Statistical Thermodynamics

— Connect the atomistic understanding of materials to thermodynamic principles.

Macroscopic thermodynamic parameters

— U, V, S, N, T, P, C_v or C_p

Atomistic description of materials

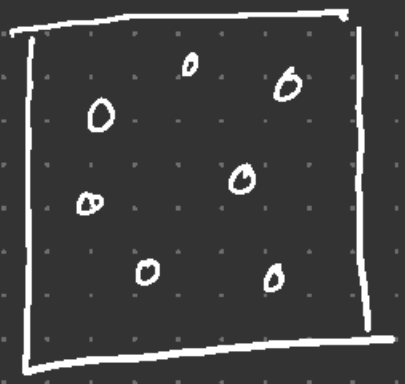
— atoms / molecules

Monoatomic gas — helium, argon, neon

$PV = NRT$

Macroscopic equation of state

U, V



1 mole of Gas atoms — 6.023×10^{23} of atoms

Atomistic description

— mass of each atom m

— position in space x, y, z

— velocity $\vec{v}$ v_x, v_y, v_z

Translational Kinetic Energy

$$\frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

Entropy $S(U, V, N)$

$S \leftrightarrow C_V$ or C_p

$$dS \geq \frac{\delta q}{T}$$

S, C_V or C_p $\rightarrow \langle m, x, y, z, v_x, v_y, v_z \rangle$

Statistical mechanical description of matter which relates microscopic quantities to macroscopic thermodynamic parameters

Equipartition Theorem

Relation between temperature of a system with its average energies

Every atom of an inert noble gas that is in thermal equilibrium at T has an average translational kinetic energy $\frac{3}{2} k_B T$ $\quad k_B = R/N_A$

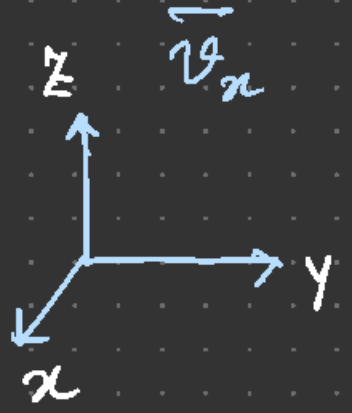
— Boltzmann's constant

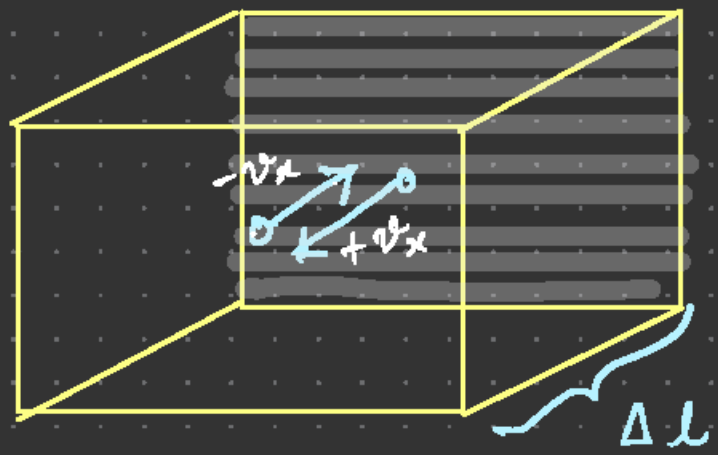
Kinetic energy $= \frac{1}{2} m \bar{v}^2$

$\bar{v}$ – Average velocity of a collection of atoms

$= \frac{1}{2} m \bar{v}_x^2 + \frac{1}{2} m \bar{v}_y^2 + \frac{1}{2} m \bar{v}_z^2$

$= \frac{3}{2} k_B T$





Volume $V = \Delta l \, A$

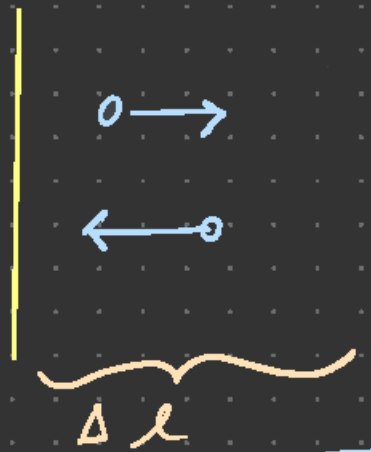
$A \rightarrow$ area of cross section

$n_T = n N_A$

– no. of gas molecules

rms $\bar{v}_x = \sqrt{\frac{v_{x1}^2 + v_{x2}^2 + \cdots v_{xn_T}^2}{n_T}}$

Over a time period Δt, on an average,



$\frac{n_T}{2}$ atoms move towards Wall

$\frac{n_T}{2}$ atoms move opposite to wall

$+x$

$\bar{v}_x$ — rms velocity along $+x$

$-\bar{v}_x$ — rms velocity along $-x$

m is the mass of atom

Change in momentum upon elastic collision with wall

$$m\bar{v}_x - (-m\bar{v}_x) = 2m\bar{v}_x$$

Rate of change of momentum

$$= \frac{2m\bar{v}_x}{\Delta t}$$

Δl - distance

$$\Delta l = \bar{v}_x \Delta t$$

$$V = \Delta l \cdot A = \bar{v}_x \Delta t A$$

$$V = A \bar{v}_x \Delta t$$

$$F = \frac{A\bar{v}_x \Delta t}{V} \frac{n_T}{2} \frac{2m\bar{v}_x}{\Delta t}$$

Pressure

$$\therefore P = F/A = m\bar{v}_x^2 \frac{n_T}{V}$$

$$\therefore n_T = n N_A$$

$$\therefore PV = mn N_A \bar{v}_x^2$$

$N_A \rightarrow$ Avogadro number

But $PV = nRT$ — Equation of state

$= mn N_A \bar{v}_x^2$ — Microscopic description

$$k_B = \frac{R}{N_A}$$

$$\therefore \quad m\bar{v}_x^2 = \frac{R}{N_A} T = k_B T$$

$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$$

$\therefore$ the probability of motion along each direction is equal

$$\bar{v}_x = \bar{v}_y = \bar{v}_z$$

$$\therefore \quad \bar{v}^2 = 3\bar{v}_x^2$$

$$m\overline{v_x}^2 = k_B T$$

Average energy of each atom

$$u_a = \frac{1}{2} m \overline{v}^2 = \frac{1}{2} m 3 \overline{v_x}^2$$

$$U \left(\text{per mole}\right) = N_A \langle E \rangle = \frac{3}{2} m \overline{v_x}^2$$

