

Statistical Mechanics --- First Steps

Goal. Form a microscopic description of accessible states of a system and use Boltzmann's hypothesis to calculate entropy. (Accessible means that the states are consistent with constraints: E, V etc. fixed.)

Outcome of experiment gives an event and these events will specify system as completely as possible

- A. Specify microstate or quantum state as completely as possible.
- B. If not possible to specify completely, use classical probability. (List all outcomes of measurement and assign equal probability.)
- C. If there are W possible quantum states, assign probability $p=1/W$.

Boltzmann hypothesis:

Entropy of system related to being in a quantum state.

If there are W states, probability $p=1/W$. Entropy $S = \varphi(W)$ some function to be determined.

Now use general arguments to find form of φ .

Consider two separate systems:



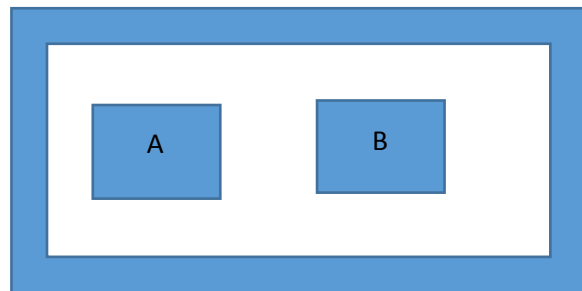
Separate systems: Entropies $S_A = \varphi(W_A)$ $S_B = \varphi(W_B)$

Now consider composite system A + B

$S_{AB} = S_A + S_B$ (additive) or
 $\varphi(W_{AB}) = \varphi(W_A) + \varphi(W_B)$

BUT $W_{AB} = W_A W_B$, thus
 $\varphi(W_A W_B) = \varphi(W_A) + \varphi(W_B)$

ONLY solution



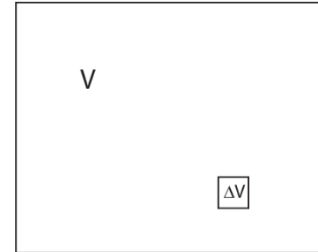
$$S = k \ln W$$

Now some fun

Consider number of ways of putting gas molecule in a box of volume V

Small volume ΔV : no of ways of putting a molecule in ΔV
 $=V/\Delta V$

For N molecules $W = \left(\frac{V}{\Delta V}\right)^N$



Entropy

$$S = kN \ln \left(\frac{V}{\Delta V} \right)$$

ΔV is arbitrary, and only differences in S matter

$$S_f - S_i = kN \ln \left(\frac{V_f}{V_i} \right)$$

Now use one of our results from thermodynamics

$$P = T \left(\frac{\partial S}{\partial V} \right)_T$$

Thus find $P = kNT/V$, identify k as Boltzmann's constant k_B

Spin system.

Spins up + or down -

+ - + + - + +

+ + + - - + +

Entropy determined by counting number of ways to place n_1 up spins and n_2 down spins on N lattice sites

Constraint: $n_1 + n_2 = N$ N fixed

n_1 spins energy $-\varepsilon$, n_2 spins $+\varepsilon$, $n_2 = N - n_1$

Internal energy: $U = -(n_1 - n_2)\varepsilon = -(2n_1 - N)\varepsilon$

$$S = k_B \ln W$$

No of ways arranging spins

$$W = \frac{N!}{(n_1)!(n_2)!} = \frac{N!}{(n_1)!(N - n_1)!}$$

Need Stirling's approximation: $\ln N! = N \ln N - N$

$$S = k_B [N \ln N - N - n_1 \ln(n_1) + n_1 - (N - n_1)(\ln(N - n_1) + (N - n_1))]$$

or

$$S = k_B [-n_1 \ln(n_1) - (N - n_1) \ln(N - n_1)]$$

Let $\frac{n_1}{N} = \frac{1-x}{2}$, find $\frac{n_2}{N} = \frac{N-n_1}{N} = \frac{1+x}{2}$ and $\frac{n_1-n_2}{N} = -x$

Find $U = N\varepsilon x$

$$\text{Entropy } S = -Nk_B \left\{ \left(\frac{1+x}{2} \right) \ln \left(\frac{1+x}{2} \right) + \left(\frac{1-x}{2} \right) \ln \left(\frac{1-x}{2} \right) \right\}$$

Now use one of our thermodynamic relations

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V = \left(\frac{\partial S}{\partial x} \right) \left(\frac{\partial x}{\partial U} \right) = \frac{1}{N\epsilon} \left(\frac{\partial S}{\partial x} \right)$$

