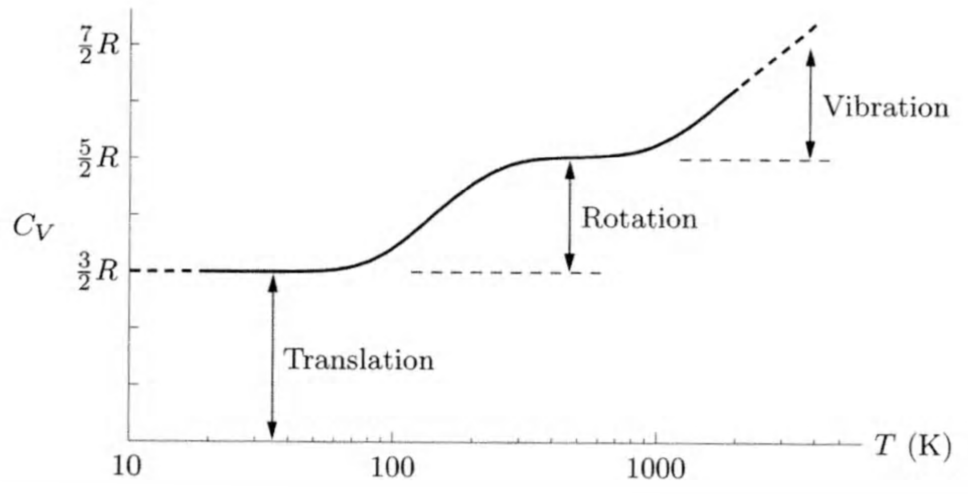
Frozen degrees of freedom

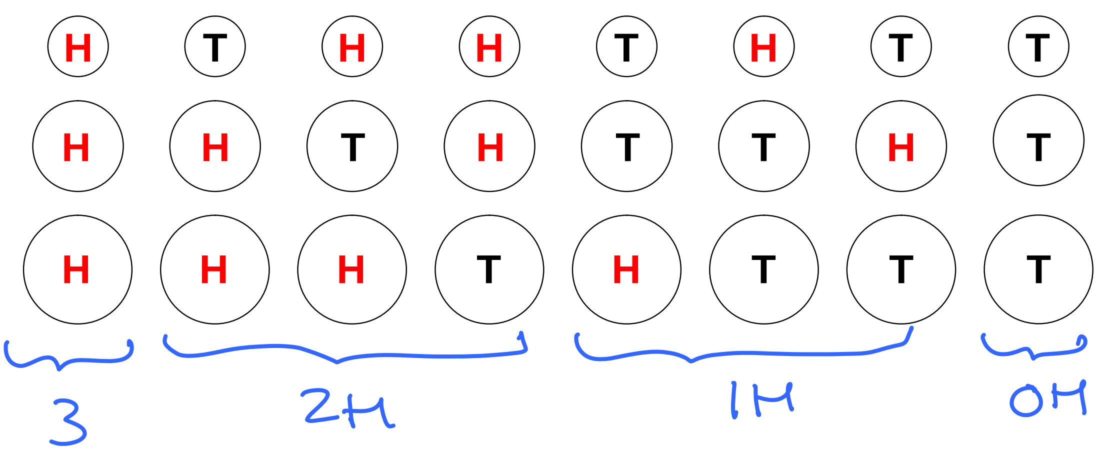
- Example of H_2 molecule



- Need Quantum and Statistical Mechanics!

Example - Coin flip

- Starting with a dime, a quarter and a loonie:
  - Flip all three - what are possible outcomes?



Some definitions for these "States"

microstate → specify state of each particle

macrostate → overall state (e.g. HHT)

multiplicity → number of microstates that correspond to a given macrostate

$\Omega(3H) = 1$ or $\Omega(2H) = 3$

total multiplicity $\Omega(\text{all}) = 8$

probability of getting particular macrostate (n heads) $= \dfrac{\text{multiplicity}}{\text{total multiplicity}} = \dfrac{\Omega(n)}{\Omega(\text{all})}$

Considering a larger system…

- If you have 10 coins, how do you calculate Ω(n)?
  - 0H: Ω(0) = 1
  - 1H: Ω(1) = 10
  - 2H: Ω(2) = $\dfrac{10 \times 9}{2}$
  - 3H: Ω(3) = $\dfrac{10 \times 9 \times 8}{3 \times 2 \times 1}$