$$\langle E \rangle = \frac{3}{2} k_B T$$

$$= N_A \cdot \frac{3}{2} k_B T$$

$$= \frac{3}{2} RT \qquad \therefore k_B = \frac{R}{N_A}$$

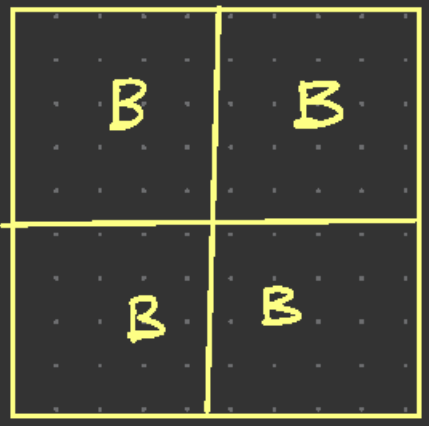
Connection between the microscopic world of atoms & macroscopic thermodynamics

$$\delta q^{rev} = TdS$$



4 A atoms

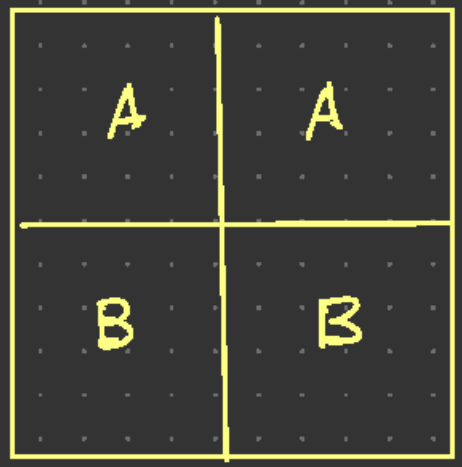
4 A's are identical or indistinguishable

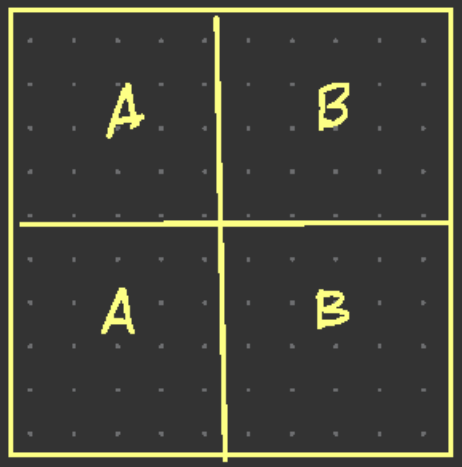


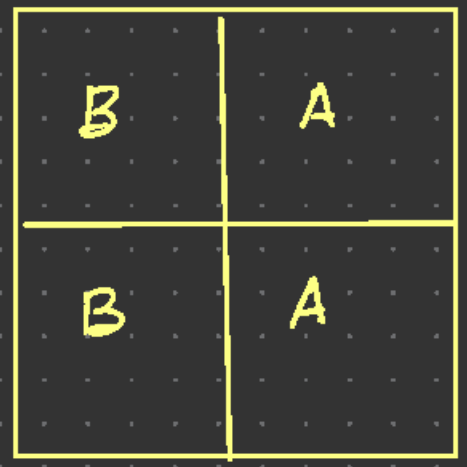
B atoms

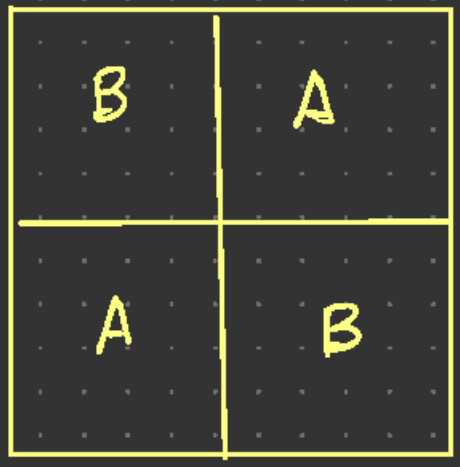
Are these distinguishable?

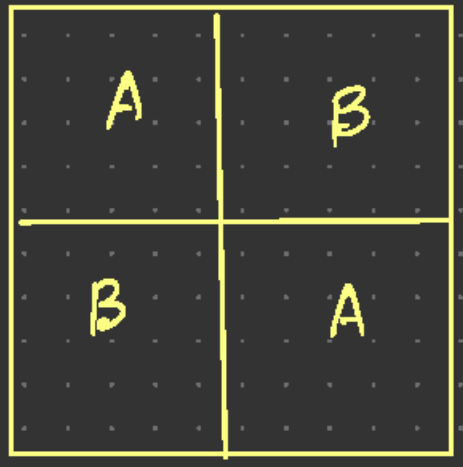
A — distinguishable from B

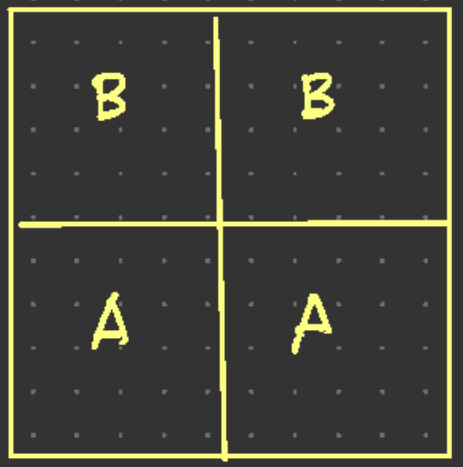












2 A's and 2 B's

4 placeholders

6 ways to arrange them

A B C D — 4 distinguishable atoms

4! ways

_ _ _ _ = 24 ways

Why?

$n! = n \cdot n-1 \cdot n-2 \cdot \cdots 3 \cdot 2 \cdot 1$

different

A — B — C — D

A can be placed in any of the 4 empty placeholders, B can be arranged in 3 ways in the 3 remaining placeholders, 2 remaining placeholders, 1 remaining

$4 \times 3 \times 2 \times 1$

$= 4!$

Problem – Statistical interpretation of entropy

Arrange n_1 elements of type 1
n_2 elements of type 2
n_3 elements of type 3
$\vdots$
n_k elements of type k

in N positions.

Each type is distinct or distinguishable from the other

Constraint:

$$n_1 + n_2 + n_3 + \cdots + n_k = N$$

Macrostates — State of a simple system

U_{sys}, T_{sys}, V_{sys}, ...

