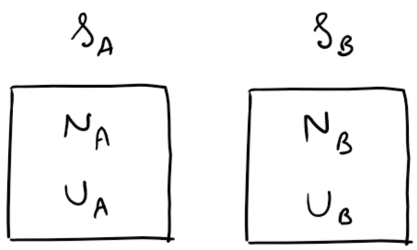
Lecture 3 – Thermal equilibrium & temperature

LAST TIME: we considered closed (or isolated) systems – no interactions with surroundings, fixed U and N

TODAY: What happens when two systems can exchange energy?
Thermal contact – two systems are brought into contact such that they interact weakly and can exchange energy (no exchange of particles, yet)

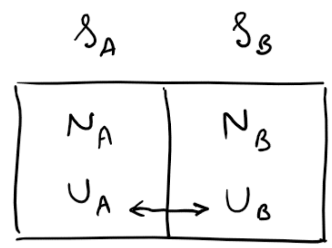
Take two systems A and B with N_A, U_A and N_B, U_B brought into thermal contact. What is the multiplicity of the combined system A + B?

Each system is closed
N_A, N_B are fixed
U_A, U_B are fixed



$$\Omega_{tot}(U_A, U_B) = \Omega_A(U_A)\Omega_B(U_B)$$

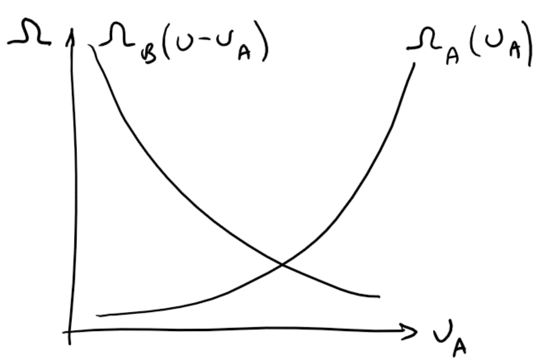
Systems are in thermal contact
N_A, N_B are fixed
U_A, U_B can vary, $U = U_A + U_B$ is fixed

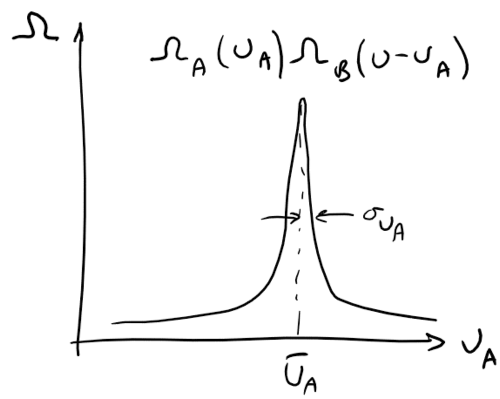


$$\Omega_{tot}(U) = \sum_{U_A} \Omega_A(U_A)\Omega_B(U - U_A)$$

What does Ω_{tot} look like for systems in thermal contact?

Take an Einstein solid as an example. $\Omega(U) \sim U^N$ is a very rapidly increasing function of U





The product $\Omega_A(U_A)\Omega_B(U - U_A)$ is very sharply peaked – peak at most likely macrostate of total combined system A + B

Question 1: Take two Einstein solids with N_A, U_A and N_B, U_B in thermal contact. At what energy is the product $\Omega_A(U_A)\Omega_B(U - U_A)$ peaked?

Hint: it's easier to consider $\ln\Omega$. If $\frac{d\Omega}{dU} = 0$, then $\frac{d\ln\Omega}{dU} = \frac{1}{\Omega}\frac{d\Omega}{dU} = 0$

$\ln\Omega_A(U_A)\Omega_B(U - U_A) = \ln\Omega_A(U_A) + \ln\Omega_B(U - U_A)$, so we're looking for energy $\bar{U}_A$ at which

$$\frac{\partial}{\partial U_A}\ln\Omega_A(U_A) + \frac{\partial}{\partial U_A}\ln\Omega_B(U - U_A) = 0$$

Since $\Omega(U) \sim U^N$ it follows that

$$\frac{N_A}{\bar{U}_A} - \frac{N_B}{U - \bar{U}_A} = 0, \quad \frac{U}{\bar{U}_A} - 1 = \frac{N_B}{N_A}, \qquad \text{so } \bar{U}_A = \frac{U}{1 + N_B/N_A} \text{ and } \bar{U}_B = \frac{U}{1 + N_A/N_B}$$

Notice that this means:

$$\frac{\bar{U}_A}{N_A} = \frac{U}{N_A + N_B} = \frac{\bar{U}_B}{N_B}$$

i.e. in the most likely macrostate, the <u>average energy per oscillator</u> in the two systems is equal. Also, if $N_A = N_B$, then $\bar{U}_A = U/2 = \bar{U}_B$.

