1}\,d\omega\right]$$

$$x = \frac{\hbar\omega}{kT}$$

$$\omega^4 = x^4\cdot\left(\frac{kT}{\hbar}\right)^4$$

$$d\omega = \left(\frac{kT}{\hbar}\right)\cdot dx$$

$$= \frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{d}{dT}\left[\frac{\hbar\omega^3}{e^{\hbar\omega/kT}-1}\right]d\omega$$

$$= \frac{9N}{\omega_D^3}\int_0^{\omega_D} -\frac{\hbar\omega^3\cdot e^{\hbar\omega/kT}\cdot\left(-\frac{\hbar\omega}{kT^2}\right)}{\left(e^{\hbar\omega/kT}-1\right)^2}\,d\omega$$

$$= \frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\left(\frac{\hbar^2}{kT^2}\right)\cdot\omega^4\, e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}\,d\omega$$

$$= \frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\left(\frac{\hbar^2}{kT^2}\right)\left(\frac{kT}{\hbar}\right)^4\cdot x^4 e^x}{\left(e^x-1\right)^2}\left(\frac{kT}{\hbar}\right)dx$$

$$= \frac{9N}{\omega_D^3}\left(\frac{\hbar}{T}\right)\left(\frac{\hbar}{kT}\right)\cdot\left(\frac{kT}{\hbar}\right)^4\left(\frac{kT}{\hbar}\right)\int_0^{\omega_D}\frac{x^4 e^x}{\left(e^x-1\right)^2}\,dx$$

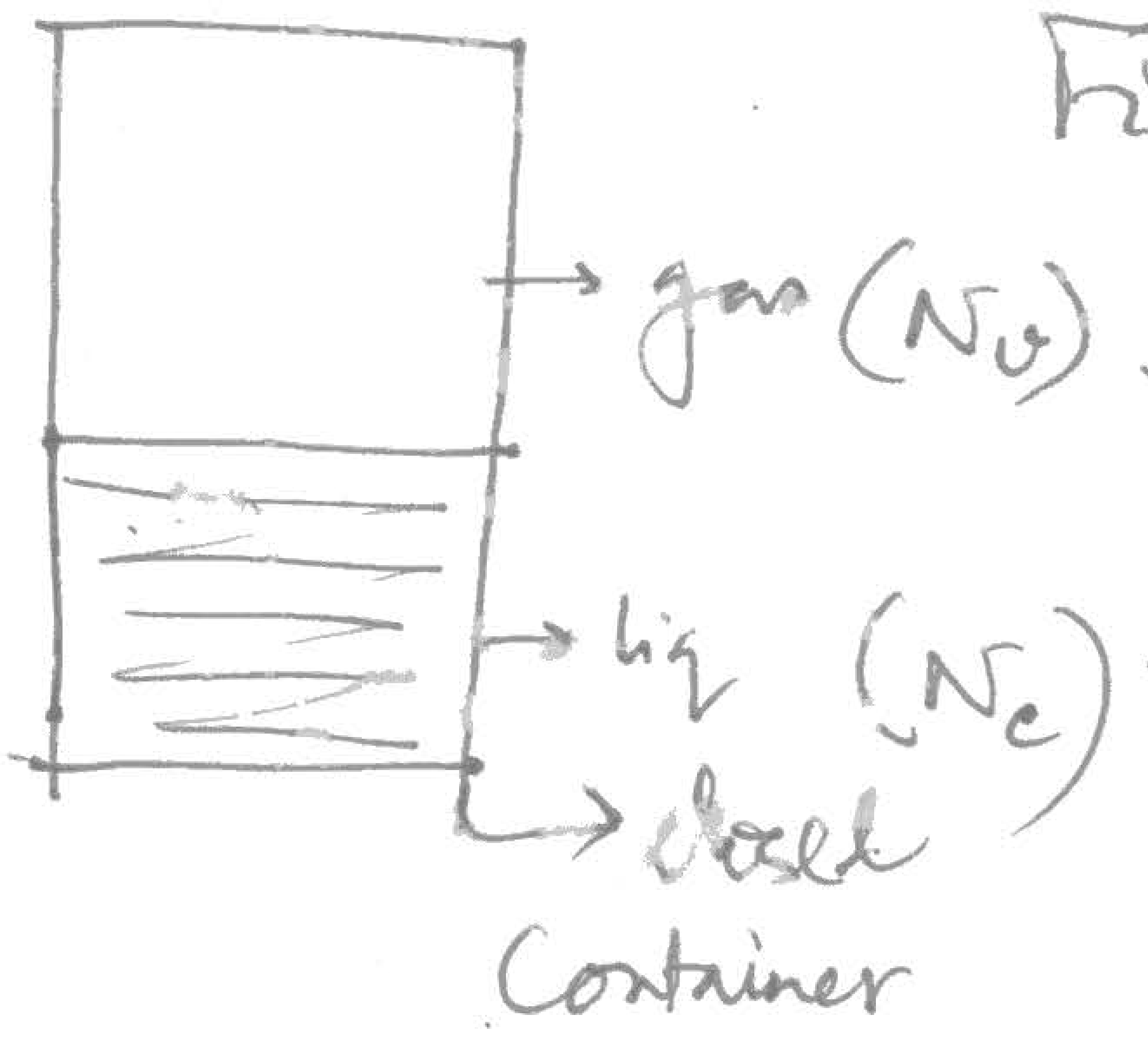
$$= \frac{9Nk}{\omega_D^3}\left(\frac{kT}{\hbar}\right)^3\int_0^{\theta_D/T}\frac{x^4 e^x}{\left(e^x-1\right)}\,dx$$

$$= 9Nk\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4 e^x}{\left(e^x-1\right)}\,dx$$

Lattice model: pure system; eqm between liquid and gas.

liq phase: attraction between molecule is large → low translational entropy
gas phase: " " " " small → large " "

gas-liq equilibrium



Fixed T and p.

→ no. of molecules in ~~gas~~ vapor and Condensed phases.

Free energy change, at constant T and P.

$$dG = -SdT + Vdp + \sum_{i=1}^{2} \mu_i dN_i$$

$$= 0 + 0 + \mu_v dN_v + \mu_c dN_c$$

Now $N = N_c + N_v \rightarrow dN = 0 = dN_c + dN_v \rightarrow dN_c = -dN_v$

$$dG = (\mu_v - \mu_c) dN_v$$

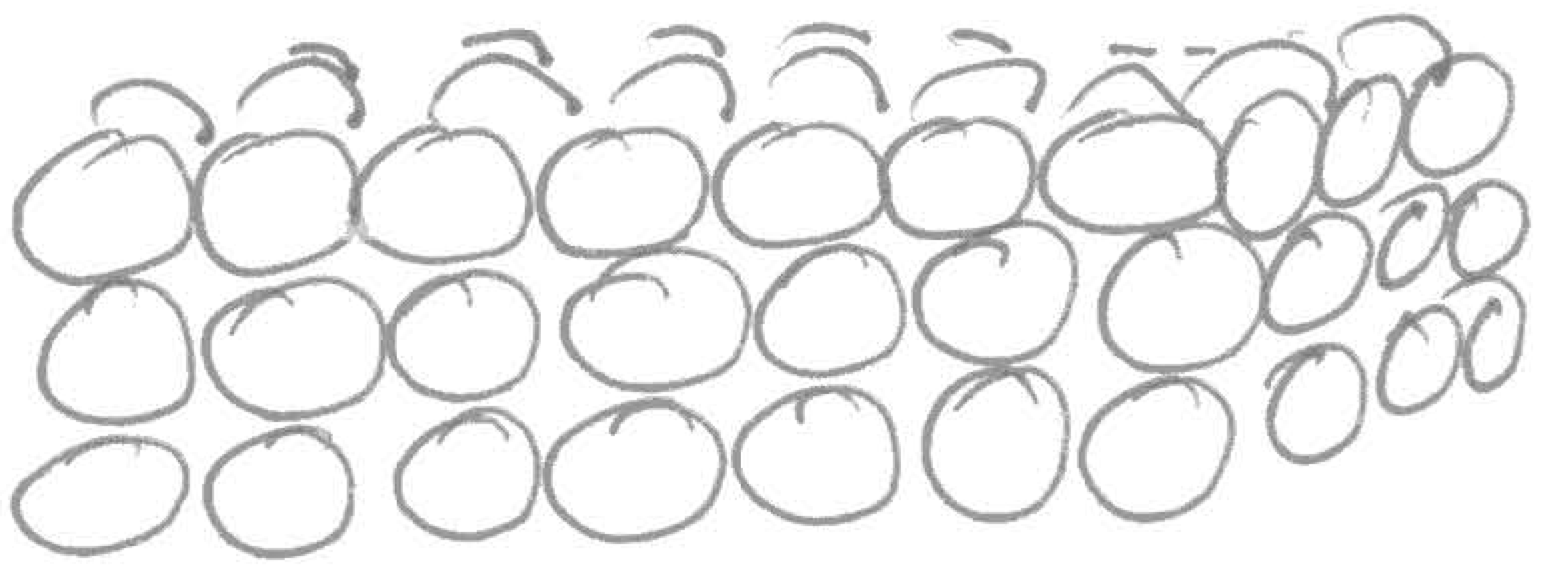
at eqm, $dG = 0$. $\longrightarrow (\mu_v - \mu_c) dN_v = 0 \rightarrow \mu_v = \mu_c$

Assuming ideal gas law for the vapor phase →

$$\mu_v = RT \ln(P/P$$

$\mu_c = ?$

Lattice model of pure liquid.