Statistical thermodynamics — probable states of particles in a system

Macrostate ≡ State in macroscopic thermodynamics — U, V, N

(Statistical Thermodynamics)

Microstate denotes the state of all particles in a system

m, v_x, v_y, v_z

x, y, z

Isolated system comprising of a gas occupying a given volume V at equilibrium

— Macrostate

Positions and velocities of all gas molecules within the system at any instant of time

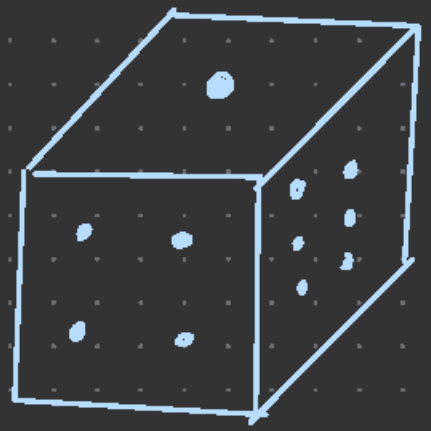
— Microstates

Macrostate passes through many microstates

Example

Use two standard (unbiased) dice that are six sided.

Labels 1 – 6



Roll both dice

Outcome – sum of numbers on both die faces

Dice I	Dice II
2	6
6	2
5	3
3	5
4	4

Sum: 8 – A macrostate

Microstates = 5

Sum = 7



$n_1 + n_2 = 7$

Dice I	Dice II
1	6
2	5
3	4
4	3
5	2
6	1

6 microstates

Sum = 12

Dice I	Dice II
6	6

1 microstate

Macrostate	Microstates	No. of microstates
2	(1,1)	1
3	(1,2) (2,1)	2
4	(1,3) (3,1) (2,2)	3
5	(1,4) (2,3) (3,2) (4,1)	4
6	(1,5) (2,4) (3,3) (4,2) (5,1)	5
7	(1,6) (2,5) (3,4) (4,3) (5,2) (6,1)	6
8	(2,6) (3,5) (4,4) (5,1) (6,2)	5
9	(3,6) (4,5) (5,4) (6,3)	4
10	(4,6) (5,5) (6,4)	3
11	(5,6) (6,5)	2
12	(6,6)	1

11 macrostates

two unbiased dice rolled

36 microstates

$$P(2) = \frac{1}{36}$$

$$P(12) = \frac{1}{36}$$

$$P(7) = \frac{6}{36} = \frac{1}{6}$$

$P(7)$ represents the probability of finding microstates corresponding to macrostate 7

7 is most likely

Balls marked as A, B, C, D

Two distinct containers I, II

2^4 microstates

Microstates I	Microstates II	# of microstates Ω	Macrostate $2 \times 2 \times 2 \times 2$
ABCD	0	1	4 in I and 0 in II
ABC	D	4	3 in I and 1 in II
BCD	A		
ABD	C		
ACD	B		
CD	AB	6	2 in I and 2 in II
AB	CD		
BC	AD		$\frac{4!}{2!\,2!}$ 6
AD	BC		
BD	AC		
AC	BD		
D	ABC	4	1 in I and 3 in II
A	BCD		
B	ABD		
0	ACD ABCD	1	0 in I and 4 in II

Ω defines the no. microstates for a given macrostate

100 distinct ball
& boxes

100 balls and 2 boxes

Total microstates = $2^{100} \sim 10^{30}$

Ω

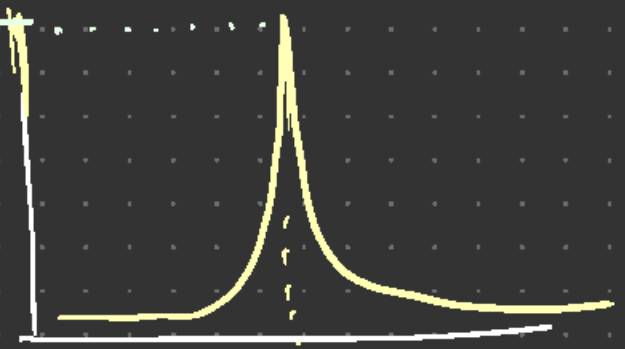
$P(A) \approx 0 \left(10^{-30}\right) \sim 1$

$P(B) = 0.00003 \sim 3 \times 10^{25}$

$P(C) = \underline{0.1} \sim \underline{10^{29}}$

Ω_{max}

Ω ↑



Most probable macrostate

Macrostate

100 in I 0 in II - A

30 in I 70 in II - B

50 in I 50 in II - C

Macrostate C

$$\frac{100!}{50!\,50!}$$

Let there be r energy levels (boxes)

N_0 particles

$\epsilon_1 \quad \epsilon_2 \quad \cdots \quad \epsilon_r$ — r energy levels or states

$n_1 \quad n_2 \quad \cdots \quad n_r$ — distribution of particles in a given macrostate

n_i — no. of particles with energy ϵ_i

Number of microstates -

Particle '1' in any of r states — r ways

Particle '2' in any of r states — $r \cdot r = r^2$ ways

Particle '3' in any of r states — $r \cdot r \cdot r = r^3$ ways

⋮

Particle 'N_0' in any of r states - r^{N_0} ways

- Independent events

Suppose $r = 100$

$N_0 = 10^{23}$

$r^{N_0} = 100^{10^{23}}$ is enormous

How many microstates correspond to the macrostate $(n_1, n_2, \dots, n_r)$

$$\Omega = \frac{N_0!}{n_1!\, n_2! \cdots n_r!}$$ — Combinatorics

Let a set S contain n elements

Fix $k < n$ elements to form a k-element subset

$S = \{a, b, c, d\}$

2-element subsets of S: $\{a, b\}$, $\{a, c\}$, $\{a, d\}$, $\{b, c\}$, $\{b, d\}$, $\{c, d\}$

Note $\{c, d\}$ is the same as $\{d, c\}$

How to select subsets of 2-elements from a set of 4 elements is given by

$$\frac{4!}{2!\,2!} = {}^4C_2 = 6$$

$$= \frac{4!}{2!\,(4-2)!}$$

Generalize –

Select r- element subsets from an n-element set

$$C(n, r) \text{ or } C\binom{n}{r}$$

$$= \frac{n!}{r!\,(n-r)!}$$

Total no. of positions n

Arrange n_1 elements of type 1

n_2 elements of type 2

$\vdots$

n_k elements of type k on n sites or positions

such that $n_1 + n_2 + \cdots + n_k = n$

n_1 elements of type 1 can be arranged in $C(n, n_1)$ ways.

n_1 particles of type '1' arranged on n available sites in $C(n, n_1)$ ways

n_2 particles of type '2' ... $C(n-n_1, n_2)$ ways

n_3 particles of type '3' ... $C(n-n_1-n_2, n_3)$ ways

⋮

n_k particles of type 'k' ... $C(n-n_1-n_2-\cdots-n_{k-1}, n_k)$ ways.