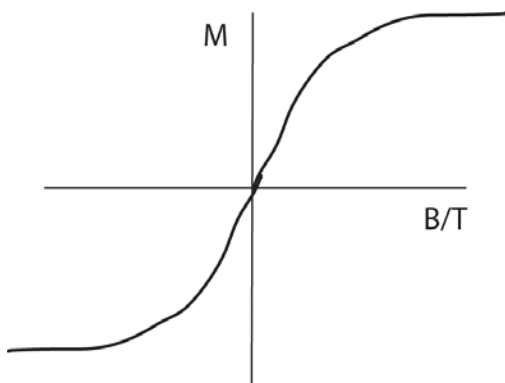
Find $\frac{1}{T} = \frac{1}{N\epsilon} \left(\frac{-Nk_B}{2} \right) \left\{ \ln \left(\frac{1+x}{1-x} \right) \right\}$

Note if $y = \ln \left(\frac{1+x}{1-x} \right)$, invert to find $x = \tanh \frac{y}{2}$

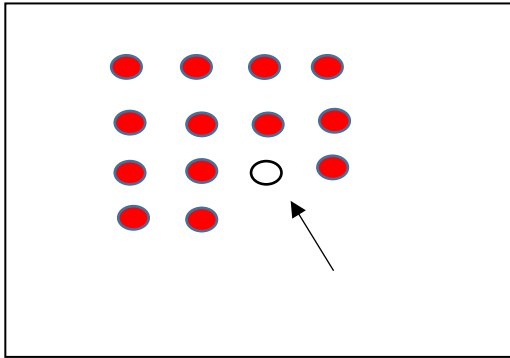
Finally have $x = \frac{U}{N\epsilon} = -\tanh \left(\frac{\epsilon}{k_B T} \right)$ Since $U = -(n_1 - n_2)\epsilon$

$$n_1 - n_2 = \tanh \left(\frac{\epsilon}{k_B T} \right)$$
$$M = (n_1 - n_2) \frac{\mu}{V} = \frac{\mu N}{V} \tanh \left(\frac{\mu B}{k_B T} \right)$$

Used $E^{up} = -\mu B, E^{dn} = +\mu B$ whence $\epsilon = \mu B$



Vacancies in crystals



N atoms, n vacancies, $N+n$ lattice sites

No of configurations $W = (N+n)! / N!n!$

Entropy $S = k_B \ln W = (N+n) \ln(N+n) - N \ln N - n \ln n$

Internal energy $U = N\varepsilon$ where ε is vacancy formation energy
(ε measured experimentally (X-rays, NMR))

Use thermodynamic RELATION

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V = \frac{\partial S}{\partial n} \frac{\partial n}{\partial U} = \frac{1}{\varepsilon} \frac{\partial S}{\partial n}$$

Thus $\frac{1}{T} = \frac{k_B}{\varepsilon} \{ \ln(N+n) - \ln(n) \} = \frac{k_B}{\varepsilon} \ln \left(1 + \frac{N}{n} \right)$

Whence
$$\frac{n}{N} = \frac{1}{e^{\frac{\varepsilon}{k_B T}} - 1}$$

OK if $\frac{n}{N} \ll 1$. At high temperature $\frac{n}{N} \sim e^{\left(-\frac{\varepsilon}{k_B T} \right)}$

Example solid ^3He , $\varepsilon = 10$ K.

At 1 K, $\frac{n}{N} = e^{-10} = 4 \cdot 10^{-5}$ Can use NMR to measure n . Vacancies move and motion contributes to relaxation rate which must be proportional to n .

Experiments show rates that are exponential per $\frac{n}{N} \sim e^{\left(-\frac{\varepsilon}{k_B T} \right)}$.

Rubber band model

n_+ steps right, n_- steps left all same length d

Total number of steps $= N = n_+ + n_-$

Extend rubber band by dl

Work done $Wk = Fl$



Change in internal energy

$$dU = TdS + Fdl$$

Force $F = -T \left(\frac{\partial S}{\partial l} \right)_U$

Number of configurations

$$W = \frac{N!}{n_+!n_-!} = \frac{N!}{n_+!(N-n_+)!} \quad S = k_B \ln W$$

Hence $F = -k_B T \left(\frac{\partial \ln W}{\partial l} \right)_L$

Length $l = (n_+ - n_-)d$ Let $\frac{n_+}{N} = \frac{1+x}{2}$ $\frac{n_-}{N} = \frac{1-x}{2}$

and thus $x = \frac{l}{Nd}$

$$\ln W = N \ln N - n_+ \ln n_+ - n_- \ln n_- = -N \left(\frac{1+x}{2} \ln \frac{1+x}{2} + \frac{1-x}{2} \ln \frac{1-x}{2} \right)$$

Now find $\frac{F}{T} = -k_B \frac{\partial \ln W}{\partial x} \frac{\partial x}{\partial l} = \frac{k_B}{2d} \ln \frac{1+x}{1-x}$

For small x , $\ln \frac{1+x}{1-x} \cong 2x$ and

$$F \cong \frac{k_B T l}{Nd^2}$$

Tension F proportional to product of T and extension l

Keep rubber band under constant F and heat, length l will decrease.

Problems at end Chap. 4

4.6 Entropy of paramagnet is given as $S = S_0 - CU^2$

Use thermodynamic relation $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V$ to find

And we have $U = -\frac{1}{2CT}$

