



Thermal & Statistical Physics

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PHYS 343

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LECTURE 5

Basic Ideas of Statistical Mechanics

- General idea
- Macrostates and microstates
- Fundamental assumptions
- A simple illustration: tossing coins
- Simple paramagnetic solid: the statistics of exceedingly big numbers
- Gaussian Distribution

Statistical Mechanics: why?

- We want to describe/explain/predict the properties of systems containing unimaginably large numbers of objects (eg $\sim 10^{23}$ atoms in a typical “lump” of solid material)
- Impossible to do this in terms of the equations of motion of individual particles: there are just far, far, too many.....
- Two approaches:



Not to worry about “microscopic” behaviour, just consider relationships between macroscopic variables.....Thermodynamics



Try to understand macroscopic behaviour on the basis of the “averaged” microscopic behaviour of the particles, using the laws of statistics.....Statistical Mechanics

(But you should think of these as complementary, rather than competing approaches: see later)

Macrostates & Microstates

Definitions

Macrostate (macroscopic state): A state of a system described by a set of macroscopic variables, eg sample of gas in a container with a fixed pressure, volume, temperature and pressure. (In fact, any macrostate can be specified by the internal energy (E), volume (V), number of particles (N) and appropriate parameters to take account of external influences (eg magnetic, electric fields)).

Microstate (microscopic state): A particular “arrangement” of the microscopic constituents of a system. For example, a specification of the positions and momenta of all the atoms or molecules of the above gas.

Fundamental Assumption of Statistical Physics

- All accessible microstates of a given system are equally likely to occur
- The most probable macrostate is the one with the most microstates.

Statistical Weight, or Multiplicity

- The number of **microstates** corresponding to a given **macrostate** is called the **STATISTICAL WEIGHT** or **MULTIPLICITY** of the macrostate
- Usually given the symbol Ω
- A given macrostate is often defined by having some number n particles with a particular state or configuration out of a total number of N particles
- Number of microstates then given by the number of ways of selecting these n particles from the total set of N particles:

$$\Omega(n) = {}^n C_N = \frac{N!}{(N-n)!n!} \quad (2\text{-state system})$$

Illustration of concepts: tossing coins

- Consider, for example, a set of 4 coins, each of which can be tossed to give a “head” or a “tail”:



Head



Tail

- The set of coins has five possible “macrostates”:
 - 4 heads
 - 4 tails
 - 3 heads, 1 tail
 - 3 tails, 1 head
 - 2 heads, 2 tails

4 heads (4H) macrostate



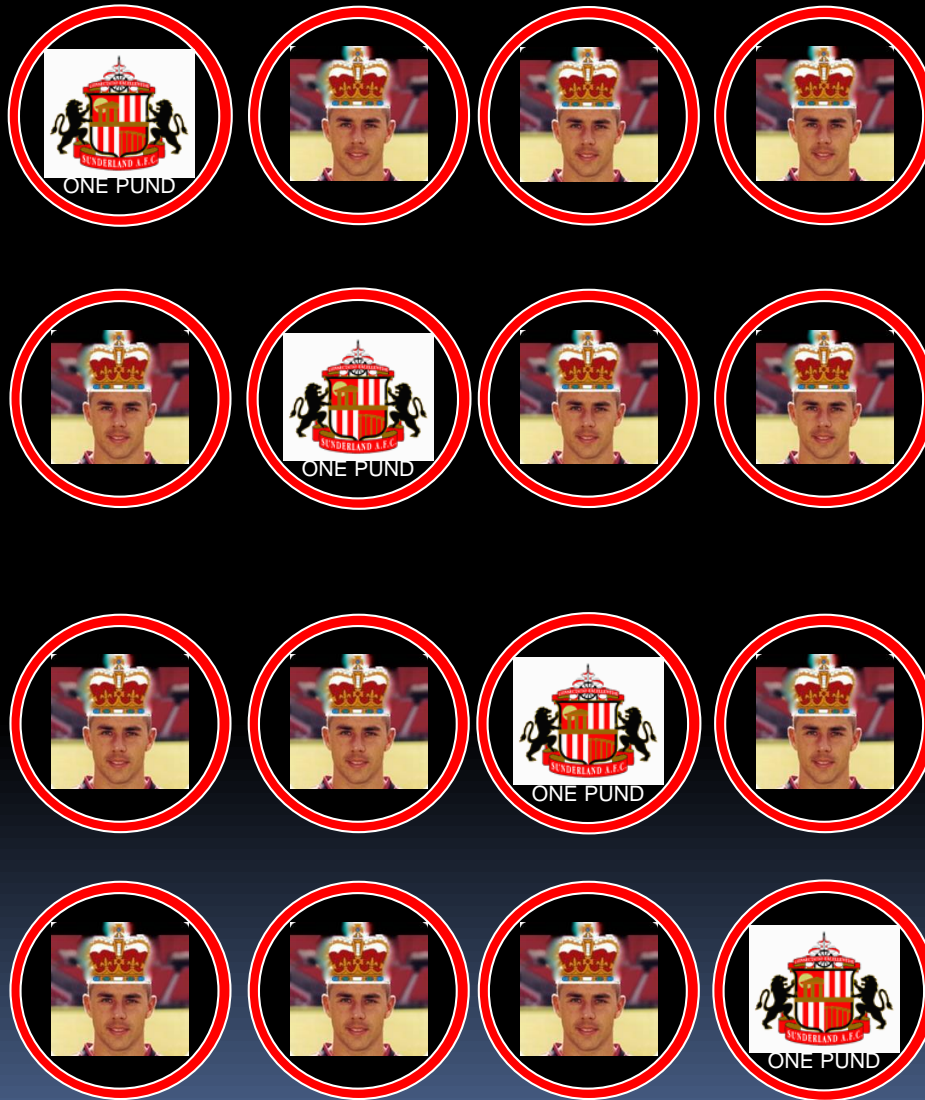
1 microstate
($\Omega(4) = 1$)