∴ Total no. of arrangements

$$\Omega = C(n, n_1) \cdot C(n-n_1, n_2) \cdots C(n-n_1-n_2-\cdots n_{k-1}, n_k)$$

Product rule

$$\Omega = \frac{n!}{n_1!(n-n_1)!}\,\frac{(n-n_1)!}{n_2!(n-n_1-n_2)!}\cdots\frac{(n-n_1-n_2-\cdots-n_{k-1})!}{n_k!(\underbrace{n-n_1-n_2-\cdots n_k}_{0!=1})!}$$

Note $n = n_1 + n_2 + \cdots + n_k$

$$= \frac{n!}{n_1!\,n_2!\cdots n_k!}$$

$n = n_1 + n_2 + \cdots + n_k$

$\therefore n - n_1 - n_2 - \cdots n_k$

$= 0$

$0! = 1$

N_0 particles, R available states

Macrostate: $(n_1, n_2, \dots, n_R)$ R sites

$$n_1 + n_2 + \dots + n_R = N_0$$

$$\Omega = \frac{N_0!}{n_1! n_2! \dots n_R!}$$

Ω — no. of microstates is the no. of microstates for the macrostate $(n_1, n_2, \dots, n_R)$

J — macrostate

$$P_J = P(n_1, n_2, \dots, n_R) = \frac{\Omega}{R^{N_0}} = \frac{N_0!}{\prod_{i=1}^{R} n_i!} \frac{1}{R^{N_0}}$$

$\nu = 1 \quad \nu = 2 \quad \nu = R$

a, b, c, d Spheren in two boxen I and II

Microntaten

	I	II
A	abcd	0
B	abc	d
C	abd	c
D	acd	b
E	bcd	a
F	ab	cd
G	ac	bd
H	ad	bc
I	bc	ad
J	bd	ac
K	cd	ab

L	a	bcd
M	b	acd
N	c	abd
O	d	abc
P	0	abcd

$2^4 = 16$ microntaten

List of macrostates

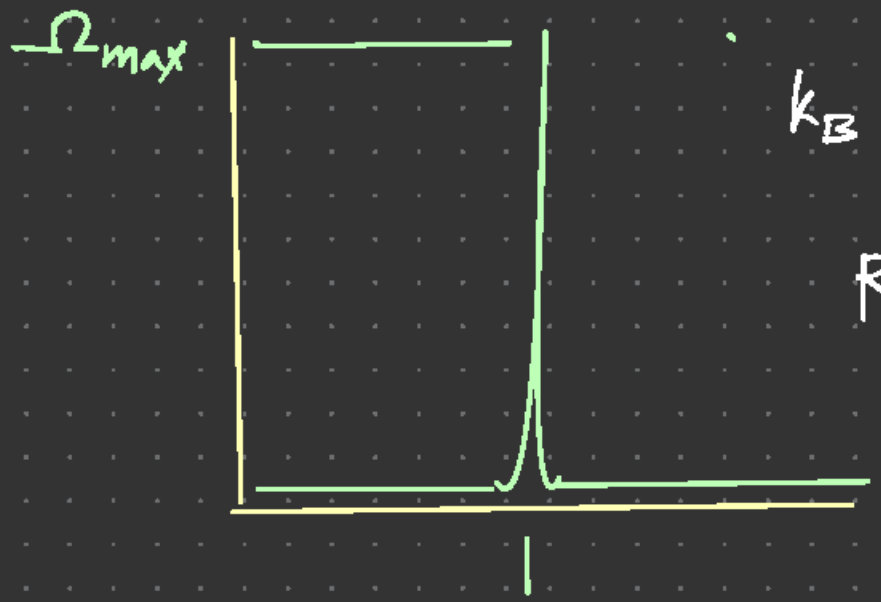
I	II	Microstates	Number	Probability
4	0	A	1	1/16
3	1	B, C, D, E	4	4/16
2	2	F, G, H, I, J, K	6	6/16
1	3	L, M, N, O	4	4/16
0	4	P	1	1/16

When $\mathcal{R}$ is large,

N_0 is large,

no. of microstates corresponding to the most likely macrostate determines the entropy of the system

$$P\left(\text{Macrostate with largest no. of microstates}\right) = \frac{\Omega_{max}}{\mathcal{R}^{N_0}}$$



k_B — $J/_{atom-K}$

R — $J/_{mol-K}$

P_{max}

Note: Ω can vary over several orders of magnitude, S varies over 1-2 orders of magnitude

$$S = k_B \ln \Omega$$

— Boltzmann hypothesis connecting atomistic description to phenomenological thermodynamics