How sharp is the multiplicity around this peak?
Look at deviations around the peak (assume for simplicity $N_A = N_B$ so $\bar{U}_A = U/2$): $U_A = \bar{U}_A + \delta U$

$$\Omega(U) = \left(\frac{eU}{N\hbar\omega}\right)^N \text{ for an Einstein solid}$$

So,

$$\begin{aligned}
\ln\Omega_A(U_A) + \ln\Omega_B(U - U_A) &= 2N + N\ln\frac{\bar{U}_A + \delta U}{N\hbar\omega} + N\ln\frac{\bar{U}_A - \delta U}{N\hbar\omega} \\
&= 2N - 2N\ln N\hbar\omega + N\ln(\bar{U}_A^2 - \delta U^2) \\
&= 2N\ln\left(\frac{e\bar{U}_A}{N\hbar\omega}\right) + N\ln\left(1 - \frac{\delta U^2}{\bar{U}_A^2}\right) \approx 2N\ln\left(\frac{e\bar{U}_A}{N\hbar\omega}\right) - \frac{N\delta U^2}{\bar{U}_A^2}
\end{aligned}$$

using $\ln(1+x) \approx x$. Exponentiating both sides

$$\Omega_A\Omega_B \approx \left(\frac{e\bar{U}_A}{N\hbar\omega}\right)^{2N} e^{-\frac{N\delta U^2}{\bar{U}_A^2}} = \left(\frac{e\bar{U}_A}{N\hbar\omega}\right)^{2N} e^{-\frac{\delta U^2}{2\sigma_{U_A}^2}}$$

This is the equation for a Gaussian peaked at $\delta U = 0$ with a half-width $\sigma_{U_A} = \bar{U}_A/\sqrt{2N}$.
The fractional width $\sigma_{U_A}/\bar{U}_A = 1/\sqrt{2N}$ is extremely small for $N >> 1$ (10^{-10} for $N \sim 10^{20}$)

So Ω_{tot} is an extremely sharp function, peaked at $U_A = \bar{U}_A$.

This is the most likely macrostate of the total system A + B, and any other macrostate is <u>extremely unlikely</u>:

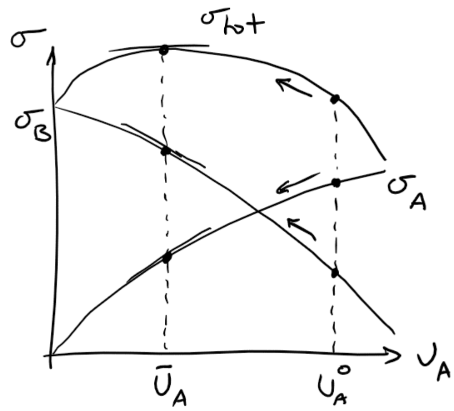
$$\Omega_{tot} = \sum_{U_A} \Omega_A(U_A)\Omega_B(U-U_A) \approx \Omega_A(\bar{U}_A)\Omega_B(U-\bar{U}_A)$$

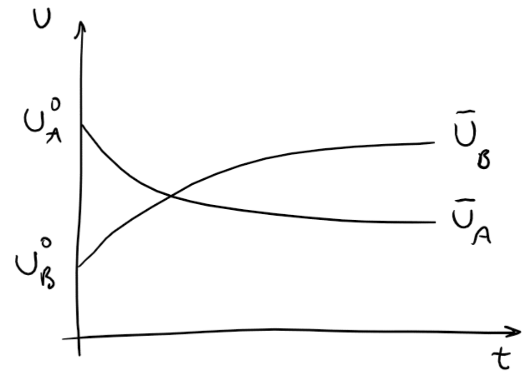
KEY CONCEPT: Thermal equilibrium

Let's look at this in terms of entropy $\sigma \equiv \ln\Omega$
Imagine two systems A + B, brought into thermal contact at t = 0

$$\sigma_{tot} = \sigma_A(U_A) + \sigma_B(U-U_A)$$

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





Initially, $\sigma_{tot} = \sigma_A(U_A^0) + \sigma_B(U-U_A^0)$. Systems evolves to $\sigma_{tot} = \sigma_A(\bar{U}_A) + \sigma_B(U-\bar{U}_A)$ where entropy is maximum and system is in likeliest macrostate – <u>2nd law of thermodynamics</u>.