4 tails (4T) macrostate



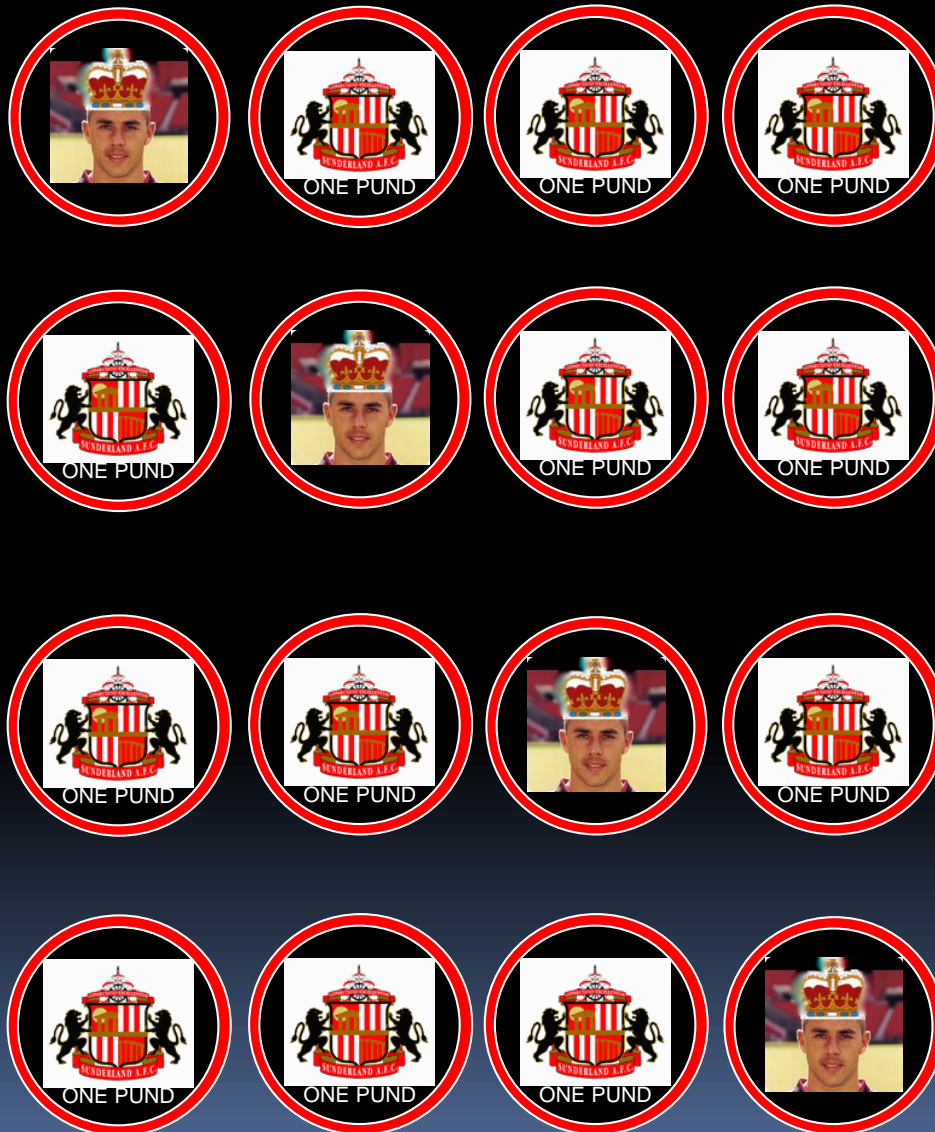
1 microstate
($\Omega(0) = 1$)