$= \dfrac{10 \times 9 \times 8 \times 7 \ldots 1}{(7 \times 6 \times 5 \times \ldots 1)(3 \times 2 \times 1)}$

$= \dfrac{10!}{7!\,3!}$

1 2 3 4 5 6 7 8 9 10

1 2 3 4 5 6 7 8 9 10
1 2 3 4 5 6 7 8 9 10

1 2 3 4 5 6 7 8 9 10
1 2 3 4 5 6 7 8 9 10
1 2 3 4 5 6 7 8 9 10
1 2 3 4 5 6 7 8 9 10
1 2 3 4 5 6 7 8 9 10
1 2 3 4 5 6 7 8 9 10

Multiplicity of a Macrostate

- Generalizing from 10 to *N*

$$\Omega(3) = \frac{10!}{7!\,3!} \Rightarrow \Omega(n) = \frac{N!}{n!\,(N-n)!} = \binom{N}{n}$$

N total number of coins

n number of coins chosen

$\Omega(n) \Rightarrow$ number of ways of chosing n objects out of N

Moving to a Model System

Another example is the two-state paramagnet

- In a paramagnetic material
  - Magnetic "dipoles" tend to align parallel to any externally applied magnetic field
- Quantized - so only certain discrete values are allowed
  - Simplest case, only two values are allowed
  - Either positive or negative orientation of dipole

$$\vec{B}\uparrow \qquad \uparrow\downarrow\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\downarrow\uparrow\downarrow$$

Two-state Paramagnet

- At a particular time,

$N_\uparrow$ upward $\quad$ $N_\downarrow$ downward

$N = N_\uparrow + N_\downarrow$

one macrostate for each $N_\uparrow$ from $0 \to N$

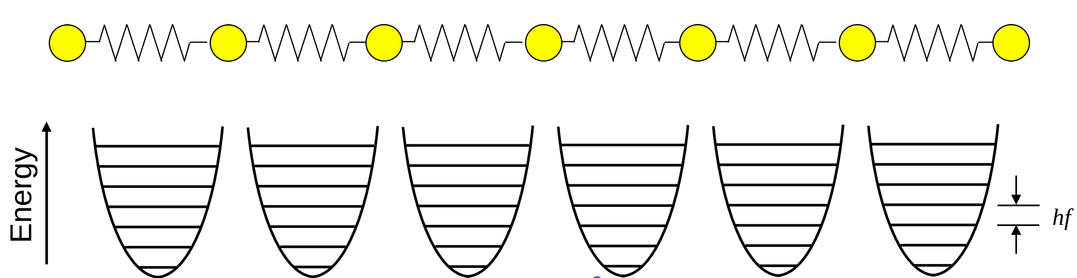
multiplicity of macrostate

$$\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!\,N_\downarrow!}$$

A more complex system

Moving to a more realistic or "physical" model system

- A set of microscopic systems that can store any number of energy "units", all of the same size
  – Such as quantum-mechanical harmonic oscillator
  – Potential energy function: $\frac{1}{2} k_s x^2$
  – Size of all energy "units": hf

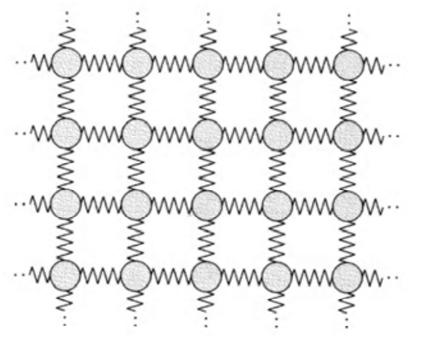


h = Planck's constant $= 6.63 \times 10^{-34}$ J·s

f = natural frequency of oscillator $= \frac{1}{2\pi}\sqrt{\frac{k_s}{m}}$

Einstein Model of a Solid

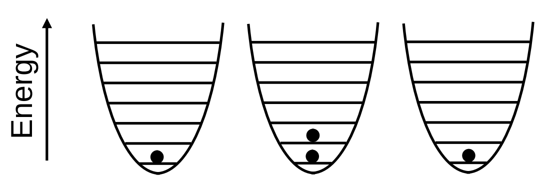
- Oscillations of atoms in a solid can be described as a collection of identical oscillators
  - In three-dimensional solid, can vibrate in three independent directions
  - *N* oscillations => only *N*/3 atoms