Consequences of Boltzmann hypothesis

N lattice sites

N_A — no. of atoms of species A

N_B — no. of atoms of species B

$N_A + N_B = N$ $\quad\therefore\quad N_A = N - N_B$

$$\Omega = \frac{N!}{N_A!\,N_B!} = C(N, N_B) = \frac{N!}{N_B!\,(N-N_B)!}$$

$$= \frac{N!}{N_A!\,(N-N_A)!}$$

$$\therefore \quad S = k_B \ln \Omega$$

$$= k_B \ln \frac{N!}{N_A!\, N_B!}$$

$$n! = n(n-1)(n-2)\cdots 3 \cdot 2 \cdot 1$$

$$\ln n! = \ln n + \ln(n-1) + \cdots + \ln 3 + \ln 2 + \ln 1$$

$$= \sum_{i=1}^{n} \ln i$$

When n is large

$$\sum_{i=1}^{n} \ln n = \int_1^n \ln x \, dx =$$

Let $z = \ln x$

$$dz = \frac{1}{x} dx$$

Integration by parts

$$\ln x \int_1^n dx - \int \left\{ \frac{d \ln x}{dx} \int dx \right\} dx$$

$$\int \ln x \, dx$$

$$= \ln x \int dx - \int \left\{ \frac{d \ln x}{dx} \int dx \right\} dx$$

$$= x \ln x - \int dx$$

$$\therefore \int_1^n \ln x \, dx$$

$$= \Big[x \ln x - x \Big]_1^n = n \ln n - n$$

$$- \ln 1 + 1$$

$$= n \ln n - n + 1$$

If n is very large,

$n \to \infty$

$$\ln(n!) = n\ln n - n + 1$$

$$\approx n\ln n - n \quad \because -n+1 \approx -n$$

$$\ln(n!) = n\ln n - n$$

— Stirling's approximation

$$\therefore \quad \ln \Omega = \ln \frac{N!}{N_A! N_B!}$$

$$X_A = \frac{N_A}{N} \qquad X_B = \frac{N_B}{N}$$

$$X_A + X_B = 1$$

$$N = N_A + N_B$$

$$= \ln(N!) - \ln(N_A!) - \ln(N_B!)$$

$$= N \ln N - N - N_A \ln N_A + N_A - N_B \ln N_B + N_B$$

$$= N \ln N - N_A \ln N_A - N_B \ln N_B + (N_A + N_B - N)$$

$$= N \ln N - N_A \ln N_A - N_B \ln N_B$$

$$= N \left(\ln N - X_A \ln N_A - X_B \ln N_B \right)$$

$$= -N \left(X_A \ln X_A + X_B \ln X_B \right)$$

$$\ln \Omega = N \ln N - N_A \ln N_A - N_B \ln N_B$$

$$N_A + N_B = N$$

$$X_A + X_B = 1$$

$$= -N \left(X_A \ln N_A - (X_A + X_B) \ln N + X_B \ln N_B \right)$$

$$= -N \left(X_A \ln \left(\frac{N_A}{N} \right) + X_B \ln \left(\frac{N_B}{N} \right) \right)$$

$$= -N \left(X_A \ln X_A + X_B \ln X_B \right)$$

$$\ln \Gamma = x_A \ln \Gamma + x_B \ln \Gamma \qquad \because x_A + x_B = 1$$

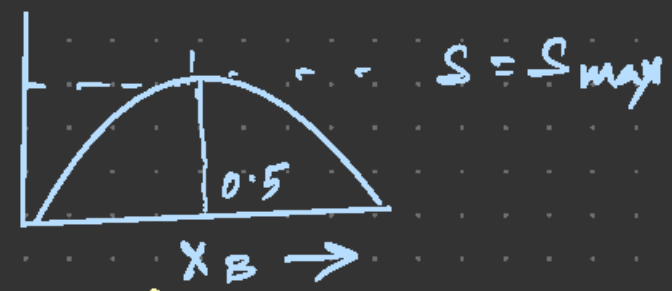
$$\therefore \Gamma \left(\ln \Gamma - x_A \ln \Gamma_A - x_B \ln \Gamma_B \right)$$

$$= \Gamma \left(x_A \ln \Gamma - x_A \ln \Gamma_A + x_B \ln \Gamma - x_B \ln \Gamma_B \right)$$

$$= -\Gamma \left(x_A \ln \frac{\Gamma_A}{\Gamma} + x_B \ln \frac{\Gamma_B}{\Gamma} \right)$$

$$= -\Gamma \left(x_A \ln x_A + x_B \ln x_B \right)$$

$$S = k_B \ln \Omega$$



$$= -k_B N \left(X_A \ln X_A + X_B \ln X_B \right)$$

ff N = Avogadro number

$$X_B = X$$

$$X_A = 1 - X$$

$$N k_B = R$$

$$\therefore \quad S = -R \left(X_A \ln X_A + X_B \ln X_B \right)$$

$S > 0$ Also $S = S_{max}$ when $X_A = X_B = \frac{1}{2}$

$$S = -R \sum_{i=1}^{k} X_i \ln X_i$$

$$S = k \ln \Omega$$

$\ln 2 = 0.693147$

$\ln 3 = 1.098612$

$\ln 4 = 1.386294$

$\ln 5 = 1.609437$

$\ln 10 = 2.302585$

High Entropy Alloy

$k = 2 \ldots . 10$

$k = A, B, C, D, E, \ldots$

$X_A = X_B = X_C = X_D = X_E$

$= 0.2$

For n- component

$$S^{conf} = R \ln 5$$

$$S = -R \sum_{i=1}^{n} x_i \ln x_i$$

$$= -R \left(\frac{1}{5} \ln \frac{1}{5} \right) X5$$

$$= -R \ln 1/5 = R \ln 5$$

x_i - mole fraction of species i

$n_1 + n_2 + n_3 + \cdots + n_r = N$

$$S = -k_B \ln \sum_{j=1}^{r} n_j \ln\left(\frac{n_j}{N}\right)$$

$$x_j = \frac{n_j}{N}$$

$\therefore R = k_B N$

$$S = -R \sum_j x_j \ln x_j$$

$$= -k_B N \sum x_j \ln x_j$$

$$= -k_B \cancel{N} \sum \frac{n_j}{\cancel{N}} \ln\left(\frac{n_j}{N}\right)$$

$$dS = -k_B\, d\left[\sum_{j=1}^{r} n_j \ln\left(\frac{n_j}{N}\right)\right]$$

$$= -k_B \sum_{j=1}^{r} d\left[n_j \ln n_j - n_j \ln N\right]$$

$$= -k_B \sum_{j=1}^{r} \left[\ln n_j\, dn_j + dn_j - \ln N\, dn_j - \frac{n_j}{N} dN\right]$$

$d \ln N = \frac{1}{N} dN$

$$d\, x_j \ln x_j$$

$$= \ln x_j \, dx_j + x_j \, d \ln x_j$$

$$= \ln x_j \, dx_j + \frac{x_j}{x_j} dx_j$$

$$= \ln x_j \, dx_j + dx_j$$

$$d \ln x_j = \frac{dx_j}{x_j}$$

$$\therefore \frac{d \ln x_j}{dx_j} = \frac{1}{x_j}$$

$$= -k_B \left[\sum_{j=1}^{r} \left(\ln n_j - \ln N \right) dn_j + \sum_{j=1}^{r} dn_j - \sum_{j=1}^{r} \left(\frac{n_j}{N} \right) dN \right]$$

