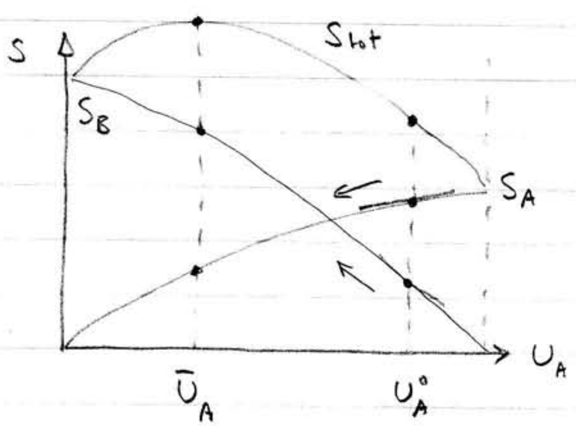
lecture 3

Last time we defined thermal equilibrium and temperature

U_A, N_A $\quad$ U_B, N_B $\qquad$ $\bar{U}_A, N_A$ $\quad$ $\bar{U}_B = U - \bar{U}_A, N_B$

At equilibrium total entropy is maximized



Assume that initially
$U_A^0 > U_B^0$

In this diagram, initially
$$\left.\frac{\partial S_A}{\partial U_A}\right|_{U_A^0} < \left.\frac{\partial S_B}{\partial U_B}\right|_{U_B^0}$$

$\therefore$ If $U_A \downarrow$, $S_A \downarrow$ less than $S_B \uparrow$
so $S_{tot} \uparrow$

Total system will spontaneously move in direction increasing S_{tot}
In this example $U_A \downarrow$ $S_A \downarrow$ but $U_B \uparrow$ $S_B \uparrow$ and $S_{tot} \uparrow$

Note: individual entropies can $\downarrow$ as long as $S_{tot} \uparrow$

Energy is transfered from $A \to B$
$\frac{1}{T} \equiv \frac{\partial S}{\partial U}$ so we say A is hotter than B initially

A hot object has a tendency to give up its energy to a cold object because $\Delta S_{hot} < \Delta S_{cold}$

How much energy is transfered?

$$\Delta S_{tot} = \Delta S_A + \Delta S_B = \frac{\partial S_A}{\partial U_A} \Delta U_A + \frac{\partial S_B}{\partial U_B} \Delta U_B$$

$$= \frac{1}{T_A} \Delta U - \frac{1}{T_B} \Delta U = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \Delta U \qquad \Delta U_A = -\Delta U_B = \Delta U$$

If $T_A > T_B$ then $\Delta U = \Delta U_A < 0$ for $\Delta S_{tot} \geq 0$ so energy transfered $A \to B$

Transfered energy is $\Delta U = T_A \Delta S_A = -T_B \Delta S_B$
This is called <u>heat</u>. We'll return to this later

One last pt:
Although $\Delta U_A = -\Delta U_B$ final energies $\bar{U}_A \neq \bar{U}_B$ necessarily

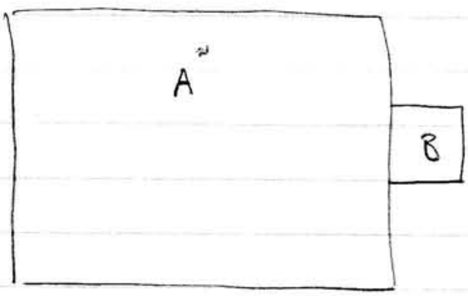
Consider Einstein solid. We showed that $U = N k_B T$ for <u>T large</u>
At equilibrium 2 Einstein solids have

$$T_A = T_B \quad \therefore \quad \frac{\bar{U}_A}{N_A} = \frac{\bar{U}_B}{N_B}$$

So final energies will depend on system sizes
This also says that at equilibrium U per oscillator of A, B systems are the same.

Heat bath or reservoir

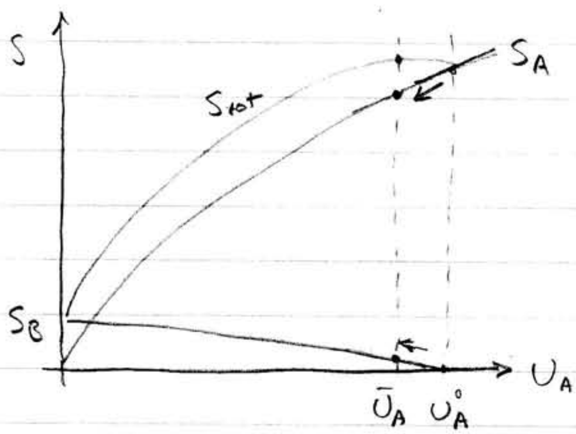
Consider now that one system (A) is much larger than the other (B):



$U_A \gg U_B$

$N_A \gg N_B$

Can expect $S_A \gg S_B$



Energy transfered going to equilibrium

$\varepsilon \ll U_A$

$$S_A(\bar{U}_A) = S_A(U_A^\circ) - \left.\frac{\partial S}{\partial U_A}\right|_{U_A^\circ} \varepsilon$$

$$S_A(\bar{U}_A) = S_A(U_A^\circ) - \frac{\varepsilon}{T_A}$$

$\uparrow$ Final entropy $\qquad$ $\uparrow$ Initial entropy

What about temperature?