3 heads, 1 tail (3H1T) macrostate



4 microstates
($\Omega(3) = 4$)

3 tails, 1 head (3T1H) macrostate



4 microstates
($\Omega(1) = 4$)

2 heads, 2 tails (2H2T) macrostate




6 microstates ($\Omega(2) = 6$)

Probability

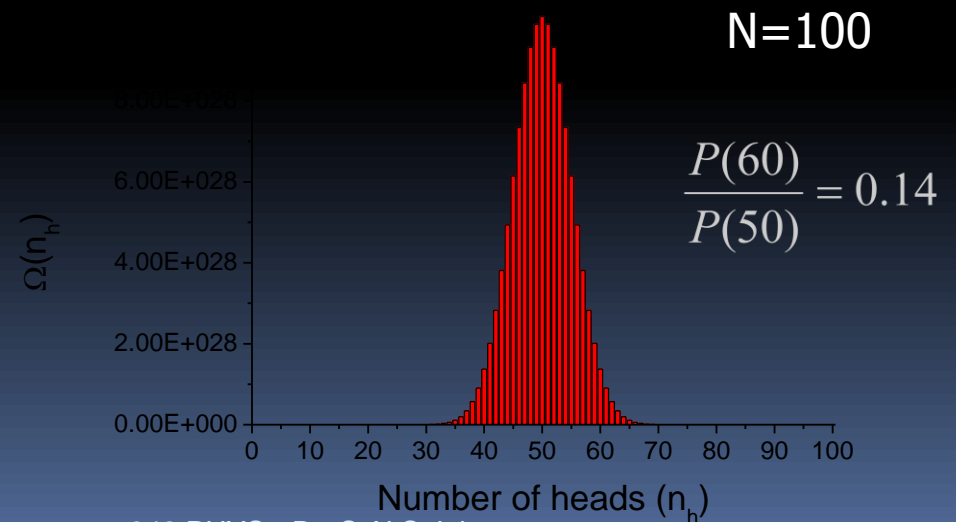