→ A lattice where at each site only one molecule can be occupied.

→ We consider (T, V, N) constant instead of (T, p, N) as the compressibility (rate of change of ~~vol~~ V with applied p) is small.

→ exchange of particles from liq. to vap. phase (or reverse) does not involve any change in the internal quantum ~~&~~ mechanical state of particles ⟶ rot, vib, nu & electronic state remain same.

→ ~~translation~~ translational entropy within liq. is 0, as W=1 → $S = k \ln W = 0$. ; particles are indistinguishable → exchange of particles ~~within~~ within liq. does not generate a ~~b~~ new configuration.

→ pairwise interaction energy: W_{AA} (<0) ~~for~~ attractive interaction.

→ for a particle with Z neighbours (coordination no.) the energy of interaction: $= W_{AA}Z$

→ For N particles: $U = \frac{NW_{AA}Z}{2}$ (2 is introduced to account for pairwise terms)

Helmholtz free energy (A)

$$A = U - TS = \left(\frac{NW_{AA}Z}{2}\right) - T \times 0 = \frac{NW_{AA}Z}{2}$$

Chemical potential in liq. $\mu_c = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \frac{1}{2}W_{AA}Z$

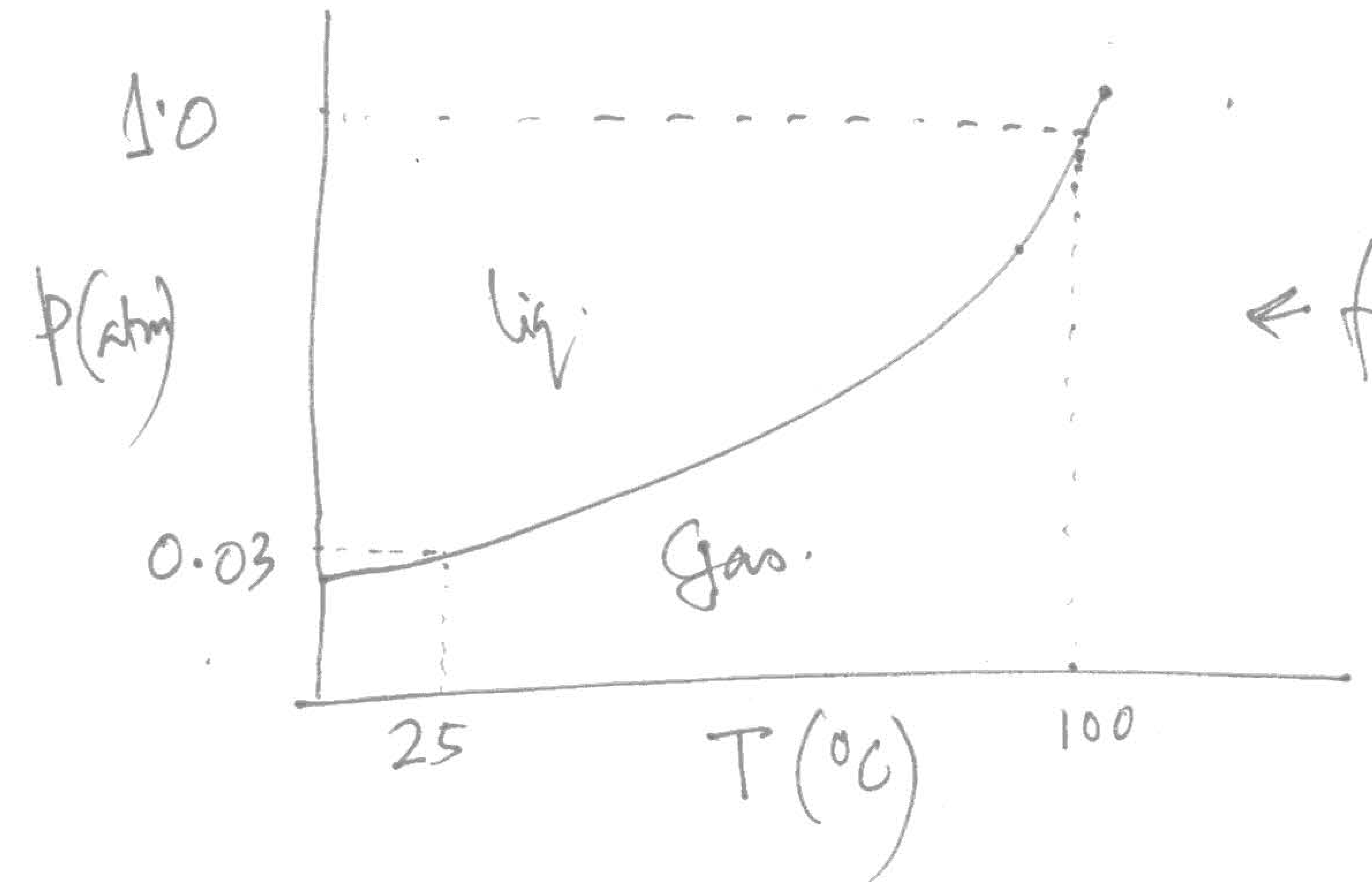
At eqm. the vapour pressure:

$$RT \ln\left(\frac{p}{p^0_i}\right) = \frac{1}{2} Z W_{AA}$$

$$\boxed{p = p^0_{int} \cdot e^{ZW_{AA}/2RT}}$$

→ Vapour pressure decreases with increasing pair-wise attraction energy.

→ Vap. pr. increases with temp. (T).



← for water

How do you find out W_{AA}?

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{ZW_{AA}}{2R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$T = 100°C$ $p = 1$ atm

$T = 25°C$ $p = 0.03$ atm

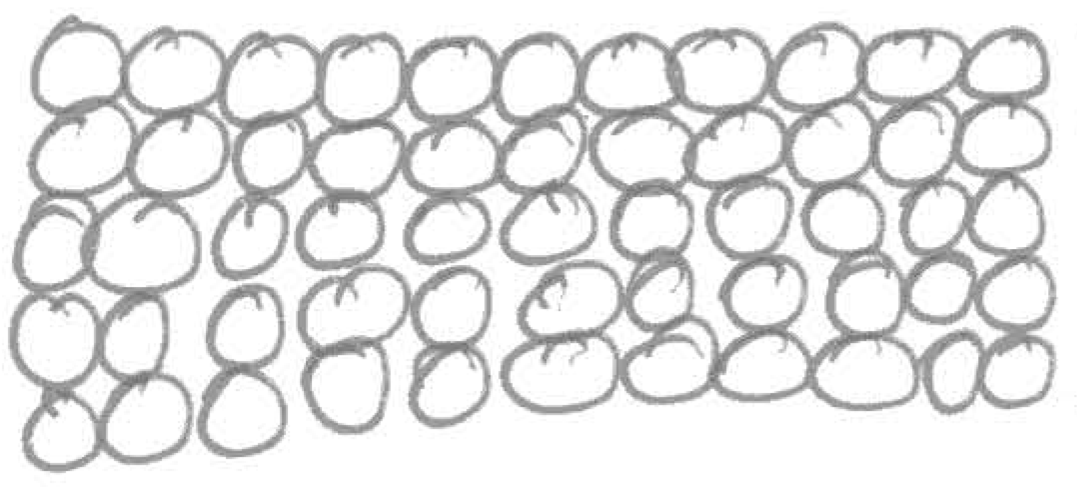
$$\frac{ZW_{AA}}{2} = 40.66 \text{ kJ/mol}$$

$Z = 4$ for H_2O in liq state.

$W_{AA} = 20.3$ kJ/mol

Surface tension:

↳ free energy cost to create/increase ~~[illegible]~~ surface area.



→ no. of molecules in surface & bulk.

Surface : $(z-1)$ neighbours

Bulk : z neighbours.

Total energy of the system (bulk + surface)

$$U = \left(\frac{z w_{AA}}{2}\right)(N-n) + \frac{(z-1) w_{AA}}{2} n$$

$$= \frac{w_{AA}}{2}(Nz-n)$$

$$A = U - TS = \left(\frac{w_{AA}}{2}\right)(Nz-n)$$

Surface tension: ~~∂A~~

$$\gamma = \left(\frac{\partial A}{\partial \sigma}\right)_{N,V,T} = \left(\frac{\partial A}{\partial n}\right)_{N,V,T} \cdot \left(\frac{\partial n}{\partial \sigma}\right)$$

$\left(\frac{\partial A}{\partial n}\right)_{N,V,T} = -\left(\frac{w_{AA}}{2}\right)$; Surface area = $n.a$ (a: area of one molecule)