$$\left.\frac{\partial S_A}{\partial U_A}\right|_{\bar{U}_A} = \left.\frac{\partial S_A}{\partial U_A}\right|_{U_A^\circ} - \left.\frac{\partial^2 S_A}{\partial U_A^2}\right|_{U_A^\circ} \varepsilon$$

$\uparrow$ Final temp. $\qquad$ $\uparrow$ Initial temp

For Einstein solid

$$\frac{\partial^2 S_A}{\partial U_A^2} = \frac{-N k_B}{U_A^2} = \frac{-N}{U_A}\frac{1}{T_A}$$

$$\frac{1}{T_A} = \frac{1}{T_A^\circ}\left(1 + \frac{\varepsilon}{U_A^\circ}\right) \approx \frac{1}{T_A^\circ}$$

so T of reservoir does not change

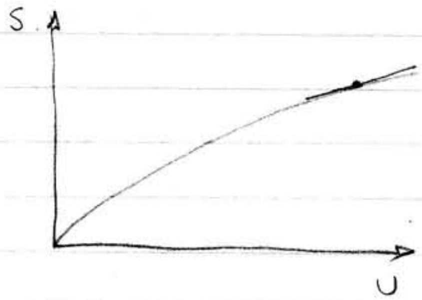
Reservoir – exchanges heat with B, sets its temperature

$T_B = T_A \approx T_A^\circ$

For many different kinds of systems

$\Omega \sim U^f$ (Einstein solid, also ideal gas – next lecture)

$\therefore \quad S \sim f \ln U \qquad T \sim \frac{U}{f}$



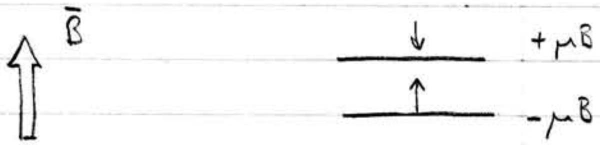
As $U \uparrow$, $S \uparrow$ and $T \uparrow$

Some systems <u>do not</u> behave this way

<u>2-state paramagnet</u>

Paramagnet made up of N spins ($\frac{1}{2}$). Each can be up or down:

$$\underbrace{\uparrow\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow}_{N = n_\uparrow + n_\downarrow}$$



In presence of B-field, spins aligned along B have a lower energy $-\mu B$

Total energy $\quad U = n_\uparrow(-\mu B) + n_\downarrow(+\mu B)$
$\qquad\qquad\qquad = -\mu B(2n_\uparrow - N)$

Multiplicity given by binomial coefficient

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

Assume $N \gg 1$, $n_\uparrow \gg 1$ and apply Stirling's approx.

$$S = k_B \ln \Omega = k_B \left(N \ln N - \cancel{N} - n_\uparrow \ln n_\uparrow - \cancel{n_\uparrow} - n_\downarrow \ln n_\downarrow - \cancel{n_\downarrow} \right)$$

$$= k_B \ln \left[N \ln N - n_\uparrow \ln n_\uparrow - (N - n_\uparrow) \ln (N - n_\uparrow) \right]$$

Find temperature

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial S}{\partial n_\uparrow} \frac{\partial n_\uparrow}{\partial U} = -\frac{1}{2\mu B} \frac{\partial S}{\partial n_\uparrow} \qquad n_\uparrow = \frac{N}{2} - \frac{U}{2\mu B}$$

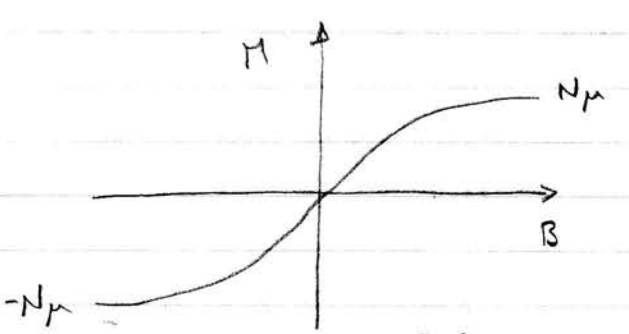
$$= \frac{k_B}{2\mu B} \left[\ln n_\uparrow + \cancel{1} - \ln(N - n_\uparrow) - \cancel{1} \right]$$

$$= \frac{k_B}{2\mu B} \ln \left(\frac{n_\uparrow}{N - n_\uparrow} \right) = \frac{k_B}{2\mu B} \ln \left(\frac{N - U/\mu B}{N + U/\mu B} \right)$$

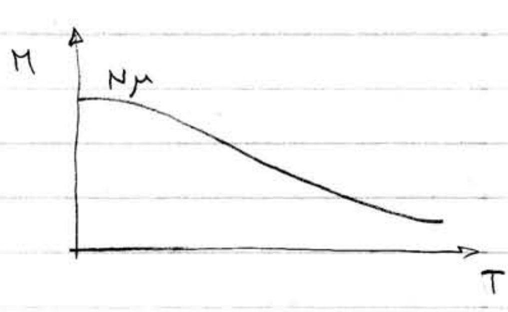
$$\therefore \quad U = -N \mu B \tanh \frac{\mu B}{k_B T}$$

