

4. The Second Law of Thermodynamics

The first law states that energy is conserved in any process. The total energy of an isolated system is constant. No change in total energy!

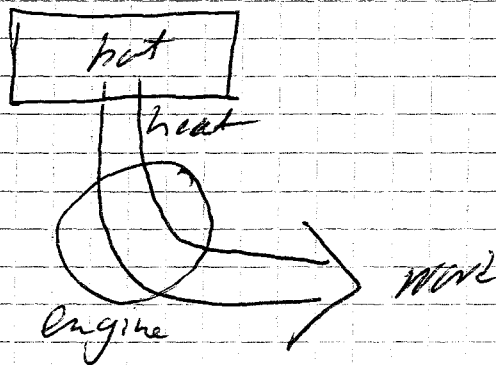
Second law determines the spontaneous direction of a change.

The Second Law:

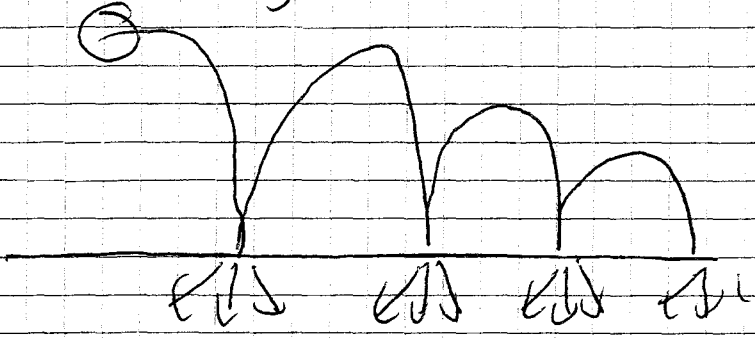
No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work!

not possible:

(i)



bouncing ball:



heat no heat flow back into the ball!
thermal cannot be directed back into the ball

spontaneous change:

the direction of change that leads to more disorderly dispersal of the total energy of the isolated system! \Rightarrow less information

\Rightarrow more possible

states or configurations

\Rightarrow self assembly is not possible in an isolated system!

\Rightarrow Entropy S

first law uses the internal energy to identify permissible changes; the second law uses the entropy to identify the spontaneous changes among those permissible changes

The entropy of an isolated system in the course of a spontaneous change:

$$\Delta S_{tot} > 0$$

thermodynamic definition:

$$dS = \frac{dq_{rev}}{T}$$

$$\Delta S = \int \frac{dq_{rev}}{T}$$

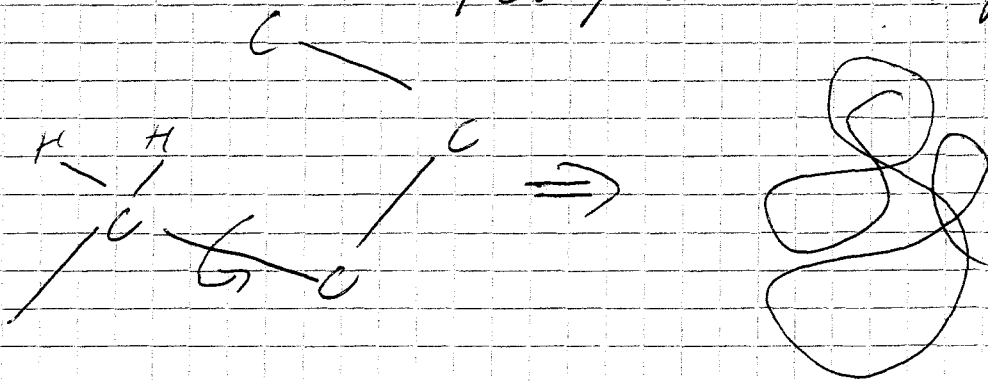
Work does not
bring disorder

Molecular interpretation

1) The molecules in a system at high temperature are highly disorganized. A small additional transfer of energy will result in a relatively small additional disorder. In contrast, the molecules in a system at low temperature have access to far fewer energy states and the same quantity of heat will have a pronounced effect.

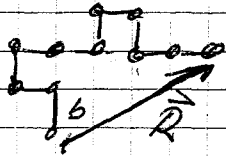
2) Entropy of a flexible polymer chain

(Doi, Introduction to Polymer Physics)



⇒ polymer chain performs a random walk!
since bending costs no energy

N monomers = N steps



end-to-end vector

probability distribution that polymer end being at \vec{R} :

$$P(\vec{R}, N) = \frac{1}{Z} \sum_{i=1}^Z P(\vec{R} - \vec{b}_i, N-1)$$

\uparrow
 possible
 directions
 for polymer
 bond

$$N \gg 1 \quad |\vec{R}| \gg |b|$$

$$P(\vec{R} - \vec{b}_i, N-1) = P(\vec{R}, N) - \frac{\partial P}{\partial N} - \frac{\partial P}{\partial R_x} b_{ix} + \frac{1}{2} \frac{\partial^2 P}{\partial R_x \partial R_x} b_{ix} b_{ix}$$

$$\frac{1}{Z} \sum_{i=1}^Z b_{ix} = 0$$

$$\frac{1}{Z} \sum_{i=1}^Z b_{ix} b_{ix} = \frac{b^2}{3}$$

$$\Rightarrow \frac{\partial P}{\partial N} = \frac{b^2}{6} \frac{\partial^2 P}{\partial \vec{R}^2}$$

and $R = 0$ for $N = 0$

$$\Rightarrow P(\vec{R}, N) = \left(\frac{3}{2\pi N b^2} \right)^{3/2} e^{-\frac{3 \vec{R}^2}{2 N b^2}}$$

\uparrow
not normalized!

\uparrow
Gaussian distribution
as predicted by
central limit theorem

⇒ number of possibilities to achieve an end-to-end ^{distance} vector \vec{R} :

$W(\vec{R}) \approx 2^N \frac{R^2}{(2\pi N b^2)^{3/2}} e^{-\frac{3R^2}{2Nb^2}}$

↑ overall number of configurations the polymer chain can assume

⇒ entropy of the polymer chain with an end-to-end distance R :

$S_{chain} = -k_B \ln W(\vec{R})$

⇒ thermal energy stored: $-k_B T \ln W(\vec{R})$

⇒ total energy of the polymer:

$A_{chain} = -k_B T \ln W(\vec{R}) + \text{constant} = \frac{3k_B T}{2Nb^2} R^2 + \text{constant}$

⇒ tension pulling on the ends is F

$f = -\frac{\partial A_{chain}}{\partial R} = \frac{3k_B T}{Nb^2} R$

⇒ Entropic Force!