Einstein Solid

- Each oscillator can have multiple energy units
  - Example: 3 oscillators
    - 0 units of energy (0*hf*): $\Omega(0) = 1$
    - 1 unit of energy (*hf*): $\Omega(1) = 3$
    - 2 units of energy (2*hf*): $\Omega(2) = 6$ (3) (2,0,0) (3) (1,1,0)
    - 3 units of energy (3*hf*): $\Omega(3) = 10$

(3) (3,0,0) (6) (2,1,0) (1) (1,1,1)



Larger Einstein Solid

- In general, for *N* oscillators with *q* energy units:

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!\,(N-1)!}$$

using • energy unit q
| line for partition $N-1$

for oscillators

• | • | • $(1,1,1)$

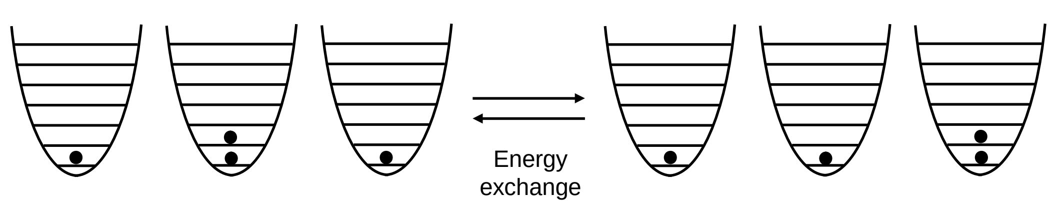
• • | | • $(2,0,1)$

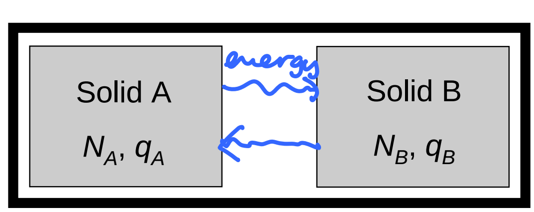
↑ 5 other arrangements of this microstate

Interacting Systems

Two Einstein solids that can share energy back and forth - A & B

- Assuming weakly coupled systems
  - Exchange of energy between atoms in each solid is much faster than between the two - U_A and U_B





System of Two Einstein Solids

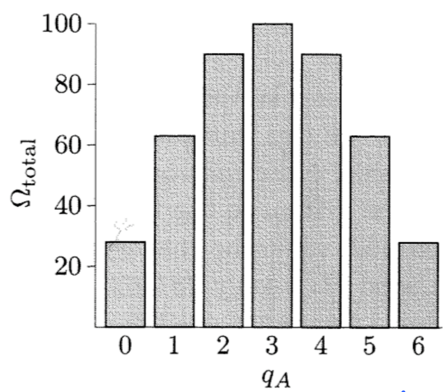
- Each solid has 3 harmonic oscillators (N_A, N_B) and they contain a total of six units of energy (q_{total})

$N_A = N_B = 3$ $\quad\quad$ $q_{total} = q_A + q_B = 6$

to calculate energy
need $U = q\,hf$ ← harmonic oscillator

System of Two Einstein Solids

q_A	Ω_A	q_B	Ω_B	$\Omega_{\text{total}} = \Omega_A \Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28
				$462 = \binom{6+6-1}{6}$



Ω_{total} depend on number of ways of chosing A & B $\quad \Omega = \binom{q+N-1}{q}$

for each of Ω_A microstates of A there are Ω_B microstates available for B

System of Two Einstein Solids

q_A	Ω_A	q_B	Ω_B	$\Omega_{\text{total}} = \Omega_A \Omega_B$
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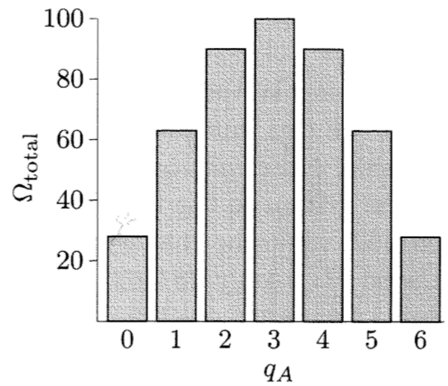

- Fundamental assumption of Statistical Mechanics
  - In an isolated system in thermal equilibrium, all accessible microstates are equally probably

Probabilities of Macrostates

- If all *microstates* are equally probable, some *macrostates* will be more probable than others