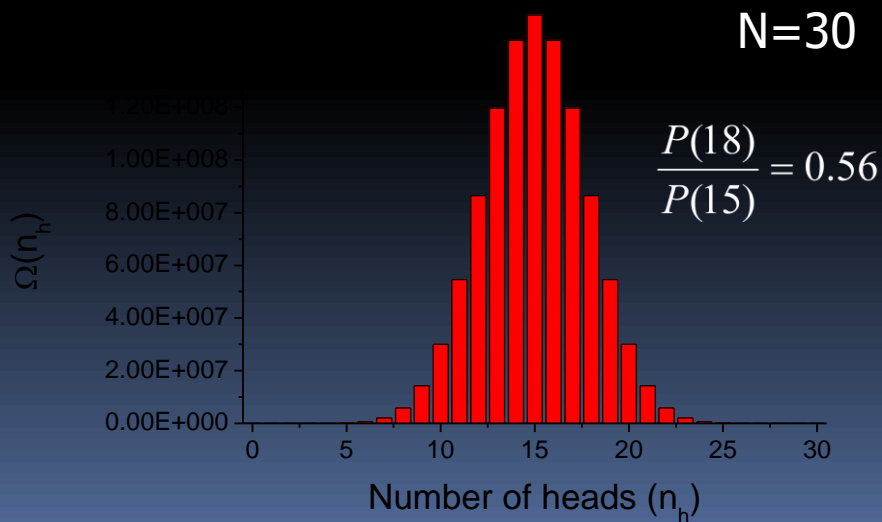
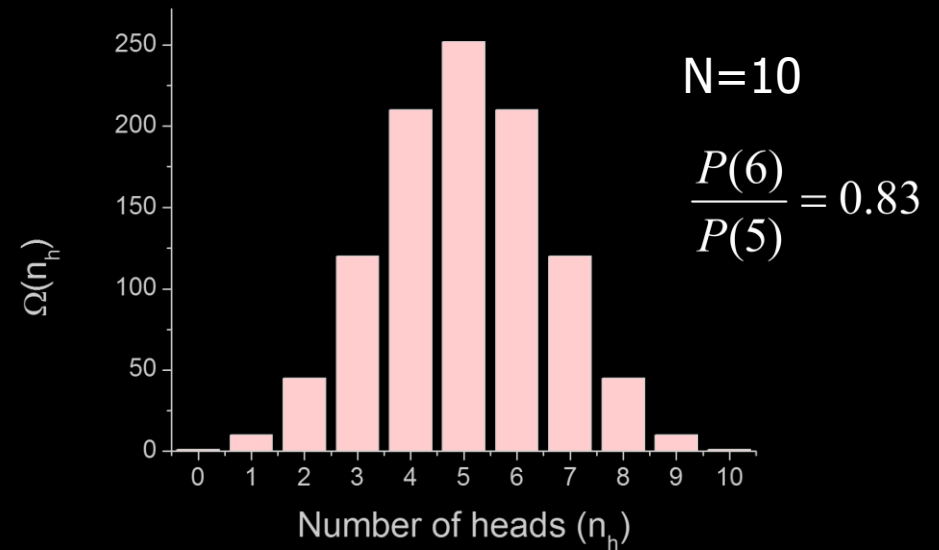
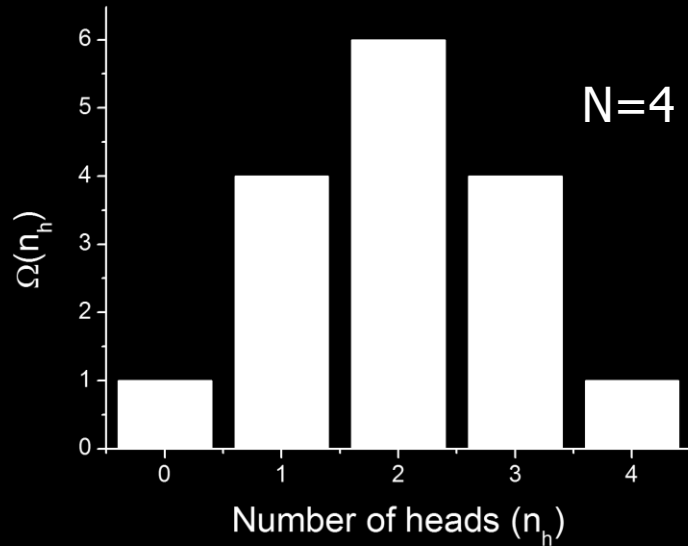
Probability of an event occurring = number of ways the event can occur ÷ total number of possible outcomes