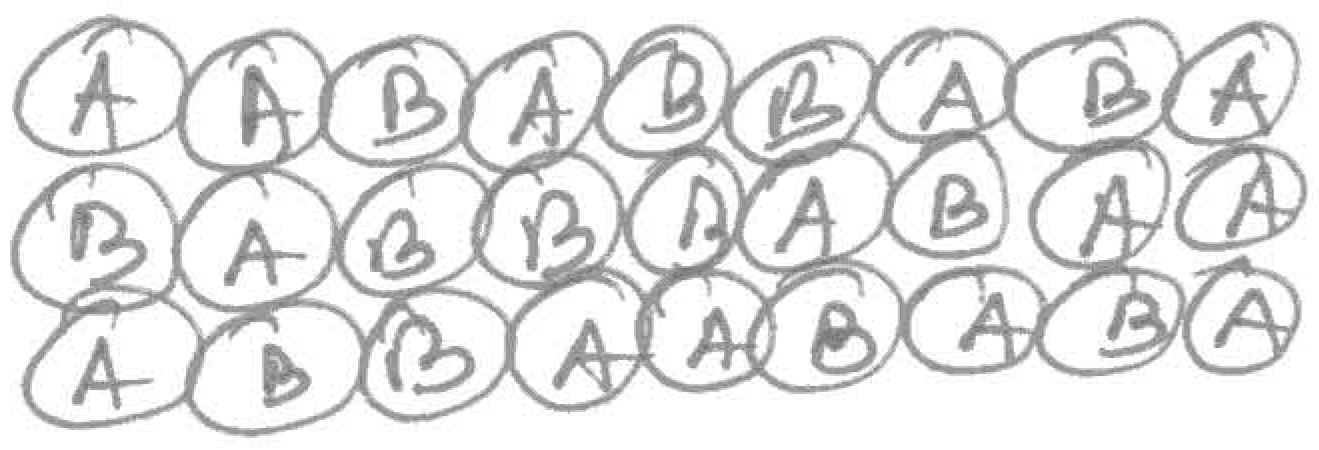
$$\left(\frac{\partial \sigma}{\partial n}\right) = \frac{\partial (na)}{\partial n} = a \longrightarrow \left(\frac{\partial n}{\partial \sigma}\right) = \frac{1}{a}$$

$$\boxed{\gamma = -\frac{w_{AA}}{2a}}$$

as $w_{AA} < 0 \longrightarrow \gamma > 0$
↓
becomes large for large w_{AA}.

Lattice model of solutions and mixture

→ Model: Lattice model of liq. mixture



→ Fixed (T, V, N) assuming low compressibility of liq.

→ Calculate $A = U - TS$

Entropy

→ Unlike pure system, S is not zero here.

$$N = N_A + N_B$$

$$W = \frac{N!}{N_A!\,N_B!}$$

$$S_{sol} = k\ln W = k\ln\left(\frac{N!}{N_A!\,N_B!}\right)$$

$$= k\left[\ln N! - \ln N_A! - \ln N_B!\right]$$

$$= k\left[N\ln N - N - N_A\ln N_A + N_A - N_B\ln N_B + N_B\right]$$ [large N, N_A, N

$$= k\left[N\ln N - N_A\ln N_A - N_B\ln N_B\right]$$

$$= k\left[N_A\ln N + N_B\ln N - N_A\ln N_A - N_B\ln N_B\right]$$

$$= k\left[N_A\ln\left(\frac{N}{N_A}\right) + N_B\ln\left(\frac{N}{N_B}\right)\right]$$

$$= -Nk\left[\left(\frac{N_A}{N}\right)\ln\left(\frac{N_A}{N}\right) + \left(\frac{N_B}{N}\right)\ln\left(\frac{N_B}{N}\right)\right]$$

$$= -Nk\left[x_A\ln x_A + x_B\ln x_B\right]$$

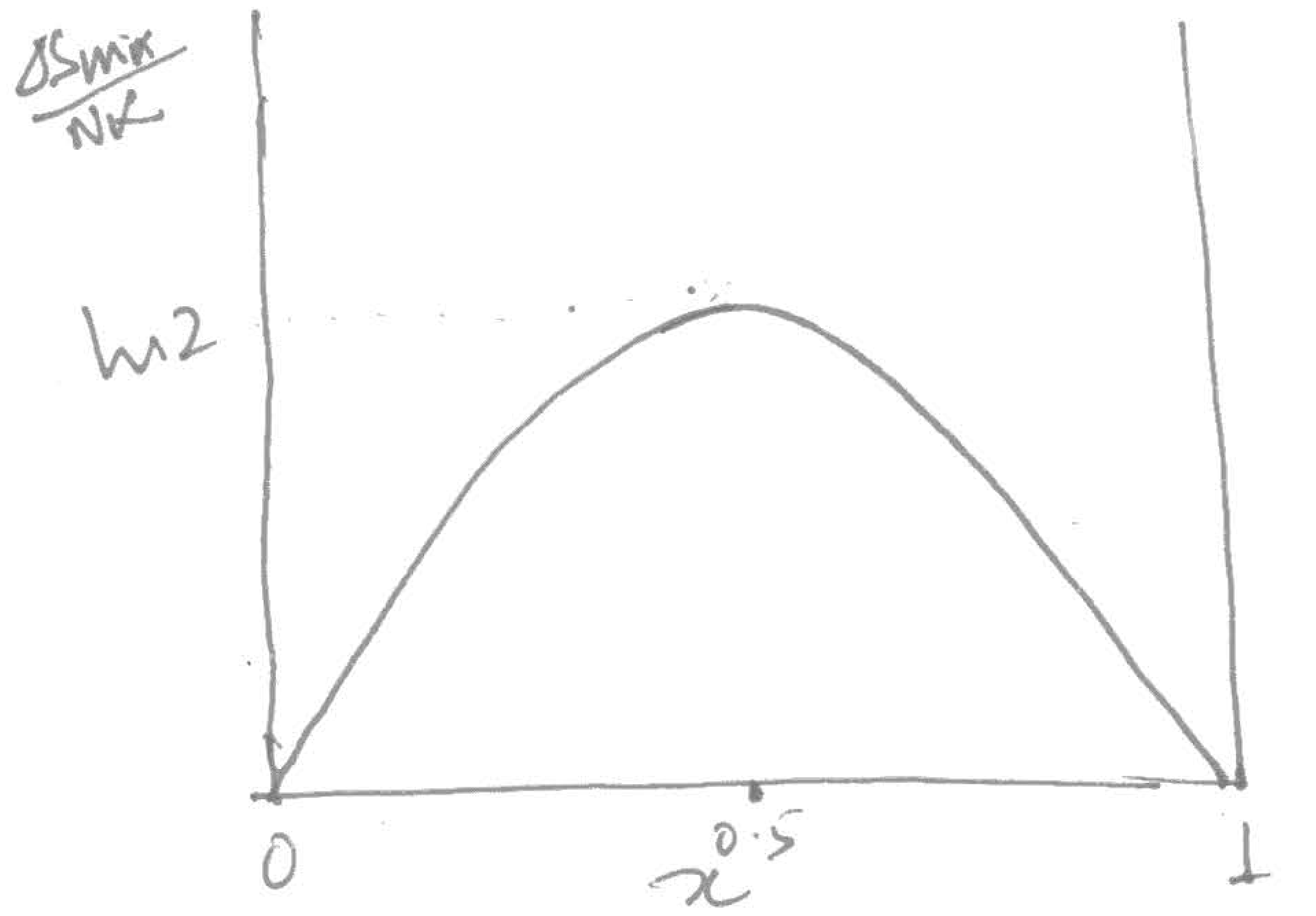
$$\Delta S_{sol} = S_{sol} - (S_A + S_B)$$

$$= S_{sol}$$

$$= -Nk\left[x\ln x + (1-x)\ln(1-x)\right] = -Nk\left[\frac{N_A}{N}\ln\left(\frac{N_A}{N}\right) + \frac{N_B}{N}\ln\left(\frac{N_B}{N}\right)\right]$$

$$= -k\left[N_A\ln(N_A/N) + N_B\cdot\ln\left(\frac{N_B}{N}\right)\right]$$

$$\boxed{\frac{\Delta S_{sol}}{Nk} = -x\ln x - (1-x)\ln(1-x)}$$



Entropy at $x = 0.5$ is maximum
→ as the multiplicity is maximum at that mole fraction.

Energy of solution

→ There are three types of mutual interactions:

A — A ; B — B and A − B

ⒶⒶ ⒷⒷ ⒶⒷ

→ Total energy of the system:

$$U = m_{AA}w_{AA} + m_{BB}w_{BB} + m_{AB}w_{AB}$$

no. of AA interactions

no. of BB interactions

no. of AB interactions.

w_{AA} : energy ~~for~~ of one AA interaction

w_{BB} : " " " BB "

w_{AB} : " " " AB "

→ finding these no.s is difficult task!

$Z N_A = 2m_{AA} + m_{AB}$ and $Z N_B = 2m_{BB} + m_{AB}$.

$m_{AA} = \frac{Z N_A - m_{AB}}{2}$ $\quad$ $m_{BB} = \frac{Z N_B - m_{AB}}{2}$

Thus the energy

$$U = \left(\frac{Z N_A - m_{AB}}{2}\right)\omega_{AA} + \left(\frac{Z N_B - m_{AB}}{2}\right)\omega_{BB} + m_{AB} \omega_{AB}$$

$$= \left(\frac{Z\omega_{AA}}{2}\right) N_A + \left(\frac{Z\omega_{BB}}{2}\right) N_B + \left(\omega_{AB} - \frac{\omega_{AA} + \omega_{BB}}{2}\right) m_{AB}.$$

Ⓐ Calculation of m_{AB} using Bragg-Williams mean-field approximation:

→ The value of m_{AB} depends on arrangement of A and B in the lattice

example
2A and 2B

$m_{AB} =$ ① $m_{AB} = 3$ $m_{AB} = 3$

→ difficult task to determine all possible arrangements.

→ solution: mean-flied approximation.

- assumption: A and B are mixed randomly and uniformly

① Probability that there is a B adjacent to A is p_B.