In order to maximize the total entropy σ_{tot}, energy is transferred between systems until

$$\frac{\partial \sigma_{tot}}{\partial U_A} = 0 = \frac{\partial \sigma_A}{\partial U_A} + \frac{\partial \sigma_B}{\partial U_A}$$

$$= \frac{\partial \sigma_A}{\partial U_A} + \frac{\partial \sigma_B}{\partial U_B}\underbrace{\frac{\partial U_B}{\partial U_A}}_{-1}$$

so $\dfrac{\partial \sigma_A}{\partial U_A} = \dfrac{\partial \sigma_B}{\partial U_B}$. This condition is called <u>thermal equilibrium</u>.

Formal definition of <u>fundamental temperature</u>:

$$\frac{1}{\tau} \equiv \left(\frac{\partial \sigma}{\partial U}\right)_N \qquad \text{(subscript reminds us that } N \text{ is fixed)}$$

and $\tau_A = \tau_B$ at thermal equilibrium.

Note: if system A is in thermal equilibrium with systems B and C, then B and C must be in thermal equilibrium (i.e. $\tau_A = \tau_B = \tau_C$) – 0^{th} law of thermodynamics

Note: the fundamental temperature τ has units of energy because entropy σ is unitless.
Absolute temperature T in units of degrees Kelvin is defined as:

$$\tau \equiv k_B T$$

where $k_B = 1.381 \times 10^{-23}$ J/K is the Boltzmann constant.
Conventional definition of entropy:

$$S \equiv k_B \ln \Omega, \qquad \text{such that } \frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_N$$

K & K use σ and τ, but we will use the conventional S and T for the rest of the semester

To summarize:

- In this example $T_A > T_B$ initially because $\left.\frac{\partial S_A}{\partial U_A}\right|_{U_A^0} < \left.\frac{\partial S_B}{\partial U_B}\right|_{U_A^0}$.
- The total system A + B spontaneously evolves to maximize S_{tot} by transferring energy. Because $\left.\frac{\partial S_A}{\partial U_A}\right|_{U_A^0} < \left.\frac{\partial S_B}{\partial U_B}\right|_{U_A^0}$, S_{tot} increases by U_A decreasing and U_B increasing, i.e. energy flows from the "hotter" system A to the "colder" system B. Thermal equilibrium is reached when $T_A = T_B$ (notice that $\bar{U}_A$ is not necessarily equal to $\bar{U}_B$, though)
- A "hot" object has a tendency to give up its energy to a "cold" object because $|\Delta S_{hot}| < \Delta S_{cold}$
- The individual entropies S_A and S_B can decrease, so long as the total entropy S_{tot} increases to its maximum. Here, S_A, T_A, and U_A decrease, S_B, T_B, and U_B increase.

How much energy is transferred in reaching thermal equilibrium?

$$\Delta S_{tot} = \Delta S_A + \Delta S_B = \frac{\partial S_A}{\partial U_A}\Delta U_A + \frac{\partial S_B}{\partial U_B}\Delta U_B = \frac{1}{T_A}\Delta U_A + \frac{1}{T_B}\underbrace{\Delta U_B}_{-\Delta U_A}$$

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

Therefore if $T_A > T_B$ then $\Delta U_A < 0$ and $\Delta U_B > 0$ (energy flows from hot to cold).
Energy transferred is $\Delta U_A = T_A \Delta S_A = -T_B \Delta S_B = -\Delta U_B$. This form of energy transfer is called heat Q – 1^{st} law of thermodynamics

Question 2: Relate the energy *U* of an Einstein solid to its temperature *T* using the definition of temperature

$\Omega \sim U^N$ so $S = Nk_B \ln U +$ terms independent of U

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_N = Nk_B \frac{\partial}{\partial U} \ln U = \frac{Nk_B}{U}$$

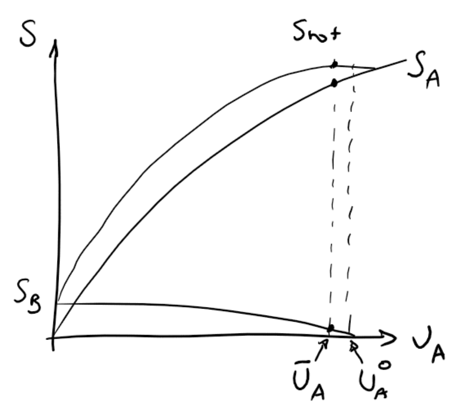
$$U = Nk_B T$$

This result will be re-derived later in the semester using the <u>equipartition theorem</u>. Note that it says that the energy per oscillator is on average $k_B T$. Two Einstein solids in thermal equilibrium with each other have the same average energy per oscillator.

