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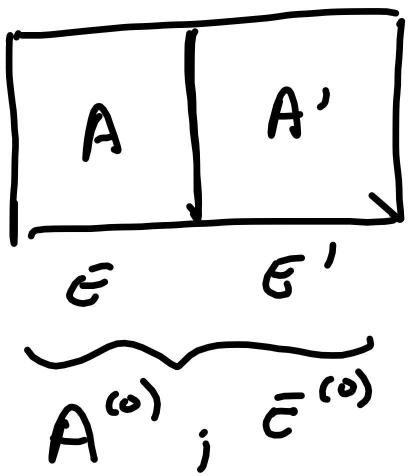
Last time:



Energy could be exchanged

$$E^{(0)} = E + E'$$

We found that

$$P(E) = C\,\Omega(E)\,\Omega(E^{(0)} - E)$$

$P(E)$ has a large peak at $E = \tilde{E}$.

Order of magnitude of the peak in $P(E)$:

If $\Omega \propto E^f$ and $\Omega' \propto E'^{f'}$

and $P(E) = C\,\Omega(E)\,\Omega'(E')$ (1)

$\ln P(E) = \ln C + \ln \Omega + \ln \Omega' =$ $E' = E^{(0)} - E$

$\approx \ln C + f \ln E + f' \ln E' =$

$= f \ln E + f' \ln (E^{(0)} - E) + \text{constant}.$

$\ln P(E)$ has a single maximum at a value $E = \tilde{E}$.

Let's find $\tilde{E}$:

$$0 = \frac{\partial \ln P}{\partial E}\bigg|_{\tilde{E}} = \frac{1}{P}\frac{\partial P}{\partial E}\bigg|_{\tilde{E}} .$$

$$E' = E^{(0)} - E \quad (2)$$

$$\frac{\partial \ln \Omega(E)}{\partial E}\bigg|_{\tilde{E}} + \frac{\partial \ln \Omega'(E')}{\partial E'} \underbrace{\frac{\partial E'}{\partial E}}_{-1}\bigg|_{\tilde{E}} = 0$$

Then

$$\frac{\partial \ln \Omega}{\partial E}\bigg|_{\tilde{E}} = \frac{\partial \ln \Omega'}{\partial E'}\bigg|_{\tilde{E}}$$

Define:

$$\beta = \frac{\partial \ln \Omega}{\partial E}$$

$$\boxed{\beta = \beta'}$$

$$\beta(E) = \frac{\partial \ln \Omega(E)}{\partial E} \quad (3)$$ has units of E^{-1}

$[\beta] = E^{-1}$ (units)

Define:

$$kT = \frac{1}{\beta}$$

T is dimensionless

$[k] = E$ (units of energy).

(we will see that k is Boltzmann's constant).

$$T = \frac{1}{k\beta} \overset{(3)}{=} \frac{1}{k \frac{\partial \ln \Omega}{\partial E}} = \frac{1}{\frac{\partial k \ln \Omega}{\partial E}} \overset{(4)}{=} \frac{1}{\frac{\partial S}{\partial E}}$$

Define:

$S = k \ln \Omega$ entropy (4)

Then

$$k\beta = \frac{\partial S}{\partial \bar{E}} \quad \text{or} \quad \boxed{\frac{\partial S}{\partial \bar{E}} = \frac{1}{T}}$$

already found in thermodynamics if T is the temperature.

We see that the equilibrium condition between A and A' means that:

- $P(\bar{E})$ is maximum.
- $P(\bar{E})$ max means that $S + S'$ is a maximum.
- It also means that $T = T'$. Both systems end up with the same temperature.

Since at equilibrium $S+S'$ is a maximum we know that:

$$S(E_f) + S'(E_f') \geqslant S(E_i) + S'(E_i')$$

or

$$S_f + S_f' \geqslant S_i + S_i'$$

$$S_f - S_i \geqslant S_i' - S_f'$$

$$\Delta S \geqslant -\Delta S'$$

$$\boxed{\Delta S + \Delta S' \geqslant 0}$$

and since $E_f + E_f' = E_i + E_i'$ Ⓐ $E^{(0)}$ is conserved

All the energy change is related to heat (the wall is fixed):

$$\left.\begin{aligned} Q &= \bar{E}_f - \bar{E}_i \\ Q' &= \bar{E}'_f - \bar{E}'_i \end{aligned}\right\} \text{ since } W = 0 \qquad \text{(B)}$$

$Q + Q' = 0$ using (A) and (B).