② p_B is the fraction of sites occupied by B.

$$p_B = \frac{N_B}{N} = x_B = (1-x)$$

③ Average no. of AB contacts made by an A $= Z p_B = Z(1-x)$

④ Total no. of AB contacts by N_A no. of A molecules.

$$\omega_{AB} = N_A Z p_B = Z N_A (1-x) = Z N x(1-x) = Z \cdot N_A \cdot N_B / N$$

$$U = \left(\frac{zW_{AA}}{2}\right)N_A + \left(\frac{zW_{BB}}{2}\right)N_B + \left(\overset{W_{AB}}{\cancel{zNx(1-x)}} - \frac{W_{AA}+W_{BB}}{2}\right)\cdot\frac{zN_AN_B}{N}$$

$$= \left(\frac{zW_{AA}}{2}\right)N_A + \left(\frac{zW_{BB}}{2}\right)N_B + RT\cdot\frac{z}{RT}\left(W_{AB} - \frac{W_{AA}+W_{BB}}{2}\right)\frac{N_AN_B}{N}$$

$$\boxed{U = \left(\frac{zW_{AA}}{2}\right)N_A + \left(\frac{zW_{BB}}{2}\right)N_B + RT\,\chi_{AB}\cdot\frac{N_AN_B}{N}}$$

$$\left.\begin{matrix}\text{Structure}\\ \text{parameter}\end{matrix}\right\}\quad \chi_{AB} = \frac{z}{RT}\left(W_{AB} - \frac{W_{AA}+W_{BB}}{2}\right)$$

Now the Helmholtz free energy.

For solution: $A_{Sol} = U - TS = A_{Sol}(N_A, N_B)$

$$= \left(\frac{zW_{AA}}{2}\right)N_A + \left(\frac{zW_{BB}}{2}\right)N_B + RT\chi_{AB}\cdot\frac{N_AN_B}{N} + RT\left[N_A\cdot\ln\left(N_A/N\right) + N_B\ln\left(\frac{N_B}{N}\right)\right]$$

For pure systems.

$$A(N_A, 0) = \left(\frac{zW_{AA}}{2}\right)N_A\quad,\quad A(0, N_B) = \left(\frac{zW_{BB}}{2}\right)N_B$$

$$\Delta A_{Sol} = A_{Sol}(N_A, N_B) - A(N_A, 0) - A(0, N_B)$$

$$= RT\chi_{AB}\cdot\frac{N_AN_B}{N} + RT\left[N_A\ln\left(N_A/N\right) + N_B\ln\left(N_B/N\right)\right]$$

$$\frac{\Delta A_{Sol}}{RT} = \chi_{AB}\frac{N_AN_B}{N} + N_A\ln\left(N_A/N\right) + N_B\ln\left(N_B/N\right)$$

$$\boxed{\frac{\Delta A_{Sol}}{NRT} = \chi_{AB}\cdot x(1-x) + x\ln x + (1-x)\ln(1-x)} \longrightarrow$$

Regular solution model by Hildebrand (1929)

Chemical potential

$$\mu_A = \left(\frac{\partial A}{\partial N_A}\right)_{T,V,N_B} \rightarrow \frac{\mu_A}{RT} = \left[\frac{\partial}{\partial N_A}\left(\frac{A}{RT}\right)\right]_{T,V,N_B}$$

* note that the derivative is calculated at constant N_B but not at constant N.

$$\frac{\mu_A}{RT} = \cancel{\frac{1}{RT}}\,\frac{\partial}{\partial N_A}\left[\underbrace{N_A \cdot \ln\left(\frac{N_A}{N}\right)}_{①} + \underbrace{N_B \ln\left(\frac{N_B}{N}\right)}_{②} + \underbrace{\left(\frac{zw_{AA}}{2RT}\right)N_A}_{③} + \underbrace{\left(\frac{zw_{AA}}{2RT}\right)N_B}_{④} + \underbrace{\chi_{AB}\frac{N_A N_B}{N}}_{⑤}\right]$$

Retivative of term ①.

~~$= \ln(N_A/N) + N_A \cdot \frac{1}{N_A} = \ln(N_A/N) + 1$~~

$$\frac{\partial}{\partial N_A}\left[N_A \ln N_A - N_A \ln(N_A+N_B)\right]$$

$$= \ln N_A + N_A \cdot \frac{1}{N_A} - \ln N - N_A \cdot \frac{1}{(N_A+N_B)} = \ln\left(\frac{N_A}{N}\right) + 1 - \frac{N_A}{N}$$

Derivative of term ②

$$\frac{\partial}{\partial N_A}\left[N_B \cdot \ln(N_B/N)\right]$$

$$= \frac{\partial}{\partial N_A}\left[N_B \ln N_B - N_B \ln(N_A+N_B)\right]$$

$$= -\frac{N_B}{N_A+N_B} = -\frac{N_B}{N}$$

Derivative of term ③

$$= \frac{zw_{AA}}{2RT}$$

Derivative of term ④ $= 0$

Derivative of term ⑤

$$\chi_{AB} N_B \frac{\partial}{\partial N_A}\left[\frac{N_A}{N_A+N_B}\right]$$

$$= \chi_{AB} \cdot N_B \frac{\partial}{\partial N_A}\left[\frac{N_A+N_B-N_B}{N_A+N_B}\right]$$

$$= \chi_{AB} N_B \cdot \frac{\partial}{\partial N_A}\left[1 - \frac{N_B}{N_A+N_B}\right]$$

$$= \chi_{AB} N_B \left[\frac{N_B}{(N_A+N_B)^2}\right]$$

$$= \chi_{AB}\left(\frac{N_B}{N}\right)^2$$

$$= \chi_{AB}(1-x_A)^2$$

$$\frac{\mu_A}{RT} = \ln\left(\frac{N_A}{N}\right) + 1 - \frac{N_A}{N} - \frac{N_B}{N} + \frac{zw_{AA}}{2RT} + \chi_{AB}(1-x_A)^2$$

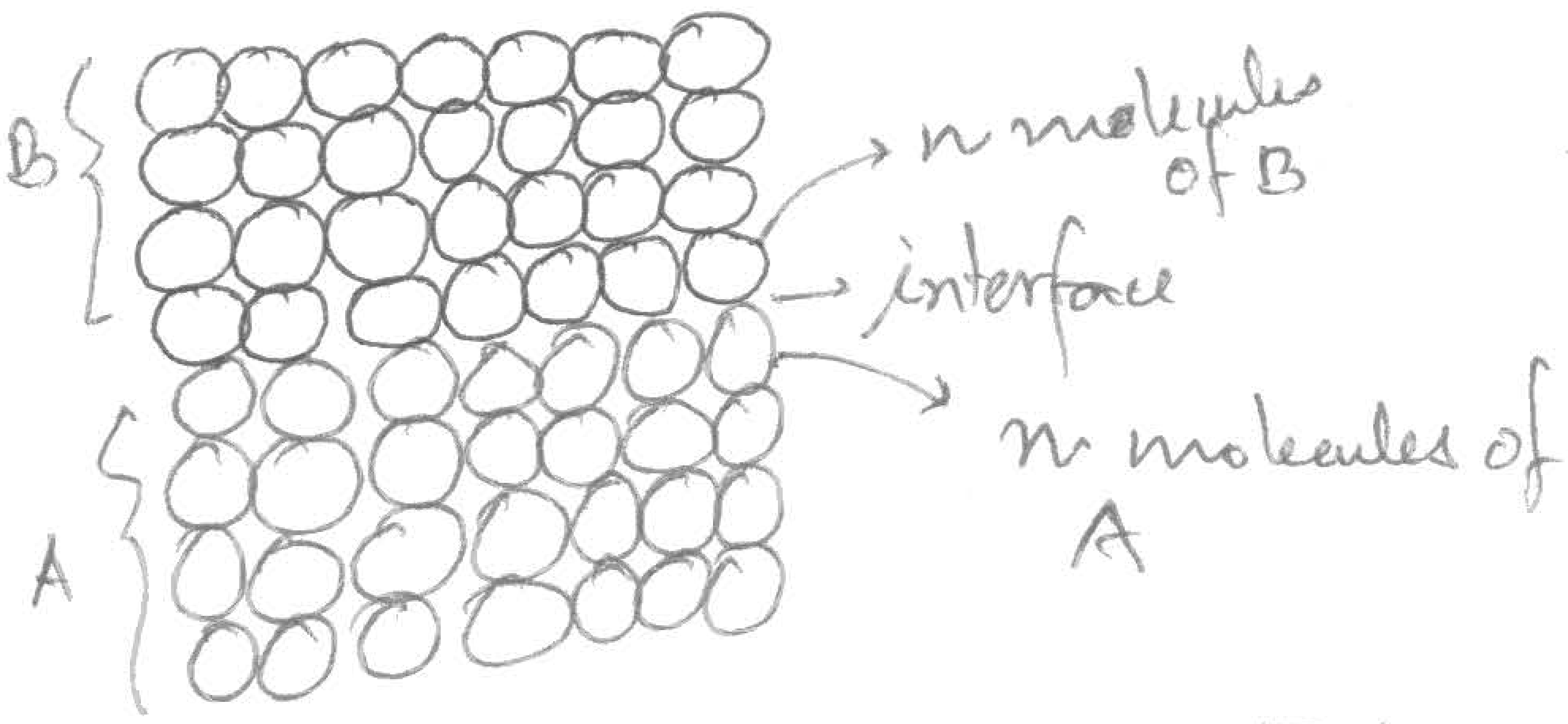
$$\boxed{\frac{\mu_A}{RT} = \ln x_A + \frac{zw_{AA}}{2RT} + \chi_{AB}(1-x_A)^2}$$

Similarly for B the chemical potential

$$\boxed{\frac{\mu_B}{RT} = \ln x_B + \frac{zw_{BB}}{2RT} + \chi_{AB}(1-x_B)^2}$$

Interfacial tension

Interface: the boundary between two condensed phases:



interfacial tension (γ_{AB}): free energy cost of increasing surface area between A and B.