As we discussed in Lect. 2, many systems have multiplicity $\Omega \sim U^f$ with $f \propto N$, so $S \sim fk_B \ln U$ and $k_B T \sim U/f$. As U increases, so does S and T.

KEY CONCEPT: <u>Heat bath</u> or <u>heat reservoir</u>

Consider now that system A is much, much larger than system B: $U_A \gg U_B$, $N_A \gg N_B$



Assuming system A is such that $\Omega \sim U^f$ with $f \propto N$, then can also expect $S_A \gg S_B$.

Initially, systems have energy U_A^0 and U_B^0

Putting system A + B in thermal contact, energy (or heat) transferred $\Delta U_A = -\Delta U_B$ is such that:

$$|\Delta U_A| \ll U_A^0$$

How much does the entropy of A change in reaching equilibrium?

$$S_A(\bar{U}_A = U_A^0 + \Delta U_A) \approx S_A(U_A^0) + \left.\frac{\partial S_A}{\partial U_A}\right|_{U_A^0} \Delta U_A = S_A(U_A^0) + \frac{\Delta U_A}{T_A^0}$$

How much does the temperature of A change in reaching equilibrium?

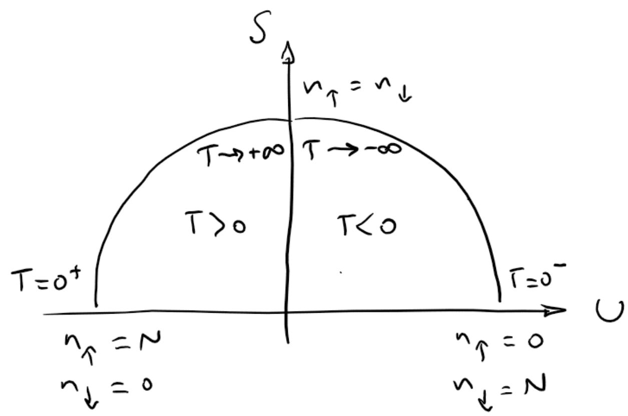
$$\left.\frac{\partial S_A}{\partial U_A}\right|_{\bar{U}_A} \approx \left.\frac{\partial S_A}{\partial U_A}\right|_{U_A^0} + \left.\frac{\partial^2 S_A}{\partial {U_A}^2}\right|_{U_A^0} \Delta U_A$$

If $\Omega_A \sim U_A^f$, then $S_A = fk_B \ln U_A + \text{const.}$, and $\dfrac{1}{T_A} = \dfrac{\partial S_A}{\partial U_A} = \dfrac{fk_B}{U_A}$ and $\dfrac{\partial^2 S_A}{\partial {U_A}^2} = -\dfrac{fk_B}{U_A^2} = -\dfrac{1}{T_A U_A}$, so

$$\frac{1}{T_A} = \frac{1}{T_A^0} - \frac{1}{T_A^0 U_A^0}\Delta U_A = \frac{1}{T_A^0}\left(1 - \frac{\Delta U_A}{U_A^0}\right) \approx \frac{1}{T_A^0}$$

i.e. the reservoir temperature does not change appreciably.
Reservoir – exchanges heat with system B, sets its temperature: $T_B = T_A \approx T_A^0$

What about systems for which Ω is not $\sim U^f$ – e.g. a paramagnet?



Entropy of N independent spin-½ particles in B-field pointing along z:

when $n_\downarrow = n_\uparrow$, absolute $T = \infty$,
when $n_\downarrow > n_\uparrow$, absolute $T < 0$!

What does it mean for $T = \infty$? Imagine putting a paramagnet with $T_A = \infty$ in thermal contact with a system at finite T_B.

$$\Delta S_{tot} = \Delta S_A + \Delta S_B = \frac{\partial S_A}{\partial U_A}\Delta U_A + \frac{\partial S_B}{\partial U_B}\Delta U_B$$
$$= \left(\cancel{\frac{1}{T_A}} - \frac{1}{T_B}\right)\Delta U_A = -\frac{1}{T_B}\Delta U_A \geq 0$$

Since $T_A = \infty$, then $\Delta U_A < 0$ and energy flows from A to B (makes sense, A is hotter).

Question 3: Now imagine putting a paramagnet with $T_A < 0$ in thermal contact with a system at finite $T_B > 0$. Which way does energy flow?

The change in entropy is

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

Since $T_A < 0$, then $\Delta U_A < 0$ and energy still flows from A to B
The system with $T < 0$ is "hotter"!