Define magnetization $M = \mu(n_\uparrow - n_\downarrow) = -\frac{U}{B}$

$$M = N\mu \tanh \frac{\mu B}{k_B T}$$



T fixed



B fixed

Spins tend to align along B. At $T=0$ all spins point along B
As $T \uparrow$ more spins point opposite B

In high T limit $\frac{\mu B}{k_B T} \ll 1$

$$M \approx \frac{N\mu^2 B}{k_B T} \qquad \text{Curie's law} \qquad M \propto 1/T$$

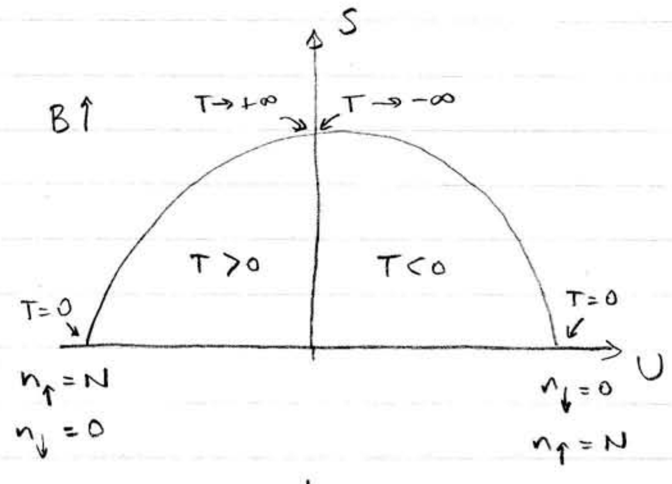
Ex: $\mu = \mu_B$ (Bohr magneton) $= \frac{eh}{4\pi m_e} = 6 \times 10^{-5}$ eV/T

Take $B = 1T$ $\quad \mu B = 6 \times 10^{-5}$ eV

$k_B T = 1/40$ eV at room temperature

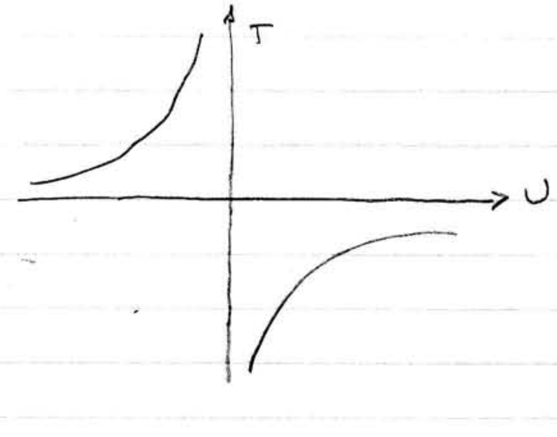
so $\frac{\mu B}{k_B T} = 2.4 \times 10^{-3} \ll 1$

What does $S(U)$ look like?



Maximum S occurs when 1/2 spins are ↑ 1/2 ↓

S = 0 both when all spins align with B (↑) and when they point opposite (↓)!



$$\frac{1}{T} = \frac{\partial S}{\partial U}$$

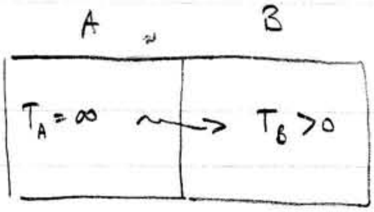
$T \to \infty$ at max S

Absolute $T < 0$ when more spins point opposite B $(n_\downarrow > n_\uparrow)$!

This is called population inversion

What does it mean for $T = \infty$?

Imagine putting the paramagnet in thermal contact with a system with finite T



$$\Delta S = \frac{\partial S_A}{\partial U_A} \Delta U_A + \frac{\partial S_B}{\partial U_B} \Delta U_B$$

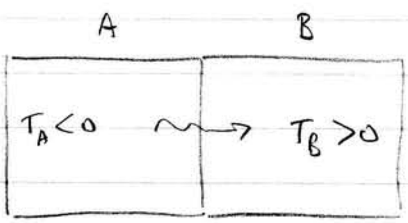
$$= \frac{1}{T_A} \Delta U_A - \frac{1}{T_B} \Delta U_A$$

$$= \Delta U_A \left(\cancelto{0}{\frac{1}{T_A}} - \frac{1}{T_B} \right) \geq 0$$

Since $T_A \to \infty$ $\Delta U_A < 0$, heat will flow $A \to B$. Makes sense

A is <u>hotter</u>

What does it mean for $T < 0$?



$$\Delta S = \Delta U_A \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \geq 0$$

$$= \Delta U_A \left(-\frac{1}{|T_A|} - \frac{1}{T_B} \right)$$

Since $T_A < 0$ $\Delta U_A < 0$, heat will flow $A \to B$.

System with negative T is <u>hotter</u> !!