→ Entropy of the individual phases are again zero.

~~The internal ener~~

→ Only U would contribute to A.

Total energy

U = Energy of bulk A + Energy of bulk B + Energy of interface A due to A-A contacts. + energy of interface B due to B-B contacts + energy for A-B contacts.

$$A = (N_A - n)\cdot\left(\frac{zw_{AA}}{2}\right) + (N_B - n)\left(\frac{zw_{BB}}{2}\right) + n\cdot\frac{(z-1)w_{AA}}{2} + n\frac{(z-1)w_{BB}}{2} + nw_{AB}$$

Total interfacial area, $\sigma = na$. → $\left(\frac{\partial n}{\partial A}\right) = \frac{1}{a}$

$$\gamma_{AB} = \left(\frac{\partial A}{\partial \sigma}\right)_{N_A,N_B,T} = \left(\frac{\partial A}{\partial n}\right)_{N_A,N_B,T} \cdot \left(\frac{\partial n}{\partial A}\right)$$

$$A = N_A\cdot\left(\frac{zw_{AA}}{2}\right) + N_B\left(\frac{zw_{BB}}{2}\right) + n\left[w_{AB} - \frac{zw_{AA}}{2} + \frac{(z-1)w_{AA}}{2} - \frac{zw_{BB}}{2} + \frac{(z-1)w_{BB}}{2}\right]$$

$$= N_A\left(\frac{zw_{AA}}{2}\right) + N_B\left(\frac{zw_{BB}}{2}\right) + n\left[w_{AB} - \frac{w_{AA}+w_{BB}}{2}\right]$$

$$= N_A\left(\frac{zw_{AA}}{2}\right) + N_B\left(\frac{zw_{BB}}{2}\right) + \frac{nzkT}{zkT}\cdot\left[w_{AB} - \frac{w_{AA}+w_{BB}}{2}\right]$$

$$= N_A\left(\frac{zw_{AA}}{2}\right) + N_B\left(\frac{zw_{BB}}{2}\right) + \frac{nkT}{z}\chi_{AB}$$

$$\gamma_{AB} = \frac{RT}{Z}\chi_{AB}\cdot\frac{1}{a}$$

↓

$$\boxed{\gamma_{AB} = \frac{RT}{aZ}\cdot\chi_{AB}}$$

$$\chi_{AB} = \frac{aZ}{RT}\cdot\gamma_{AB}$$

* χ_{AB} can be determin
from interfacial
tension expt.
data.

if $N_B = 0$, (there is no other phase) → $\omega_{AB} = 0$, $\omega_{BB} = 0$.

$$\chi_{AB} = -\frac{Z\omega_{AA}}{2RT}$$

$$\gamma_{AB} = -\frac{\omega_{AA}}{2a}$$

Problem

Determine χ_{AB} at 20°C for water – benzene interface with $\gamma_{AB} = 35$ dyne
$Z = 6$, and interfacial contact area $a = 3\mathring{A} \times 3\mathring{A} = 9\mathring{A}^2$.

$$\chi_{AB} = \frac{Za\gamma_{AB}}{RT}$$

$$= \frac{6\times(9\mathring{A}^2)\times(35\times10^{-7}\,\mathrm{J\,cm^{-2}})\left(\frac{1\,\mathrm{cm}}{10^8\,\mathring{A}}\right)^2}{(1.38\times10^{-23}\,\mathrm{JK^{-1}})\times(293\,\mathrm{K})} = 4.7$$

Lattice model of polymer solution: <u>Flory-Huggins theory.</u>

Total sites in the Lattice : M $\qquad M = Nn_p + n_s$

no. of solvent molecules = n_s

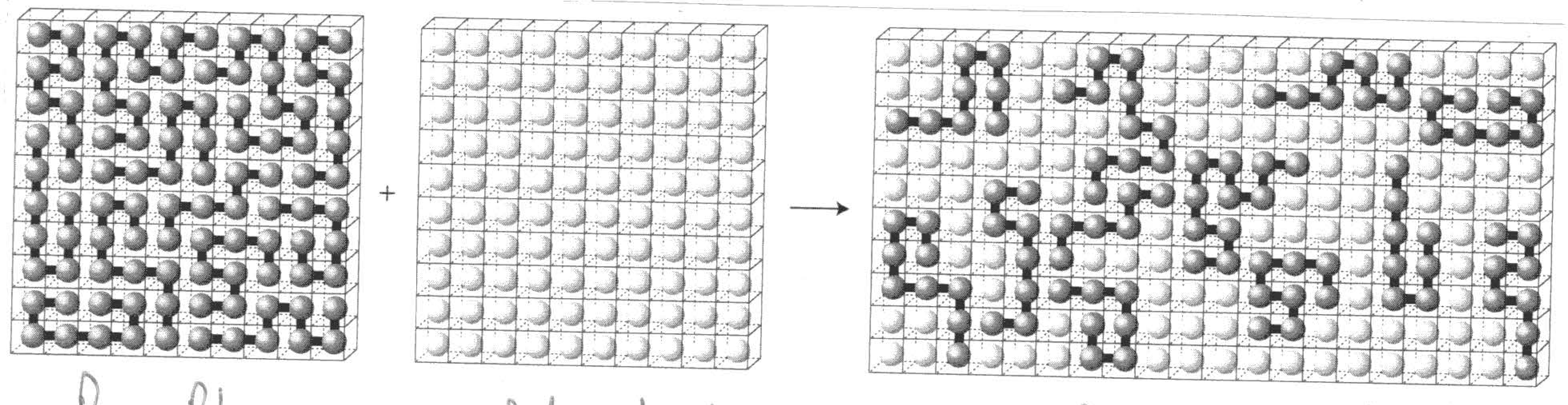
no. of polymer molecules = n_p

no. of segments in each polymer : N

Mole fraction of polymer : $x_p = \dfrac{n_p}{n_s + n_p}$; Volume fraction of polymer : $\phi_p = \dfrac{Nn_p}{M}$

mole fraction of solvent ; $x_s = \dfrac{n_s}{n_s + n_p}$ $\qquad$ Vol. fraction of solvent : $\phi_s = \dfrac{n_s}{M}$

~~Pure~~



Pure Polymer $\qquad$ Pure solvent $\qquad$ Polymer solution.

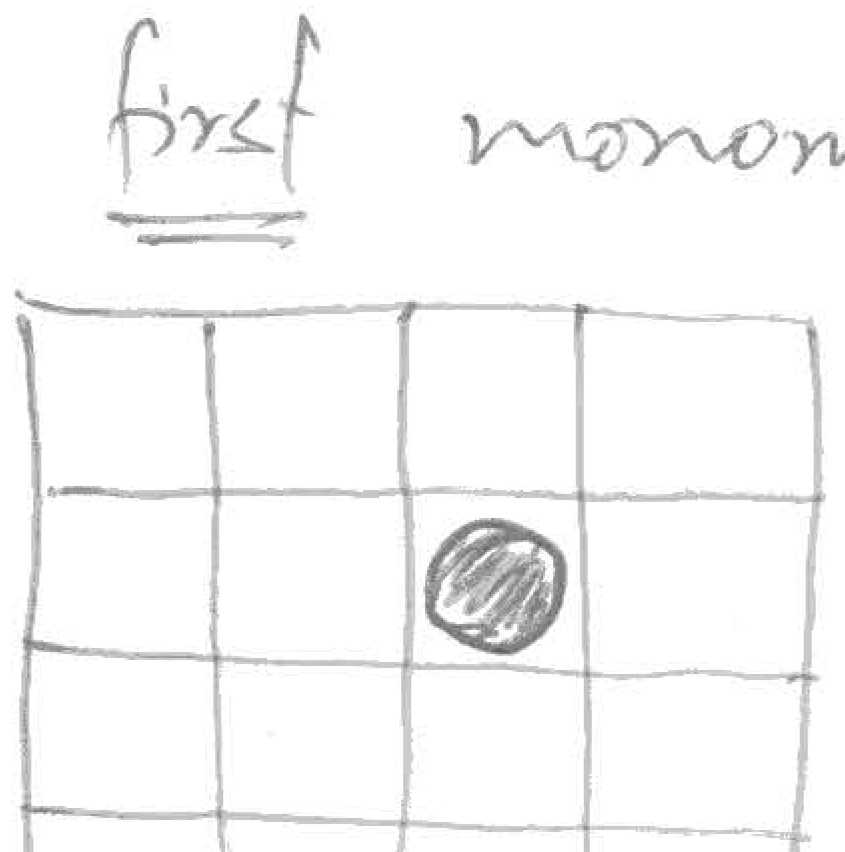
- one solvent molecule and a monomer molecule have same size.
- molecules of polymer mix with solvent randomly
- Polymer chains in sol^n are indistinguishable

Entropy of mixing:

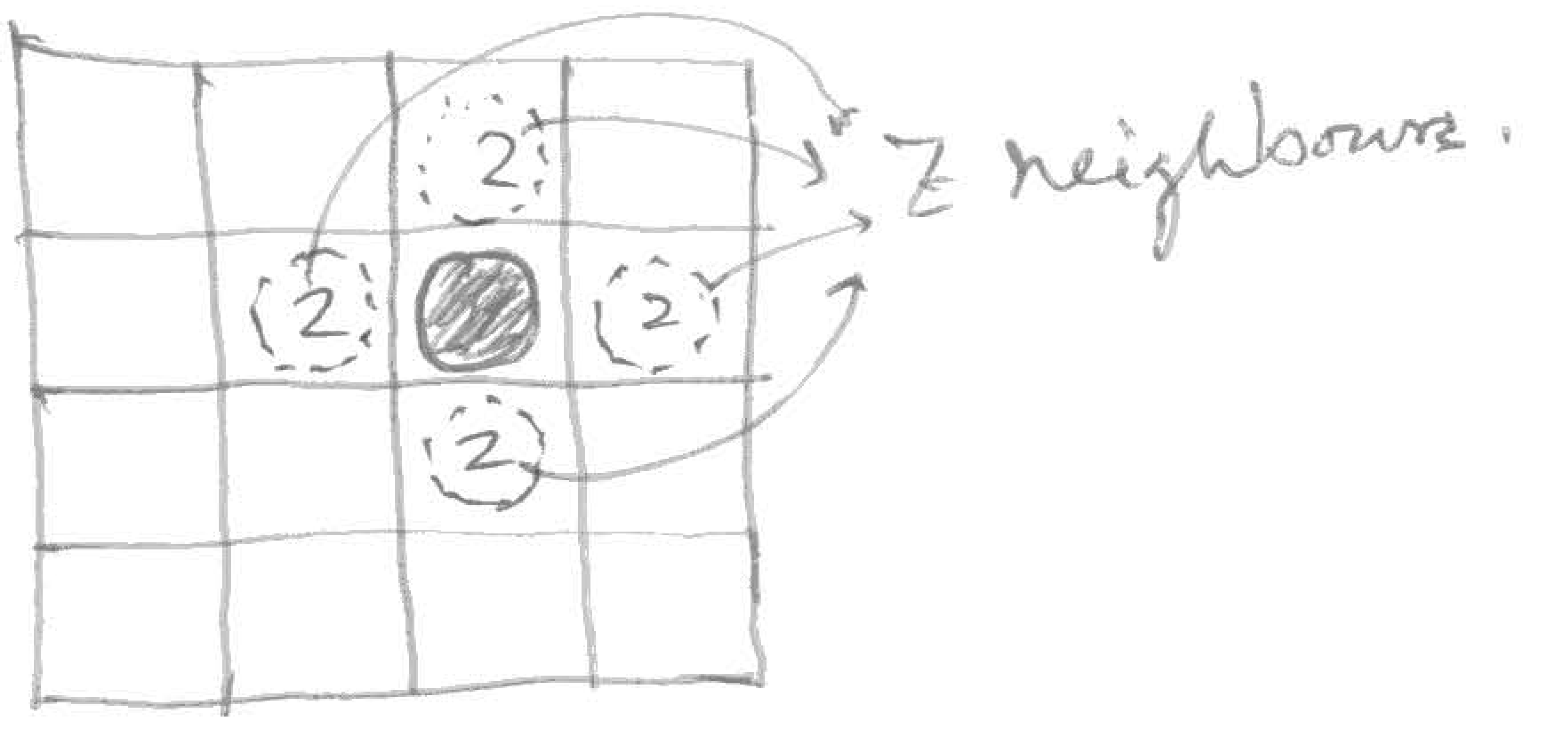
S can be calculated from $W(n_p, n_s) \rightarrow$ the no. of ways polymer chain can be arranged in the lattice.

Let's begin with one polymer chain (molecule):

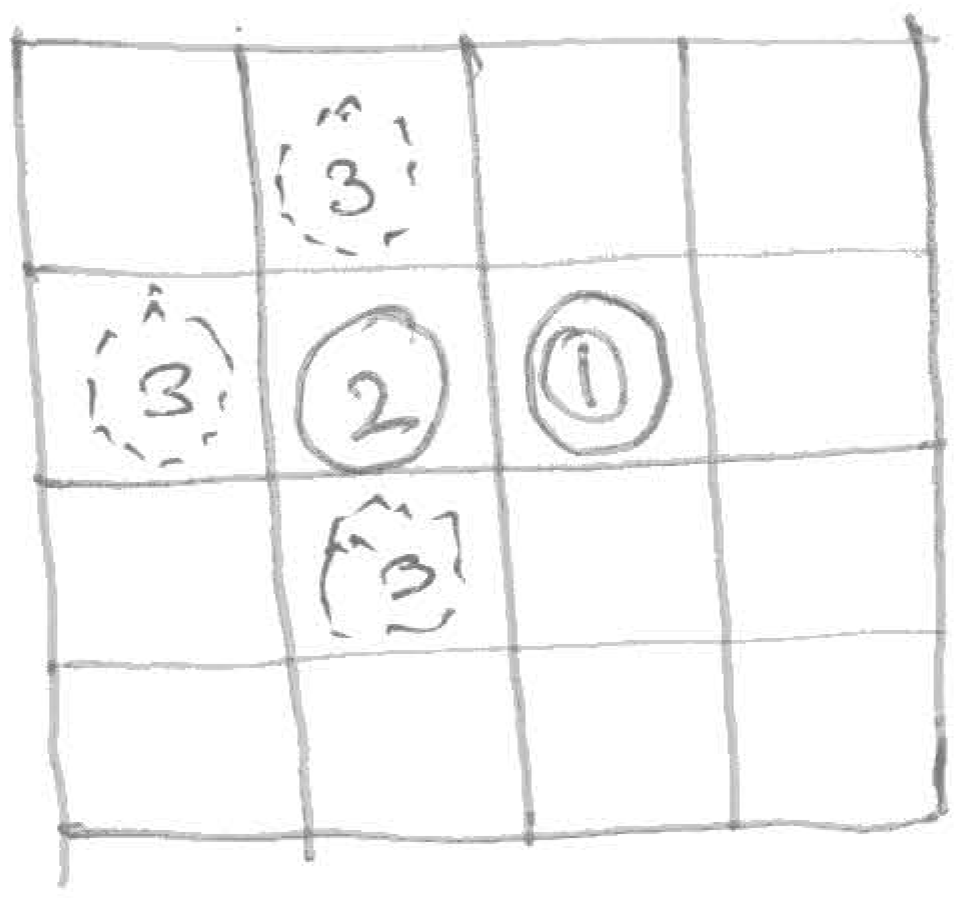
① the no. of ways the <u>first</u> monomer can be placed in lattice with M site $= M$



② The no. of ways the <u>2nd</u> monomer can be placed. = Z



③ The no. of ways the <u>3rd</u> monomer can be placed = (Z−1)



④ The no. of ways the 4th monomer can be placed = (Z−1).

⑤ Thus the total no. of ways one polymer with N segments can be placed in lattice with M sites.

$$\nu_1 = M\, Z \underbrace{(Z-1)(Z-1)\cdots\cdots(Z-1)}_{(N-2)\text{ times}}$$

$$\boxed{\nu_1 \simeq M(Z-1)^{N-1}}$$

✳ However with each monomer placed the available vol (sites) in the lattice decreases.

→ Flory & Huggins ~~assumed that~~ calculated the excluded volume (or the available vol) assuming random ~~mixing~~ dispersion of polymer in lattice.

→ based on mean field approach.

→ the available vol. for first ~~lattice~~ monomer $= \left(\frac{M}{M}\right)$

→ . . . . 2nd . . . . . $= \frac{M-1}{M}$

→ . . . . 3rd . . . . . . $= \frac{M-2}{M}$

→ . . . . Nth . . . . $M-(N-1)$, $M-N+$

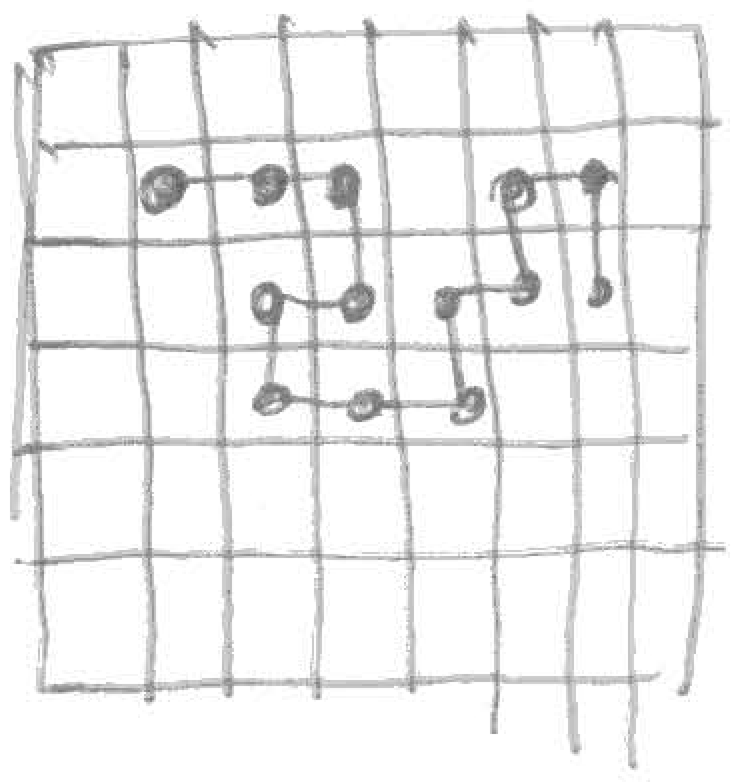
Thus,

$$\nu_1 = M\cdot\left[Z\cdot\frac{M-1}{M}\right]\left[(Z-1)\left(\frac{M-2}{M}\right)\right]\left[(Z-1)\left(\frac{M-3}{M}\right)\right]\cdots\cdots\left[(Z-1)\left(\frac{M-N+1}{M}\right)\right]$$

$$\approx \left(\frac{Z-1}{M}\right)^{N-1}\cdot M(M-1)(M-2)\cdots\cdots(M-(N-1))$$

$$= \left(\frac{Z-1}{M}\right)^{N-1}\cdot\frac{M(M-1)(M-2)\cdots(M-(N-1))(M-N)(M-N-1)(M-N-2)\cdots\cdots 1}{(M-N)(M-N-1)(M-N-2)\cdots\cdots 1}$$