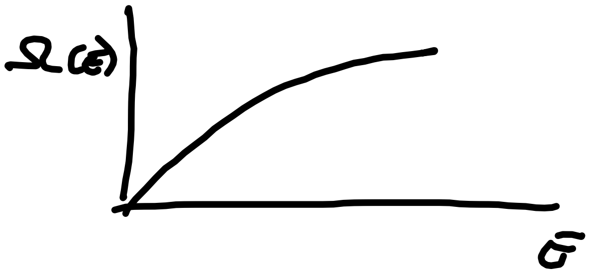
or $Q = -Q'$ the heat absorbed (or released) by A is equal to minus the heat released (or absorbed) by A'.

The system that releases heat is called warmer. The one that absorbs it is called colder.

Heat flows from the warmer to the colder system until $T = T'$.

Notice:

$$\beta = \frac{1}{kT} = \frac{1}{k}\frac{\partial S}{\partial E} = \frac{1}{k}\frac{\partial k \ln \Omega}{\partial E} = \frac{\partial \ln \Omega}{\partial E}$$



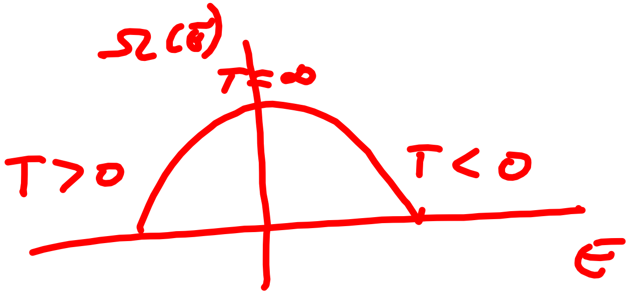
$$\beta = \frac{\partial \ln \Omega}{\partial E} > 0$$

$\therefore \beta > 0$ or $T > 0$.

In general T is positive for all systems since $\Omega(E)$ increases with E.

Exceptions

Spin systems.



$$\beta = \frac{\partial \ln \Omega}{\partial E}$$ is not always positive.

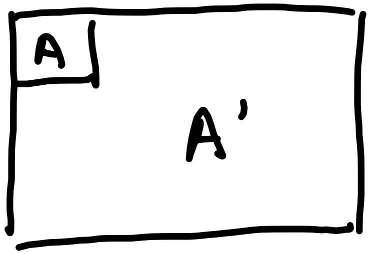
If $\Omega(E) \propto E^f \Rightarrow \ln \Omega(E) \approx f \ln E + c$

$$\therefore \quad \beta = \frac{\partial \ln \Omega}{\partial E} = \frac{f}{E} \quad (1) \qquad \therefore \quad kT \approx \frac{\bar{E}}{f}$$

(mean energy per degree of freedom)

—— x ——

Heat reservoir!



A and A' exchange energy but $\Omega' \gg \Omega$.

$\Delta E' = Q'$ $\quad Q' \approx E$ $\quad \frac{f'}{E'} = \beta'$ (1)

$$\left| \frac{\partial \beta'}{\partial E'} \Delta E' \right| = \left| \frac{\partial \beta'}{\partial E'} Q' \right| \overset{(1)}{\approx} \left| -\frac{f'}{E'^2} E \right| = \left| \beta' \frac{E}{E'} \right| \ll \beta'$$

(2)

From ② we see that A' can be consider a heat reservoir for A if $\frac{\bar{E}}{E'} \ll 1$. Because this means that β' remains approximately unchanged when A and A' get into contact with each other.

- Notice that $Q' = \Delta E'$ then

$$\underbrace{\ln \Omega'(E' + \underbrace{Q'}_{\Delta E'}) - \ln \Omega'(E')}_{\Delta S'/k} = \underbrace{\frac{\partial \ln \Omega'}{\partial E'}\Bigg|_{\bar{E}'}}_{\beta'} Q' + \frac{1}{2} \underbrace{\frac{\partial^2 \ln \Omega'}{\partial E'^2}\Bigg|_{\bar{E}'}}_{\frac{\partial \beta'}{\partial E'} \simeq 0} Q'^2 + \cdots$$

$\frac{\partial \beta'}{\partial E'} \simeq 0$ since $\beta' \simeq$ constant.