Probability of a given macrostate M occurring is given by:

$$P(M) = \frac{\Omega(M)}{\sum_m \Omega(M)} = \frac{\Omega(M)}{2^N}$$


Total number of microstates for all possible macrostates of a 2-state (binary) system of N particles

Tossing coins : effect of increasing N



- ❖ As N gets bigger, the probability of observing a deviation from the most likely macrostate ($n_h = n_t = N/2$) gets smaller
- ❖ How small does the probability of deviation get for REALLY big numbers, eg number of atoms in a macroscopic solid???
- ❖ Can't evaluate Ω numerically for $N > \sim 100$: so try to derive an **analytical** expression.....

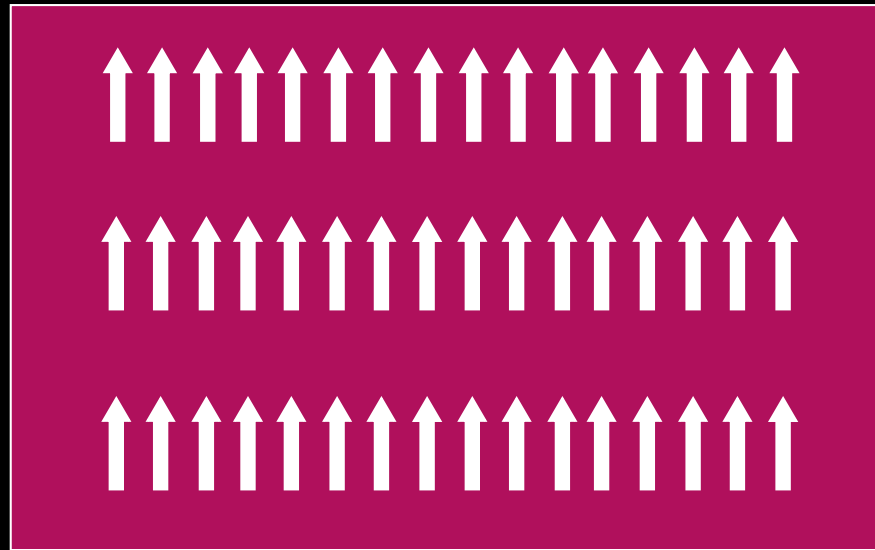
Investigate this by taking our first look at the **simple paramagnetic solid**.....

Simple Paramagnetic Solid (SPS)

- ❖ In an SPS, each atom or molecule of the solid behaves like a microscopic magnetic dipole (bar magnet). Dipoles are assumed to be independent of one another.
- ❖ Because of quantization of orbital angular momentum (spin) of electrons, dipoles have only 2 possible orientations with respect to an externally applied magnetic field (B): "up" \uparrow (parallel to field direction) or "down" \downarrow (antiparallel to field direction).
- ❖ At very low temperatures, all dipoles are aligned with field direction (\uparrow); as temperature is increased, thermal energy of crystal randomises the dipole orientation, so we have some aligned up ($N \uparrow$) and some aligned down ($N \downarrow$).
- ❖ Consider **highT, low B limit**: randomising effect of temperature far outweighs alignment effect of field.