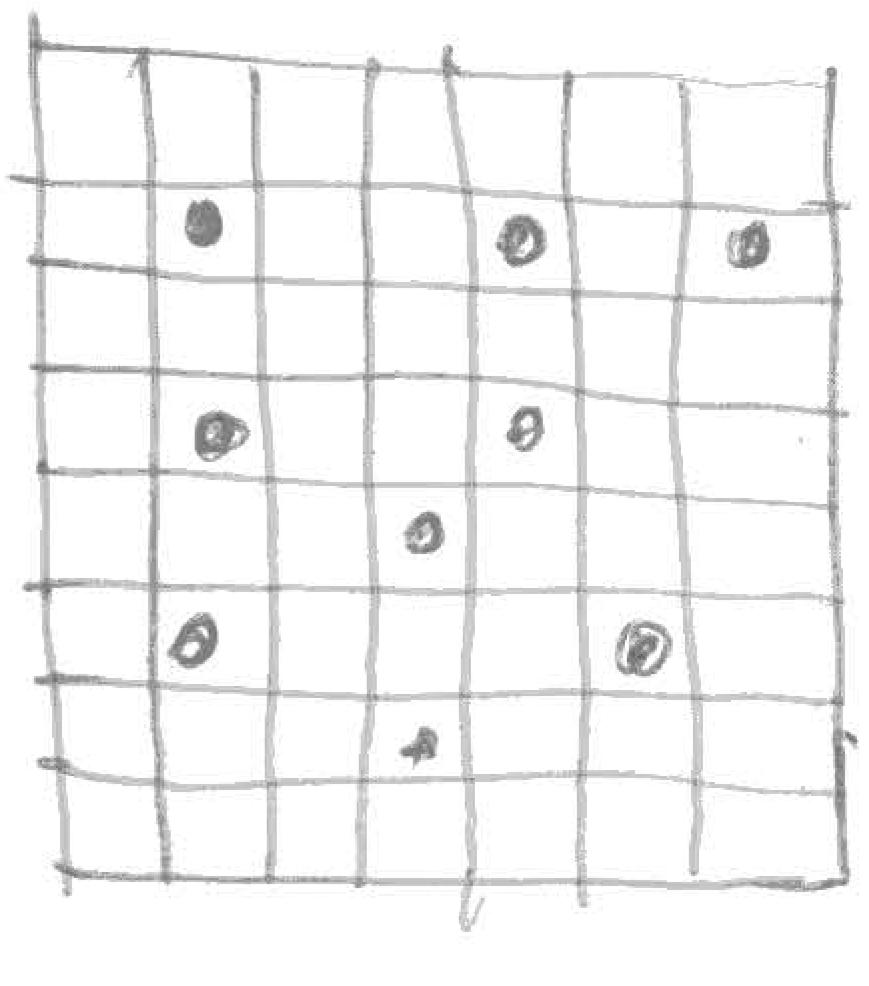
$$\boxed{\nu_1 = \left(\frac{Z-1}{M}\right)^{N-1}\cdot\frac{M!}{(M-N)!}}$$



Calculating ν_2 (for 2nd polymer), ν_3 (3rd) ... is difficult problem

<u>Alternatively,</u>

→ Put the 1st monomer of all n_p polymer molecules first in the lattice.



$$\nu_{\text{first}} = M(M-1)(M-2)\cdots\cdots(M-(n_p-1))$$

$$= \frac{M!}{(M-n_p)!}$$

→ The no. of remaining segments : $N-1$

" " " available sites : $M-n_p$

" " " monomers to be placed = $n_p(N-1)$

$$\nu_{\text{subsequent}} = \underbrace{\left[(Z-1)\cdot\left(\frac{M-n_p}{M}\right)\right]\left[(Z-1)\left(\frac{M-n_p-1}{M}\right)\right]\cdots\cdots\left[(Z-1)\frac{(M-n_p)}{M}\right.\cdots\cdots\left[(Z-1)\frac{(M-n_p)-\{n_p(N-1)-1\}}{M}\right]}_{n_p(N-1)\text{ terms.}}$$

$$= \cancel{\frac{Z-1}{M}}$$

$$= \left(\frac{Z-1}{M}\right)^{n_p(N-1)} \cdot (M-n_p)(M-n_p-1)(M-n_p-2) \cdots\cdots (M-\cancel{n_p}Nn_p+1)$$

$$= \left(\frac{Z-1}{M}\right)^{n_p(N-1)} \cdot \frac{(M-n_p)!}{(M-Nn_p)!}$$

Thus, $W(n_p, n_s) = \dfrac{\nu_{first} \cdot \nu_{subsequent}}{n_p!}$

$\longrightarrow$ to account for indistinguishabil
of polymer molecul

$$W(n_p, n_s) = \frac{M!}{(M-n_p)!} \cdot \left(\frac{Z-1}{M}\right)^{n_p(N-1)} \cdot \frac{(M-n_p)!}{(M-Nn_p)!\, n_p!}$$

$$= \left(\frac{Z-1}{M}\right)^{n_p(N-1)} \cdot \frac{M!}{(M-Nn_p)!\, n_p!} = \left(\frac{Z-1}{M}\right)^{n_p(N-1)} \cdot \frac{M!}{n_s!\, n_p!}$$

For pure polymer.

$$W(n_p, 0) = \left(\frac{Z-1}{Nn_p}\right)^{n_p(N-1)} \cdot \frac{(Nn_p)!}{n_p!} \qquad \begin{bmatrix} n_s = 0 \\ M = n_p N \end{bmatrix}$$

For pure solvent $W(0, n_s) = 1$

$$\Delta S_{mix} = S_{Sol^n} - (S_{Solvent} + S_{Polymer})$$

$$= k \ln W(n_p, n_s) - (k \ln W(0,n_s) - k \ln W(n_p, 0))$$

$$= k \cdot \ln \frac{W(n_p, n_s)}{W(0,n_s)\, W(n_p,0)}$$

$$= k \ln \frac{W(n_p, n_s)}{W(n_p, 0)}$$

$$\frac{W(n_p, n_s)}{W(n_p, 0)} = \left(\frac{Z-1}{M}\right)^{n_p(N-1)} \cdot \frac{M!}{n_s!\, n_p!} \cdot \left(\frac{Nn_p}{Z-1}\right)^{n_p(N-1)} \cdot \frac{n_p!}{(Nn_p)!}$$

$$= \left(\frac{Nn_p}{M}\right)^{n_p(N-1)} \cdot \frac{M!}{(Nn_p)!\, n_s!}$$

$$= \frac{\left(M/e\right)^{M}}{\left(Nn_p/e\right)^{Nn_p} \cdot \left(n_s/e\right)^{n_s}} \cdot \left(\frac{Nn_p}{M}\right)^{n_pN} \cdot \left(\frac{M}{Nn_p}\right)^{n_p}$$

Stirling's approximation.
$N! = \left(\frac{N}{e}\right)^{N}$

$$= \frac{M^{M}}{(Nn_p)^{Nn_p} \cdot n_s^{n_s}} \cdot \left(\frac{Nn_p}{M}\right)^{n_pN} \cdot \left(\frac{M}{Nn_p}\right)^{n_p}$$

$$= \frac{M^{n_pN} \cdot M^{n_s}}{(Nn_p)^{Nn_p} \cdot (n_s)^{n_s}} \cdot \left(\frac{Nn_p}{M}\right)^{Nn_p} \cdot \left(\frac{M}{Nn_p}\right)^{n_p}$$