Then

$$\frac{\Delta S'}{k} = \beta' Q' = \frac{Q'}{kT'}$$

or

$$\boxed{\Delta S' = \frac{Q'}{T'}}$$

for a heat reservoir (known from thermodynamics).

For any system that absorbs any infinitesimal amount of heat $đQ$ we obtain that:

$$dS = \frac{đQ}{T}$$

Notice that $đQ$ is not an exact differential (unless $đW = 0$) but $\frac{đQ}{T}$ is an exact differential.

Sharpness of $P(E)$ is given by

$$\frac{\Delta^* E}{\bar{E}} \approx \frac{1}{\sqrt{f}} \approx 10^{-12} \quad \text{if } f \sim 10^{23}$$

(see section 3.7 for derivation).

Thermodynamic laws and statistics:

- Zeroth law: If 2 systems are in thermal equilibrium with a third system they must be in thermal equilibrium with each other.

Since if $\beta = \beta'$ the two systems are already in equilibrium and have the same temperature.

- First law: A macrostate of a system is characterized by $\bar{E}$ (internal energy) so that:

$\bar{E}$: constant if the system is isolated,

or

$\Delta \bar{E} = -W + Q$ change in $\bar{E}$ when a system is allowed to interact.

work done by the system due to change in external parameters.

heat absorbed by the system.

Conservation of energy.

- Second law: $S = k \ln \Omega$ is the entropy.

statistical definition that relates microscopic properties to macroscopic ones.

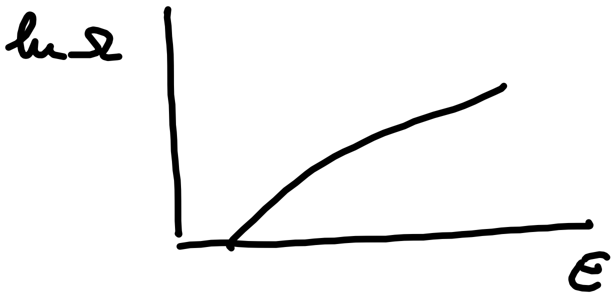
$\Delta S \geq 0$ in a thermally isolated system that changes macrostate ($\Delta Q = 0$).

If the process is quasistatic and reversible then $\Delta S = 0$. otherwise, $\Delta S > 0$.

(S always increases because Ω has to become maximum to achieve equilibrium).

$dS = \frac{đQ}{T}$ change in entropy for a non-isolated system in a quasi-static process in which $đQ$ heat is exchanged.

• Third law:



as $T \to 0^+$ $S \to S_0$

S_0 is either 0 or a very small number independent on the size of the system.

If a system as a non-degenerate ground state $\Omega = 1$ for $T \to 0$ then $\ln\Omega = 0$ and $S = 0$.

For a spin system $\Omega \sim N$ (or some small number) then for $T \to 0^+$ (small but finite T) $S \to S_0$ (small).

Statistical Calculation of Thermodynamic Properties.

- We have defined: $S = k \ln \Omega$ (1)
- Also we know that $P \propto \Omega \propto e^{S/k}$
- We defined $\beta = \frac{\partial \ln \Omega}{\partial E} = \frac{1}{kT}$.

Notice that

$$dS = \frac{dQ}{T} = \frac{1}{T}\Big(d\bar{E} + \underbrace{\sum_{\alpha=1}^{n} \bar{X}_\alpha \, d\bar{x}_\alpha}_{dW \text{ (generalized)}} \Big)$$

$$\therefore \left.\frac{\partial S}{\partial \bar{x}_\alpha}\right|_{\bar{E}} = \frac{1}{T} \bar{X}_\alpha \quad \text{Then} \quad \bar{X}_\alpha = T \left.\frac{\partial S}{\partial \bar{x}_\alpha}\right|_{\bar{E}} \overset{(1)}{=} T \frac{d(k \ln \Omega)}{d\bar{x}_\alpha}$$

Then

$$\bar{X}_\alpha = kT \frac{\partial \ln \Omega}{\partial x_\alpha} = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial x_\alpha}$$

If $x_\alpha = V$ then

$$\bar{X}_\alpha = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial V} = \bar{p}.$$