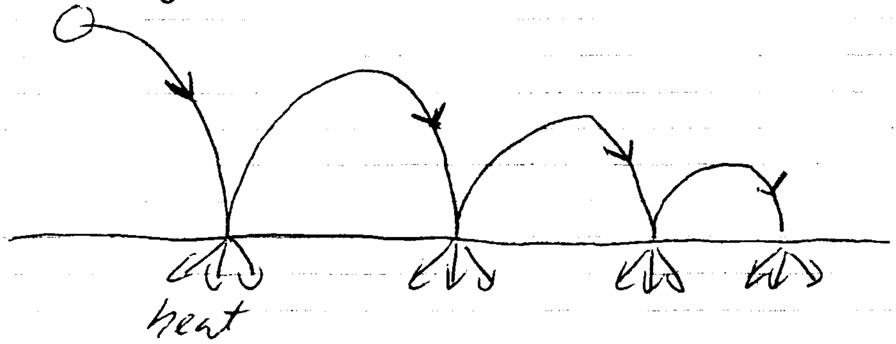
1.5. Entropy

bouncing ball:



no heat flow back into the ball!

⇒ spontaneous change:
the direction of change that leads to more disorderly disposal of the total energy of the isolated system!
⇒ less information
⇒ more possible states or configurations
⇒ selfassembly is not possible in an isolated system!

Entropy S

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

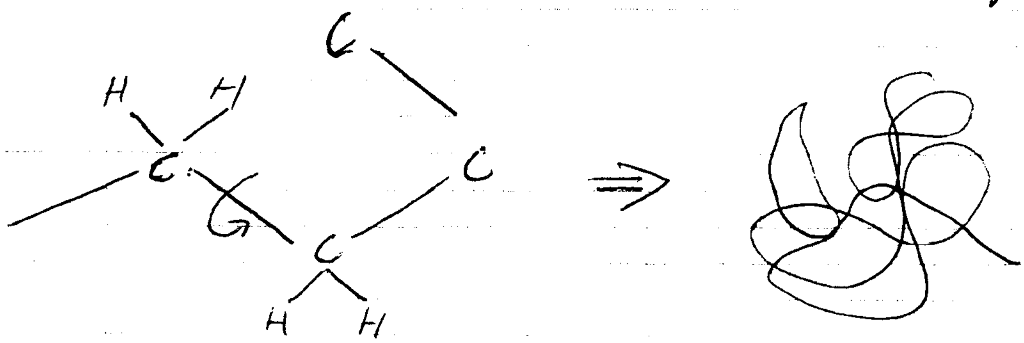
$$\Delta S_{tot} > 0$$

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 fewer energy states and the same quantity of heat will have a pronounced effect.

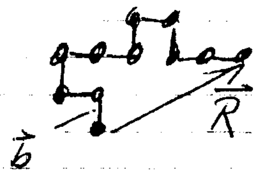
$$\boxed{dq_{rev} = T\,dS}$$

2) Entropy of a flexible polymer chain
(Doi, Introduction to Polymer Physics)



$\Rightarrow$ polymer chain performs a random walk since bending costs no energy!

N monomer = N random steps



$\vec{R}$ end-to-end vector

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

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

Z: possible directions for last polymer segment in 3 dimensions; $Z = 6$

$N \gg 1$, $|\vec{R}| \gg |b|$:

$$P(\vec{R} - \vec{b}_i, N-1) = P(\vec{R}, N) - \frac{\partial P}{\partial N} - \sum \frac{\partial P}{\partial R_\alpha} b_{i\alpha} + \sum \frac{1}{2} \frac{\partial^2 P}{\partial R_\alpha \partial R_\beta} b_{i\alpha} b_{i\beta}$$

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

$$\frac{1}{Z} \sum_{i=1}^{Z} b_{i\alpha} b_{i\beta} = \frac{\delta_{\alpha\beta} b^2}{3}$$

$$\Rightarrow \frac{\partial P}{\partial N} = \frac{b^2}{6} \frac{\partial^2 P}{\partial \vec{R}^2} \quad , \quad R = 0 \text{ for } N = 0$$

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

not normalized

Gaussian distribution as predicted by central limit theorem

$\Rightarrow$ number of possibilities to achieve an end-to-end distance $|\vec{R}|$:

$$W(R) \sim \underset{\substack{\uparrow \\ \text{overall number of configurations} \\ \text{the polymer chain can assume}}}{z^N} \overset{\text{Kugeloberfläche}}{R^2} \cdot P(\vec{R}, N) = z^N R^2 \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-\frac{3R^2}{2Nb^2}}$$

$\Rightarrow$ entropy of the polymer chain with an end-to-end distance R:

$$S_{chain} = -k_B \ln W(R) \Rightarrow \text{thermal energy stored: } -k_B T \ln W(R)$$

$\Rightarrow$ total energy of the polymer:

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

$\Rightarrow$ tension pulling on the ends is

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

$\Rightarrow$ Entropic force!