$$= \left(\frac{M}{n_s}\right)^{n_s} \cdot \left(\frac{M}{Nn_p}\right)^{n_p}$$

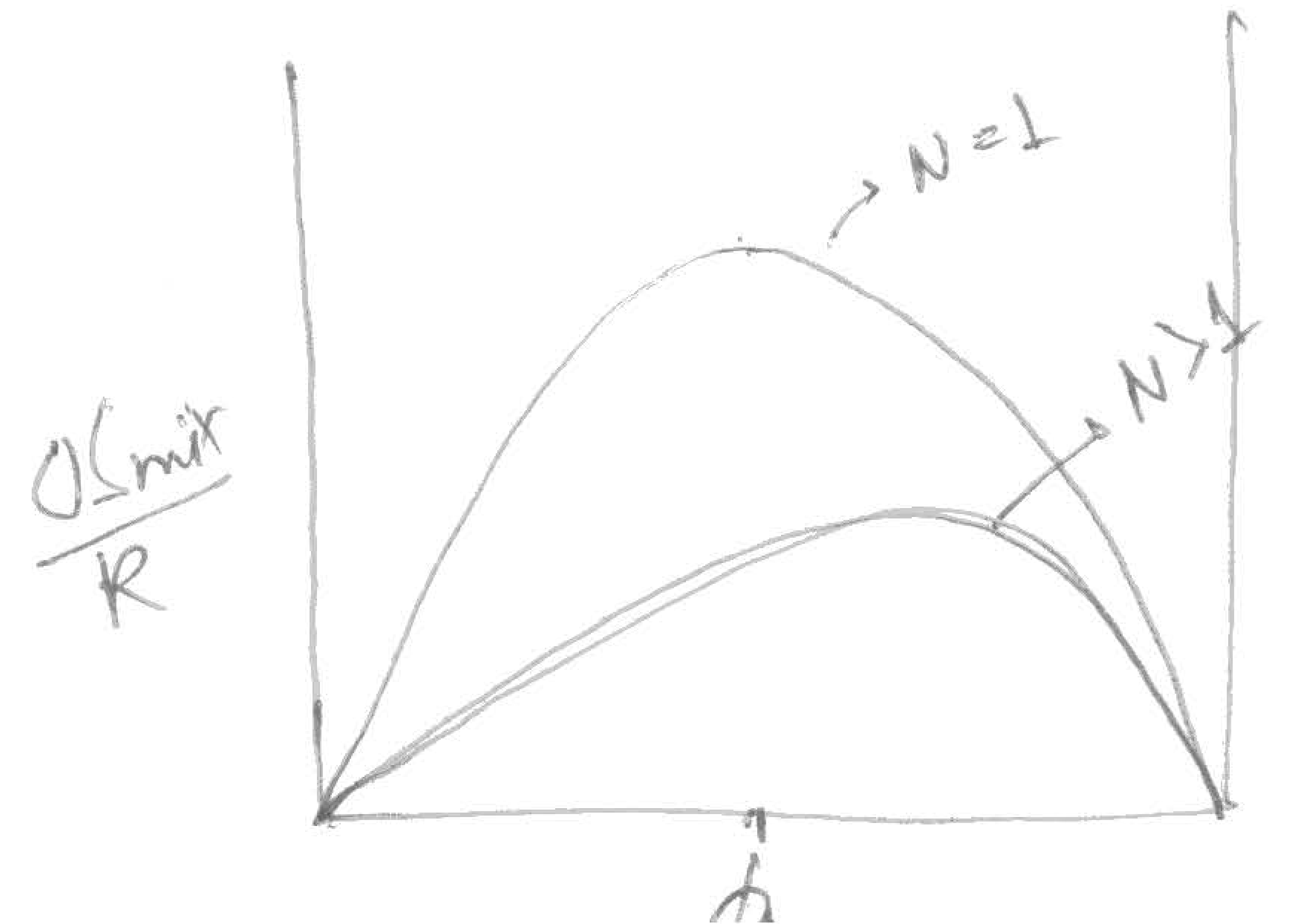
$$\Delta S_{mix} = R \cdot \ln\left[\left(\frac{M}{n_s}\right)^{n_s} \cdot \left(\frac{M}{Nn_p}\right)^{n_p}\right]$$

$$\frac{\Delta S_{mix}}{R} = -\ln\left(\frac{n_s}{M}\right)^{n_s} - \ln\left(\frac{Nn_p}{M}\right)^{n_p}$$

$$\boxed{\frac{\Delta S_{mix}}{R} = -n_s \ln \phi_s - n_p \ln \phi_p}$$

when $N = 1$

$$\frac{\Delta S_{mix}}{R} = -n_s \ln x_s - n_p \ln x_p$$



Energy of mixing

Total energy of contact

$$U = m_{ss}\omega_{ss} + m_{pp}\omega_{pp} + m_{sp}\omega_{sp}$$

solvent-solvent contact

monomer - monomer contact

solvent-monomer contact

Based on conservation of no. of contacts. for solvent.

$$Z n_s = 2m_{ss} + m_{sp} \longrightarrow m_{ss} = \frac{1}{2}(Z n_s - m_{sp})$$

and for monomers.

$$(Z-2)N n_p = 2m_{pp} + m_{sp}$$

* $(Z-2)$ term originates from the fact that a monomer ~~two~~ is ~~two~~ connected to tw other monomers except for the termin monomer.

approximately → $Z N n_p = 2m_{pp} + m_{sp}$

$$\longrightarrow m_{pp} = \frac{1}{2}(Z N n_p - m_{sp})$$

Now for monomer - solvent contact; apply mean field approximation of Bragg - William.

m_{sp} = (no. of solvent molecules) × (no. of neighbours per solvent) × (av. no. of monomer per solvent)

$$= n_s \times Z \times \frac{N n_p}{M} \longrightarrow \boxed{m_{sp} = \frac{n_s Z N n_p}{M}}$$

$$U = \frac{1}{2}(Z n_s - m_{sp})\omega_{ss} + \frac{1}{2}(Z N n_p - m_{sp})\omega_{pp} + \cancel{\frac{n_s Z N n_p}{M}\omega_{sp}}\; m_{sp}\omega_{sp}$$

$$= \left(\frac{Z\omega_{ss}}{2}\right)n_s + \left(\frac{Z\omega_{pp}}{2}\right)N n_p + \left(\omega_{sp} - \frac{\omega_{ss}+\omega_{pp}}{2}\right)m_{sp}$$

$$= \left(\frac{z\omega_{ss}}{2}\right)n_s + \left(\frac{z\omega_{pp}}{2}\right)Nn_p + z\left(\omega_{sp} - \frac{\omega_{ss}+\omega_{pp}}{2}\right)\frac{n_s n_p N}{M}$$

→ $\frac{U}{\cancel{RT}}$ The total energy of polymer solution.

$$\boxed{U(n_p, n_s) = \left(\frac{z\omega_{ss}}{2}\right)n_s + \left(\frac{z\omega_{pp}}{2}\right)Nn_p + RT\chi_{sp}\frac{n_s n_p N}{M}}$$

where $\chi_{sp} = \frac{z}{RT}\left(\omega_{sp} - \frac{\omega_{ss}+\omega_{pp}}{2}\right)$

energy of pure solvent

$$U(0, n_s) = \left(\frac{z\omega_{ss}}{2}\right)n_s$$

Energy of pure polymer.

$$U(n_p, 0) = \left(\frac{z\omega_{pp}}{2}\right)Nn_p$$

$$\Delta U_{mix} = U(n_p, n_s) - \left[U(n_p, 0) + U(0, n_s)\right]$$

$$\boxed{\Delta U_{mix} = RT\chi_{sp}\frac{n_s n_p N}{M}}$$

Change in Helmholtz free energy: (ΔA_{mix})

$$\Delta A_{mix} = \Delta U_{mix} - T\Delta S_{mix}$$

$$= RT\chi_{sp}\frac{n_s N n_p}{M} + RT\left[n_s \ln\phi_s + n_p \ln\phi_p\right]$$

$$= MRT\left[\chi_{sp}\left(\frac{n_s}{M}\right)\left(\frac{Nn_p}{M}\right) + \left(\frac{n_s}{M}\right)\ln\phi_s + \left(\frac{Nn_p}{NM}\right)\ln\phi_p\right]$$

$$= MRT\left[\chi_{sp}\phi_s\phi_p + \phi_s\ln\phi_s + \frac{\phi_p}{N}\ln\phi_p\right]$$

→ $$\boxed{\frac{\Delta A_{mix}}{MRT} = \chi_{sp}\phi_s\phi_p + \phi_s\ln\phi_s + \frac{\phi_p}{N}\ln\phi_p}$$

Energy of mixing

Total energy of contact

$$U = \underbrace{m_{ss}\omega_{ss}}_{\text{solvent-solvent contact}} + \underbrace{m_{pp}\omega_{pp}}_{\text{monomer-monomer contact}} + \underbrace{m_{sp}\omega_{sp}}_{\text{solvent-monomer contact}}$$

Based on conservation of no. of contacts for solvent.

$$Zn_s = 2m_{ss} + m_{sp} \rightarrow m_{ss} = \frac{1}{2}(Zn_s - m_{sp})$$

and for monomers

$$(Z-2)Nn_p = 2m_{pp} + m_{sp}$$

* $(Z-2)$ term originates from the fact that a monomer ~~has~~ is ~~two~~ connected to tw other monomers except for the termin monomer.

approximately → $ZNn_p = 2m_{pp} + m_{sp}$

$$\rightarrow m_{pp} = \frac{1}{2}(ZNn_p - m_{sp})$$

Now for monomer-solvent contact; apply mean field approximation of Bragg-William.

m_{sp} = (no. of solvent molecules) × (no. of neighbours per solvent) × (av. no. of monomer per solvent)

$$= n_s \times Z \times \frac{Nn_p}{M} \rightarrow \boxed{m_{sp} = \frac{n_s Z N n_p}{M}}$$

$$U = \frac{1}{2}(Zn_s - m_{sp})\omega_{ss} + \frac{1}{2}(ZNn_p - m_{sp})\omega_{pp} + \cancel{\frac{n_s Z N n_p}{M}\omega_{sp}}\, m_{sp}\omega_{sp}$$

$$= \left(\frac{Z\omega_{ss}}{2}\right)n_s + \left(\frac{Z\omega_{pp}}{2}\right)Nn_p + \left(\omega_{sp} - \frac{\omega_{ss}+\omega_{pp}}{2}\right)m_{sp}$$

Mixing two different polymers (polymer blend):

$$M = n_A N_A + n_B N_B \quad , \quad \phi_A = \frac{n_A N_A}{M} \, , \quad \phi_B = \frac{n_B N_B}{M}$$

$$\boxed{\frac{\Delta A_{mix}}{MRT} = \chi_{AB}\phi_A\phi_B + \frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B}$$