$$= -k_B \sum_{i=1}^{r} \ln\left(\frac{n_j}{N}\right) dn_j + dN - dN$$

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

$$\therefore dN = dn_1 + dn_2 + \cdots + dn_j = \sum_{j=1}^{r} dn_j$$

$$= -k_B \sum_{j=1}^{r} \ln\left(\frac{n_j}{N}\right) dn_j$$

$$\sum_{i=1}^{r} \left(\frac{n_j}{N}\right) = 1 \quad (\text{Why?})$$

$$\frac{n_j}{N} = x_j$$

$$\sum_{j=1}^{r} x_j = 1$$

$$dS = -k_B \sum_{j=1}^{r} \ln\left(\frac{n_j}{N}\right) dn_j$$

ϵ_j – energy of jth level – fixed

Assume an isolated system

– Total U and total N cannot change

$$U = \sum_{j=1}^{r} \epsilon_j n_j$$

n_1 atoms of type 1 in ϵ_1

n_2 atoms of type 2 in ϵ_2

$\epsilon_j \rightarrow$ Energy of level j

$$dU = \sum_j \epsilon_j \, dn_j = 0 \quad \therefore \; n_j \, d\epsilon_j = 0$$

$$dN = \sum_j dn_j = 0$$

S of the isolated system at equilibrium

$dS = 0$ with constraints

$dU = 0$

$dN = 0$

Use Lagrange Multipliers method

$$dS + \alpha\, dN + \beta\, dU = 0$$

α, β – Lagrange multipliers

$$- k_B \sum_j \ln\left(\frac{n_j}{N}\right) dn_j + \alpha \sum_j dn_j + \beta \sum_j \epsilon_j dn_j = 0$$

$$\Rightarrow \sum_j \left[- k_B \ln\left(\frac{n_j}{N}\right) + \alpha + \beta \epsilon_j \right] dn_j = 0$$

What does this mean?

$$-k_B \ln\left(\frac{n_j}{N}\right) + \alpha + \beta \epsilon_j = 0$$

$$j = 1, 2, \cdots, n$$

$$\therefore \quad k_B \ln\left(\frac{n_j}{N}\right) = \alpha + \beta \epsilon_j$$

$$\ln\left(\frac{n_j}{N}\right) = \frac{\alpha}{k_B} + \frac{\beta}{k_B} \epsilon_j$$

$$\frac{n_j}{N} = e^{\left\{ \alpha/k_B + \beta/k_B \epsilon_j \right\}}$$

$$e^{A} e^{B} = e^{A+B}$$

$$\therefore \frac{n_j}{N} = e^{\alpha/k_B} e^{\frac{\beta \epsilon_j}{k_B}}$$

Note $\sum_j \frac{n_j}{N} = X_1 + X_2 + \cdots + X_n$

$$= 1$$

$$\therefore \sum_j e^{\alpha/k_B} e^{\beta \epsilon_j/k_B} = 1$$

or,

$$e^{\alpha/k_B} = \frac{1}{\sum_j \left(e^{\beta \epsilon_j/k_B}\right)}$$

Define partition function p (Italic 'p')

$$p = \sum_{i=1}^{n} e^{\frac{\beta \epsilon_i}{k_B}}$$

$$\therefore \quad e^{\alpha/k_B} = \frac{1}{p}$$

$$\therefore \quad \frac{n_j}{N} = e^{\alpha/k_B} e^{\frac{\beta \epsilon_j}{k_B}}$$

$$= \frac{1}{p} e^{\frac{\beta \epsilon_j}{k_B}}$$

$$dS = -k_B \sum_i \ln\left(\frac{n_i}{N}\right) dn_i \qquad \ln e^x = x$$

$$= -k_B \sum_i \ln\left(\frac{1}{p} e^{\frac{\beta \epsilon_i}{k_B}}\right) dn_i$$

$$= -k_B \sum_i \left(\frac{\beta \epsilon_i}{k_B} - \ln p\right) dn_i$$

$$= -\beta \sum_i \epsilon_i dn_i + k_B \ln p \sum_i dn_i$$

$$= -\beta dU + k_B \ln p \, dN$$

Microscopic (particle-based)

$$dS = -\beta\, dU + k_B \ln p\, dN \quad - (micro)$$

Macroscopic

$$S = S(U, V, N) \qquad dU = T dS - p dV + \mu dN$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{S,V} dN$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN \quad - (macro)$$

Compare:

$$\beta = -\frac{1}{T} \qquad -\frac{\mu}{T} = k_B \ln p$$

$$\mu = -k_B T \ln p$$

partition function

$$\mathcal{p} = \sum_i e^{-\frac{\epsilon_i}{k_B T}} \qquad \beta = -\frac{1}{T}$$

$$\frac{n_i}{N} = \frac{1}{\mathcal{p}} e^{-\epsilon_i / k_B T}$$

$$S = -k_B \sum_i n_i \ln\left(\frac{n_i}{N}\right) = -k_B \sum_i n_i \ln\left[\frac{1}{\mathcal{p}} e^{-\frac{\epsilon_i}{k_B T}}\right]$$

$$\sum_i n_i = N$$

$$S = \frac{U}{T} + k_B N \ln \mathcal{p} \qquad = -k_B \sum_i n_i \left[-\frac{\epsilon_i}{k_B T} - \ln \mathcal{p}\right]$$

$$\mathcal{p} = \sum_i e^{-\epsilon_i / k_B T} \qquad = \frac{1}{T} U + k_B \ln \mathcal{p} \sum_i n_i$$

$$= \frac{U}{T} + k_B N \ln \mathcal{p}$$

Helmholtz free energy

$$F = U - TS$$

$$S = \frac{U}{T} + k_B N \ln p$$

$$\therefore \quad F = U - T\left[\frac{U}{T} + k_B N \ln p\right]$$

$$= \quad - N k_B T \ln p$$

$$dF = -S\,dT - P\,dV + \mu\,dN$$

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

$$S = -\left[\frac{\partial}{\partial T}\left(-N k_B T \ln p\right)\right]$$

$$= N k_B \ln p + N k_B T \left(\frac{\partial \ln p}{\partial T}\right)_{V,N}$$

$$U = F + TS$$

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

$$= N k_B T^2 \left(\frac{\partial \ln p}{\partial T}\right)_{V,N}$$

$$\therefore \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

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

In all these derivations, we are using discrete energy levels ϵ_i that are accessible by particles

A distribution $\{n_1, n_2, \ldots, n_R\}$ of N particles occupying discrete energy levels ϵ_i with fixed total internal energy U is a macrostate

— Many possible microstates or distributions of particles associated with N particles possessing same energy U

$\{n_1, n_2, \ldots, n_R\}$ $\epsilon_1, \epsilon_2 \ldots, \epsilon_{100}$

U

All accessible microstates with the same energy U are equally probable

Total no. of microstates — most probable macrostate with the greatest no. of microstates

$\mathcal{R}$ energy levels
N particles
$\mathcal{R}^N$

How does the system evolve?