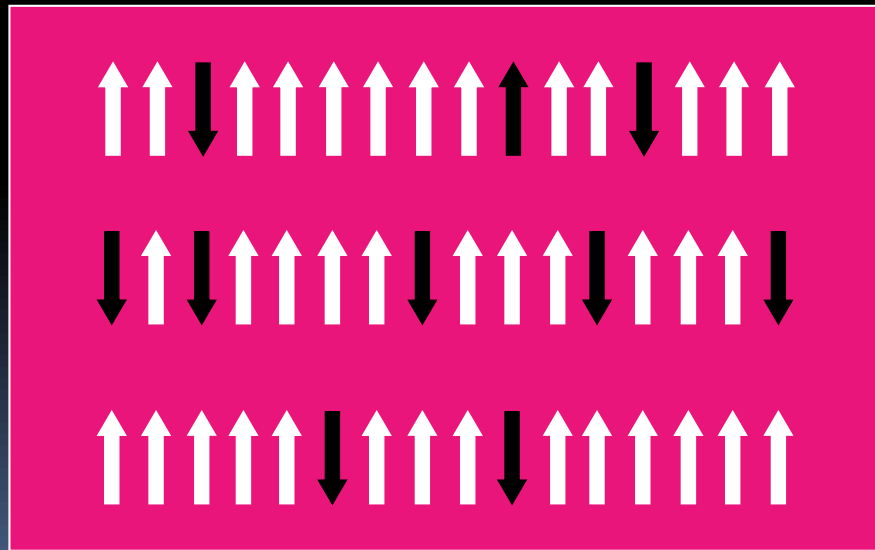
B



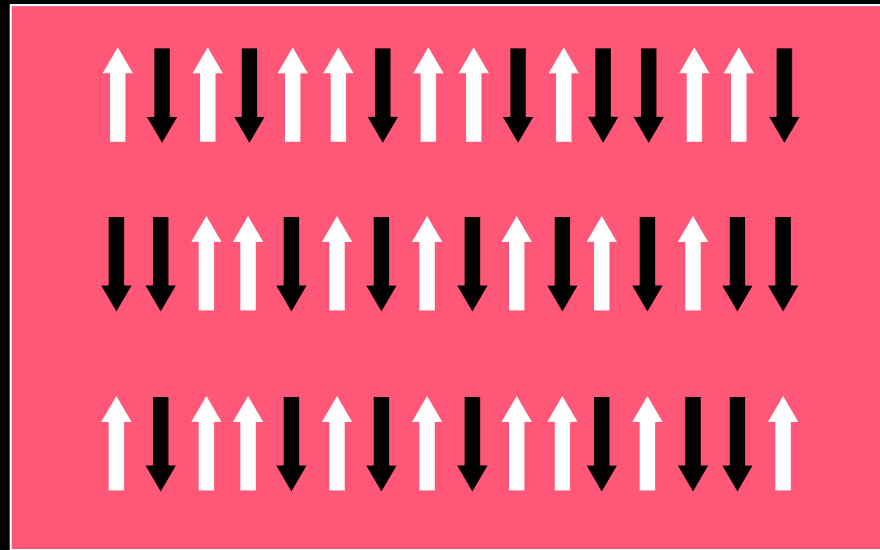
High B, low T



B



Moderate B, T



Low B, high T

Simple Paramagnetic Solid (SPS)

To evaluate the number of microstates for a given number of “up” dipoles ($N \uparrow$) in a total number N we use the “standard” formula ■

$$\Omega(N \uparrow) = \frac{N!}{N \uparrow!(N - N \uparrow)!} = \frac{N!}{N \uparrow!N \downarrow!}$$

- Because we want to work large numbers, it's convenient to use logs
- We also make use of **Stirlings approximation**: for large x :

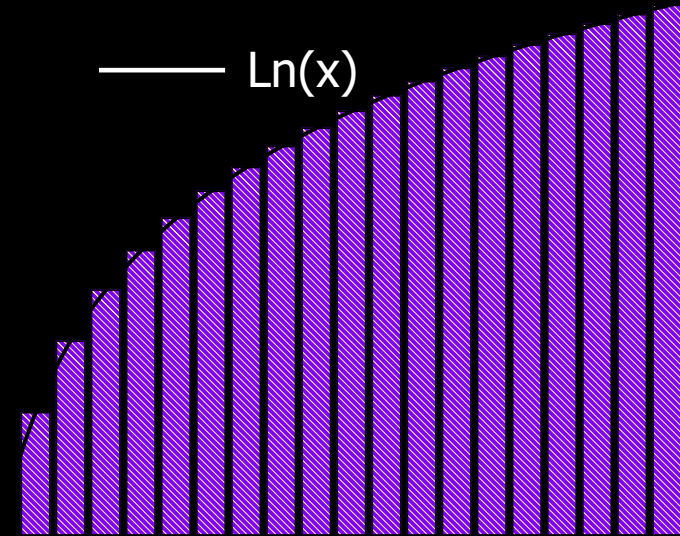
$$\ln(x!) \approx x \ln x - x$$

Stirling's Approximation

$$\begin{aligned} \diamond \ln(N!) &= \ln 2 + \ln 3 + \ln 4 + \dots \\ &\dots \dots \dots \ln(N-1) + \ln(N) \end{aligned}$$

❖ Consider, eg $N=20$ (opposite)

$$\ln(20!) = \sum_{n=1}^{20} \ln(N) = \text{total area of "strips"}$$



• Total area of strips \approx total area under curve $y = \ln(x)$ ($1 \leq x \leq 20$)

$$A = \int_1^{20} \ln(N) dN = [N \ln N - N]_1^{20} = 20 \ln 20 - 20 + 1$$

$$\ln(20!) = 20 \ln 20 - 20 + 1$$

$$\ln(N!) \approx N \ln(N) - N$$

Taylor Expansion

$$f(x_0 + a) = f(x_0) + af'(x_0) + \frac{a^2 f''(x_0)}{2!} + \frac{a^3 f'''(x_0)}{3!} + \dots$$

