Chapter 7 The States of a System

- Any practical system can be in a large number of possible states. The number is large but finite.
- The number increases rapidly with the number of particles in the system and the number of possible states per particle.
- We talked about ways to deal with these states:

Binomial: $P_N(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$

$(\log(m!) \simeq m \ln m - m + \frac{1}{2}(2\pi m))$

Poisson: $P_N(n) \simeq \frac{(\bar{n})^n}{n!} e^{-\bar{n}}$, $p \ll 1$, $\bar{n} = pN$

Gaussian: $P(n) = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-(n-\bar{n})^2 / 2\sigma^2}$

$\sigma^2 = (n-\bar{n})^2 = Npq$, $\bar{n} = pN$

$(n-\bar{n}) \ll \sigma^2$

- Quantum mechanics assures us ~~that~~ the number of states is <u>finite</u> (though very large)

A. Equilibrium

- An isolated system is "in equilibrium" when the probabilities of it being in the various possible states do not vary in time.

- each system has a characteristic relaxation time for each process.
  - heat transfer
  - particle redistribution due to mechanical motion
  - diffusion
  - ⋮

- Thermodynamics is really Thermo "statics" or thermo "quasi-statics";

  Changes on a system level are considered to be slow w.r.t. relaxation times
  - ie quasi-static.

B. The Fundamental Postulate

$$\boxed{\text{An isolated system in equilibrium is equally likely to be in any of its accessible states.}}$$

ie $P = \dfrac{1}{\Omega_0}$

Ω_0 = # of possible states of system o

If $\Omega_i \equiv$ number of states in subset i

then P_i = prob. of system being in subset i state

$$= \frac{\Omega_i}{\Omega_0}$$

ie Life is a game (lottery)

Example:

3 coins flipped (Heads or Tails)

8 Possible outcomes:

1 T T T

2 T T H

3 T H T

4 T H H

5 H T T * ✗

6 H T H * ✓

7 H H T * ✓

8 H H H * ✗

What is prob. of getting 2 heads out of 3 given the first flip is a head? (Call this outcome 1)?

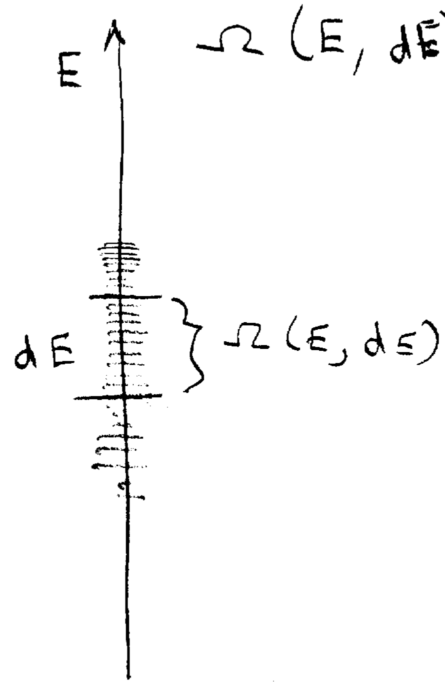
$$P_1 = \frac{\Omega_1}{\Omega_0} = \frac{2}{4}$$

C The Spacing of States

The number of possible states for, say, molecules in a room ~~so that~~ ½ are in front & ½ are in back is $\sim 10^{10^{28}}$!

Most of these states have molecules ~ same energy.
Spacing in energy $\sim 10^{-24}$ eV (quantum levels)
We can describe this using the density of states:

$$\Omega(E, dE) = g(E)\,dE$$



D. Density of States and the Internal Energy

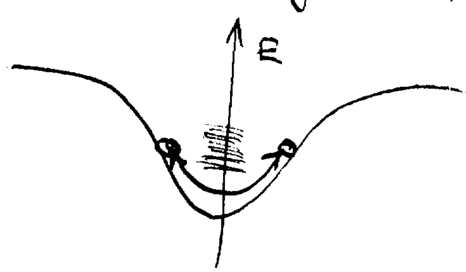
Let Ω_i = # of states in the i^{th} degree of freedom (say vibration in x direction) etc.

For each of these states there are Ω_j states in the j^{th} degree of freedom, etc.

So in total there are

$$\Omega_0 = \Omega_1 \cdot \Omega_2 \cdot \Omega_3 \cdots\cdots \Omega_{\mathcal{R}} \quad \text{states}$$
$$= \prod_{i=1}^{\mathcal{R}} \Omega_i \qquad \leftarrow \# \text{ of D.o.f.}$$

Now as E in a system ↑, there are more available states



$$\Omega_i(E) \propto E^{x} \leftarrow \text{some positive number. (typically } \tfrac{1}{2}\text{)}$$

$$\therefore \ \Omega_0 = \Omega_1 \cdot \Omega_2 \cdot \Omega_3 \cdots \propto (E^{x})^{\mathcal{R}} = E^{x\mathcal{R}}$$

Now $\mathcal{R} \sim 10^{22} \to 10^{28}$

$\therefore$ Ω_0 ↑ very rapidly as E ↑

What is χ ?

We had (see 5-1)

$$\mathcal{E} = bq^2 \quad , \quad \text{eg } \tfrac{1}{2}mv^2, \ \tfrac{1}{2}kx^2 \ldots$$

So max energy in a given D.O.F, $= b\, q^2_{max}$

$\therefore$ # of accessible states, $\Omega_i \propto q_{max} \propto E^{\frac{1}{2}}$

ie $\chi = \frac{1}{2}$.

$$\therefore \quad \Omega_0(E) = \prod_{i=1}^{\mathcal{R}} \Omega_i = \text{const} \times E^{\mathcal{R}/2}$$

$$+ \quad \Omega_0(E, dE) = \underbrace{\text{constant } E^{\mathcal{R}/2}}_{g(E)} dE$$

density of states

Example

if $\mathcal{R} = 2 \times 10^{24} \Rightarrow g(E) \propto E^{10^{24}}$!

as $E \uparrow$ $g \uparrow$ very rapidly.

Example Room full of air 10^{28} molecules
5 DOF for each molecule
(3 translational, rotational)

T increases by 1 °C.
By what factor does # states increase?

Sol'n

$T \sim 300\,K$

$E \sim kT$ so $\frac{E_2}{E_1} \sim \frac{301}{300} = 1.0033$

$$\therefore \frac{\Omega_0^{301}}{\Omega_0^{300}} = \left(\frac{E_2}{E_1}\right)^{R/2} = (1.0033)^{\frac{5}{2}\times 10^{28}}$$
$$= 10^{3.6\times 10^{26}}$$

Huge increase in # states when T ↑ by 1 degree.

$$\underline{\Omega_0^{301} = \Omega_0^{300} \times 10^{3.6\times 10^{26}}} \quad !$$