Boltzmann

$$S = k_B \ln \Omega$$

$$= k_B \ln \mathcal{Z}_{mc}$$

$\Omega = \mathcal{Z}_{mc}$ — total no. of accessible microstates

Macroscopic thermodynamic property

— average of the properties over all temporal microstates of the system

If the number of particles is very large,
number of identical systems specified
by same set of thermodynamic parameters
(number of moles N / volume V / temperature T /
pressure P / chemical potential μ / internal
energy U) is very large

Collection of large number of identical systems
is called an ensemble (Gibbs)

Different types of thermodynamic systems based on specified thermodynamic condition

1. Microcanonical (mc) Ensemble: Isolated simple systems with constant internal energy U, constant volume V and constant number of particles N

   T, P, μ can fluctuate in each system as well as from system to system

$$Z_{mc} = \Omega$$

Canonical Ensemble: A collection of closed simple systems bounded by a thermal reservoir at constant temperature T, constant volume V and constant number of particles N

U, P, μ can vary in each system and from system to system

Grand canonical ensemble: Open simple systems bounded by a thermal reservoir and a chemical reservoir

fixed parameters: T, V, μ

Variable parameters: U, P, N

Microcanonical ensemble:

Partition function Z_{mc} is the total no. of accessible microstates having same energy U, same volume V and same no. of particles N

$$Z_{mc} = \Omega \quad (\text{total no of accessible microstates})$$

Probability of accessing i^{th} microstate

$$P_i = \frac{1}{Z_{mc}}$$

$$S = k_B \ln \mathcal{Z}_{mc} \qquad \text{(Boltzmann Hypothesis)}$$

$$\mathcal{Z}_{mc} = \mathcal{Z}_{mc}(U, V, N)$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = k_B \left(\frac{\partial \ln \mathcal{Z}_{mc}}{\partial U}\right)_{V,N}$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V} = k_B \left(\frac{\partial \ln \mathcal{Z}_{mc}}{\partial N}\right)_{U,V}$$

Canonical ensemble: $\wp = \sum_i e^{-\epsilon_i / k_B T}$

$$Z_c(T, V, N) = \sum_i e^{-\frac{U_i}{k_B T}} = \sum_i e^{-\beta U_i}$$

U_i – Energy of microstate i $\qquad \beta = \frac{1}{k_B T}$

$$P_i = \frac{e^{-U_i / k_B T}}{Z_c(T, V, N)} = \frac{e^{-\beta U_i}}{Z_c}$$

$$U = \langle U_i \rangle = \sum_i P_i U_i = \sum_i \frac{e^{-\beta U_i} U_i}{Z_c} = \sum_i -\frac{\partial}{\partial \beta} \frac{\left(e^{-\beta U_i}\right)}{Z_c}$$

$$= -\frac{\partial}{\partial \beta} \frac{\sum_i e^{-\beta U_i}}{Z_c} = -\frac{\partial \ln Z_c}{\partial \beta}$$

$$-\left[\frac{\partial \ln Z_c}{\partial (1/k_B T)}\right]_{V,N} = -\frac{\partial \ln Z_c}{\partial Z_c}\frac{\partial Z_c}{\partial (1/k_B T)} \quad -(A)$$

$$\frac{\partial Z_c}{\partial (1/k_B T)} = \frac{\partial \sum_i e^{-U_i/kT}}{\partial (1/k_B T)} = \sum_i \frac{\partial e^{-U_i/kT}}{\partial (1/k_B T)}$$

From (A)

$$= -\frac{1}{Z_c}\sum_i -U_i e^{-U_i/kT} = \frac{\sum_i U_i e^{-U_i/k_B T}}{\sum_i e^{-U_i/k_B T}}$$

$$d \ln Z = \frac{\partial \ln Z}{\partial \beta} d\beta +$$

$$= -U d\beta$$

$$U d\beta = d(\beta U) - \beta dU$$

$$\therefore d(\ln Z_c) = -d(\beta U) + \beta dU$$

$$dU = \frac{1}{\beta} d(\ln Z_c) + \frac{1}{\beta} d(\beta U)$$

$$dU = TdS$$

When $T \to 0$ $\quad T = T_0$ where $T_0 \to 0$

$$S = k_B \ln Z_{mc}^{0}$$

$$\beta = \beta_0 = \frac{1}{k_B T_0}$$

$$U = U^0$$

$$\therefore \quad T dS = \frac{1}{\beta} d\left(\ln Z_c\right) + \frac{1}{\beta} d\left(\beta U\right)$$

$$dS = k_B d\left(\ln Z_c\right) + k_B d\left(\beta U\right)$$

$$S = k_B \ln Z_c + \frac{U}{T} + C$$

$$\lim_{T\to 0} \sum_i e^{-\beta U_i} = \lim_{T\to 0} Z = e^{-\beta U_0}$$

$$S = k_B \ln Z^{\circ}_{mc}$$

$$\downarrow$$

$$k \ln Z^{\circ}_{mc} = k_B \ln \left[Z^{\circ}_{mc} e^{-\beta_0 U_0} \right]^{\frac{U_0}{T}} + \frac{U_0}{T_0} + c$$

$$= k_B \ln Z^{\circ}_{mc} - \frac{U_0}{T_0} + \frac{U_0}{T_0} + c$$

$$c = 0$$

$$\therefore S = k_B \ln Z + \frac{U}{T}$$

$$\therefore F = U - TS$$

$$= -k_B T \ln Z_c$$

$$S = k_B \ln Z_c + \frac{U}{T}$$

$$\therefore TS = k_B T \ln Z_c + U$$

$$\therefore F = U - TS = -k_B T \ln Z_c$$

Grand canonical ensemble

$U(S,V,N) \longrightarrow G(T,P,N)$

System with fixed V in contact with both thermal (energy) and chemical (particle) Reservoir

$$G = H - TS = U + PV - TS$$

Grand potential (Landau potential)