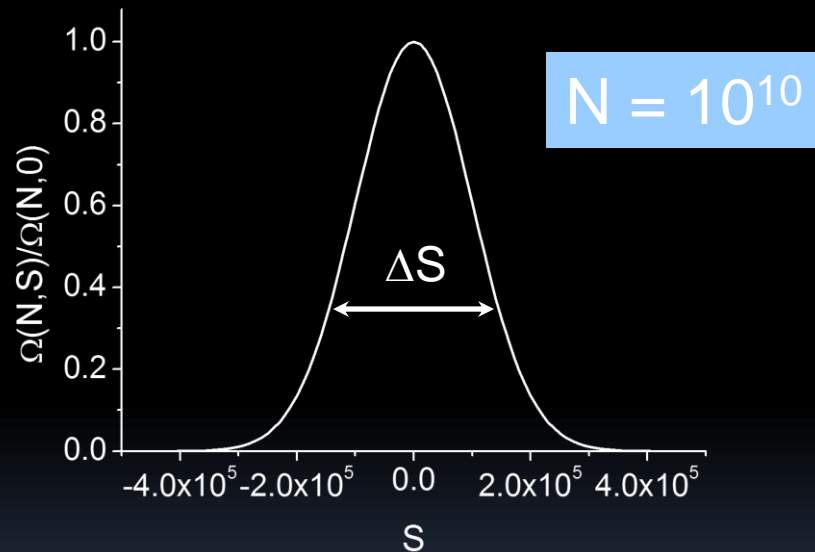
where $f'(x_0) = \left. \frac{df(x)}{dx} \right|_{x=x_0}$, ie derivative evaluated at $x = x_0$

$$f''(x_0) = \left. \frac{d^2 f(x)}{dx^2} \right|_{x=x_0} \text{ etc.....}$$

Series converges for $|a| < 1$

Simple Paramagnetic Solid: Gaussian Distribution

$$\frac{\Omega(N, S)}{\Omega(N, 0)} = e^{(-S^2/2N)}$$



- Define “half width” of the distribution from the value of S at which Ω falls to $1/e$ of its maximum value
- This is when $S^2 = 2N$, ie $S = \pm(2N)^{1/2}$
- So, “fractional” width of distribution is given by:

$$\frac{\Delta S}{N} \sim \frac{1}{\sqrt{N}}$$

Simple Paramagnetic Solid: Gaussian Distribution

$$\frac{\Omega(N, S)}{\Omega(N, 0)} = e^{-S^2/2N}$$

Thermodynamics FE review

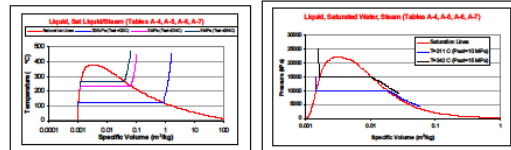
Subjects

1. Properties of Materials, Property Relations for Ideal Gases/Liquids/Solids and Liquid-Vapor Phases
2. First Law in closed and Open Systems
3. Second Law, Entropy, Heat Engine and Refrigeration Cycles

Material Properties

State postulate

P-v and T-v diagrams for two-phase systems, saturated substances, mixtures and quality



Ideal Gas Law Property Relations

$$PV = mRT$$

$$Pv = RT$$

$$P = \rho RT$$

$$PV = NR_uT$$

$$R_u = R(MW) \text{ and } N(MW) = m$$

$$\text{Isothermal: } P_1V_1 = P_2V_2$$

$$\text{Isobaric: } T_1V_2 = T_2V_1$$

$$\text{Isochoric: } P_1T_2 = P_2T_1$$

$$\text{Isentropic: } \frac{T_1}{T_2} = \left(\frac{P_2}{P_1}\right)^{\gamma} \text{ OR } \frac{T_1}{T_2} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} \text{ OR } \frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^{\gamma}$$

Specific Heat, Internal Energy and Enthalpy Relations

Ideal gases

$$\Delta u = C_v\Delta T \text{ for specific heat constant}$$

$$\Delta h = C_p\Delta T \text{ for specific heat constant}$$

$$C_p = C_v + R$$

Incompressible liquids and solids where ΔP is negligible: $\Delta h = \Delta u = C_p\Delta T$

Incompressible liquids where Δu is negligible (ΔT negligible) - pumps: $\Delta h = v\Delta P$

1

$$\frac{\Delta S}{N} \sim \frac{1}{\sqrt{N}}$$

Simple Paramagnetic Solid: Some conclusions

- We've considered the case for the weak field, high temperature limit, where thermal energy of crystal completely randomises dipole orientation, \uparrow or \downarrow (see later to deal with the situation where "ordering" due to magnetic field is significant)
- As expected, the most likely configuration is with equal numbers of dipoles up and down
- Key point is that this is **OVERWHELMINGLY** more probable than any other configuration
- Fractional fluctuations away from $N\uparrow = N\downarrow = N/2$ are exceedingly small, $\sim 1/\sqrt{N} \sim 10^{-11}$ for $N = 10^{22}$
- So, for systems with numbers of particles on this scale, the most likely **macrostate** (the one with the most **microstates**), is an entirely well defined, stable thermodynamic state.