$$\Phi = U - TS - \mu N = \Omega_{Landau}$$

$$d\Phi = -PdV - SdT - Nd\mu$$

$$\because \quad dU = TdS - PdV + \mu dN$$

$N \to \mu$

$S \to T$

$$U = U(S, V, N)$$

$$T = \frac{\partial U}{\partial S}$$

$$\mu = \frac{\partial U}{\partial N}$$

$$\Phi = U - TS - \mu N$$

$$\Phi(T, V, \mu)$$

$$-S = \frac{\partial \Phi}{\partial T}$$

$$-N = \frac{\partial \Phi}{\partial \mu}$$

$$U = \Phi + TS + \mu N$$

grand canonical

Z_G – partition function

$$Z_G = \sum_i e^{-\frac{\Phi_i}{k_B T}}$$

$$- (U_i - \mu N) / k_B T$$

$$p_i = \frac{1}{Z_G} e$$

$$\Phi = -k_B T \ln Z_G$$

p_i – probability of appearance of microstate i

$$S = -R \sum x_i \ln x_i$$

$$S = -k_B \sum p_i \ln p_i$$

$$p_i(\text{isolated}) = \frac{1}{Z_{mc}(U, V, N)}$$

$$p_i(\text{closed}) = \frac{e^{-U_i/k_B T}}{Z_c(T, V, N)}$$

Two-state system - N particles Two energy levels ϵ_0 and ϵ_1

$$p = \sum_i e^{-\epsilon_i / k_B T}$$

$$= e^{-\epsilon_0 / k_B T} + e^{-\epsilon_1 / k_B T}$$

$$\frac{n_1}{N} = \frac{e^{-\epsilon_0 / k_B T}}{p}$$

N -

$n_1 \longrightarrow \epsilon_0$

$n_2 \longrightarrow \epsilon_1$

$$\frac{n_2}{N} = \frac{e^{-\epsilon_1 / k_B T}}{p}$$

$$F = -N k_B T \ln p$$

Let $\epsilon_0 = \epsilon$

$\epsilon_1 = 2\epsilon$

$$p = e^{-\epsilon/k_B T}\left[1 + e^{-\epsilon/k_B T}\right]$$

$$\ln p = -\frac{\epsilon}{k_B T} + \ln\left(1 + e^{-\epsilon/k_B T}\right)$$

$$F = -N k_B T\left\{-\epsilon/k_B T + \ln\left(1 + e^{-\epsilon/k_B T}\right)\right\}$$

$$= N\epsilon - N k_B T \ln\left[1 + e^{-\epsilon/k_B T}\right]$$

Prove that

$$C_V = \frac{N\epsilon^2}{k_B T^2} \frac{e^{-\epsilon/k_B T}}{\left(1 + e^{-\epsilon/k_B T}\right)^2}$$

for a two-state system

$$\epsilon_0 = \epsilon$$

$$\epsilon_1 = 2\epsilon$$

Monoatomic gas

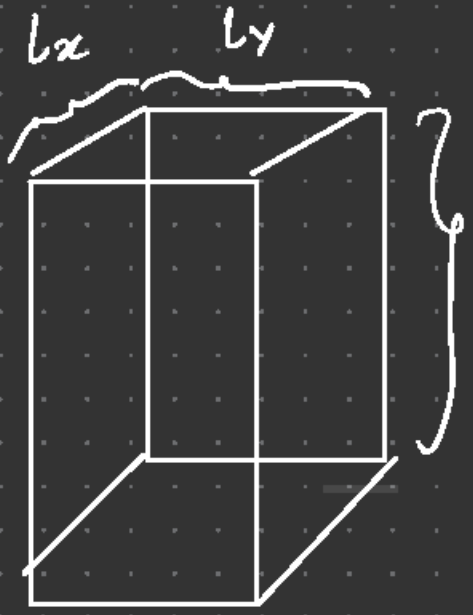
Composed of identical single atoms

Example – Argon, Neon

One particle state – $m, x, y, z, v_x, v_y, v_z$

$$\epsilon = \frac{1}{2} m v^2 = \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right)$$

The gas is in a container



$$-\infty < v_x < \infty$$
$$-\infty < v_y < \infty$$
$$-\infty < v_z < \infty$$

$$p = \int_0^{l_z}\int_0^{l_y}\int_0^{l_x}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\epsilon/k_B T}\, dv_x\, dv_y\, dv_z\, dx\, dy\, dz$$

Canonical partition function

$$p = \int_0^{l_x}\int_0^{l_y}\int_0^{l_z}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{mv_x^2}{2k_BT}} e^{-\frac{mv_y^2}{2k_BT}} e^{-\frac{mv_z^2}{2k_BT}} dv_x dv_y dv_z dx dy dz$$

$$p = \int_0^{l_x}\int_0^{l_y}\int_0^{l_z} dx dy dz \int_{-\infty}^{\infty} e^{-mv_x^2/2k_BT} dv_x$$

$$\int_{-\infty}^{\infty} e^{-\frac{mv_y^2}{2k_BT}} dv_y \int_{-\infty}^{\infty} e^{-\frac{mv_z^2}{2k_BT}} dv_z$$

$$V = \int_0^{l_x}\int_0^{l_y}\int_0^{l_z} dx dy dz$$

$$\int_{-\infty}^{\infty} e^{-ax^2}\,dx = \sqrt{\pi/a}$$

Gaussian Integral

$$a = \frac{m}{2k_B T}$$

$$\therefore \int_{-\infty}^{\infty} e^{-\frac{m v_x^2}{2k_B T}}\,dv_x = \sqrt{\frac{2\pi k_B T}{m}}$$

$$p = V\left(\frac{2\pi k_B T}{m}\right)^{3/2}$$

$$\ln p = \ln V + \frac{3}{2}\ln\left(\frac{2\pi k_B}{m}\right) + 3/2 \ln T$$

$$U = N k_B T \left(\frac{\partial \ln p}{\partial T} \right)_V = N k_B T^2 \left(\frac{3}{2} \frac{1}{T} \right)$$

$$= \frac{3}{2} N k_B T$$

$$C_V = \frac{3}{2} N k_B$$

0 0 1 2 4 2 1 0 0 0

0 1 1 2 2 2 1 1 0 0

1 $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$ $\frac{11}{2}$ $\frac{13}{2}$ $\frac{15}{2}$ $\frac{17}{2}$ $\frac{19}{2}$

$1\times0 + 1\times\frac{3}{2} + 1\times\frac{5}{2} + 2\times\frac{7}{2} + 2\times\frac{9}{2}$

$+ 2\times\frac{11}{2} + 1\times\frac{13}{2} + 1\times\frac{15}{2}$

$+ 0\times\frac{17}{2} + 0\times\frac{19}{2}$

$3 + 5 + 14 + 18 + 22 + 13 + 15$

$40 + 50 = 90$