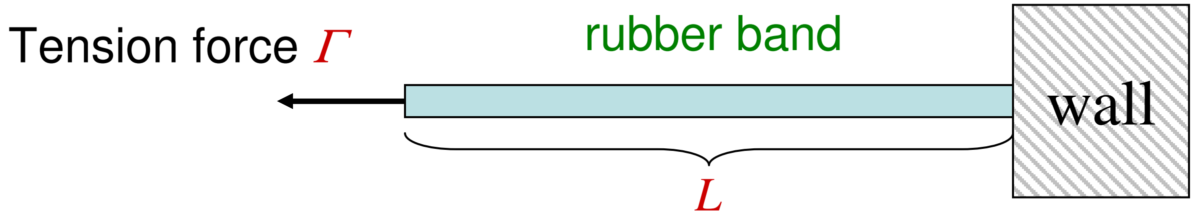
Rubber band or Polymer

This example will show spectacular macroscopic manifestations of entropy – *elasticity of an ideal rubber band is not due to "elastic energy" but is due to entropy!*



Let us chose the extensive coordinates of the system:

- Internal energy U, is always a coordinate
- Length of the rubber band L

The fundamental relation will have a form: $S(U,L)$

If we are not going to bend or twist the rubber band, we have enough coordinates to find the equilibrium state of the rubber band.

Notes

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Experimental observations:

1. Energy of the rubber band *in equilibrium with the environment* is independent on the length of the rubber band and is proportional to temperature:

$$U = cL_0T$$

- first experimental "equation of state"

where L_0 is the equilibrium length (constant)

2. Tension Γ is proportional to change in length:

$$\Gamma = f(T)\frac{(L - L_0)}{L_0}$$

- second experimental "equation of state"

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The differential form of the fundamental relation is:

$$dS = \frac{1}{T}dU - \frac{\Gamma}{T}dL$$

Since mixed second partial derivatives of S must be equal:

$$\frac{\partial}{\partial L}\left(\frac{1}{T}\right)_U = \frac{\partial}{\partial U}\left(-\frac{\Gamma}{T}\right)_L$$

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Differentiability condition:

$$\frac{\partial}{\partial L}\left(\frac{1}{T}\right)_U = \frac{\partial}{\partial U}\left(-\frac{\Gamma}{T}\right)_L$$

Equations of state:

$$\frac{1}{T} = \frac{cL_0}{U} \qquad -\frac{\Gamma}{T} = -\frac{cf(T)}{U}(L-L_0)$$

$$\frac{\partial}{\partial L}\left(\frac{1}{T}\right)_U = \frac{\partial}{\partial L}\left(\frac{cL_0}{U}\right)_U = 0 \quad \Rightarrow \quad \frac{\partial}{\partial U}\left(-\frac{\Gamma}{T}\right)_L = \frac{\partial}{\partial U}\left(-\frac{cf(T)}{U}(L-L_0)\right)_L = 0$$

$$\Rightarrow \quad \frac{\partial}{\partial U}\left(\frac{f(T)}{U}\right) = 0 \quad \Rightarrow \quad f(T) = \frac{B}{L_0}U$$

where B is a constant

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Now we can substitute the equations of state into the differential for dS:

$$dS = \frac{1}{T}dU - \frac{\Gamma}{T}dL \quad \Rightarrow \quad dS = \frac{cL_0}{U}dU - cB\frac{(L - L_0)}{L_0}dL$$

Integrating, we obtain:

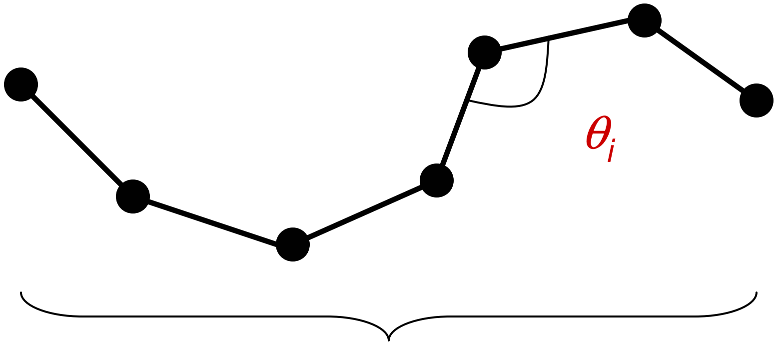
$$\boxed{S = cL_0 \ln(U) - \frac{cB}{2}\frac{(L - L_0)^2}{L_0} + const}$$

We see that entropy decreases with increasing length of the rubber band (polymer chain). Therefore, the tendency of the rubber band to shrink is driven not by minimizing elastic energy (in our model there is no elastic energy) but by maximizing entropy

Polymer : microscopic model

A model polymer consists of monomers that are connected by rigid rods. The monomers are can rotate with respect to each other at zero energy cost. This is why the energy does not depend on the macroscopic length of the polymer.

N = 7 monomers



U does not depend on θ_i

L – macroscopic length of a polymer chain

Notes

Polymer : microscopic model

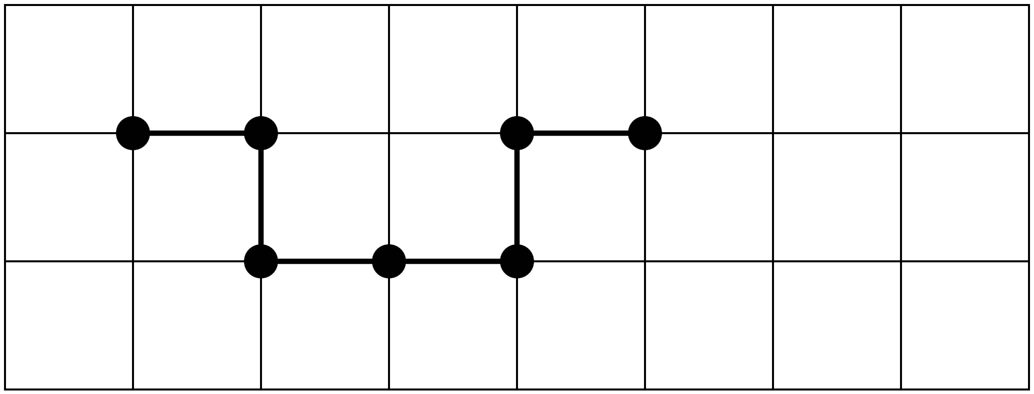
We will examine a toy model of 2D polymer where monomers sit on a square lattice

Number of monomers, N, is fixed

N = 7

Polymer length, L,
is not constrained

L = 4

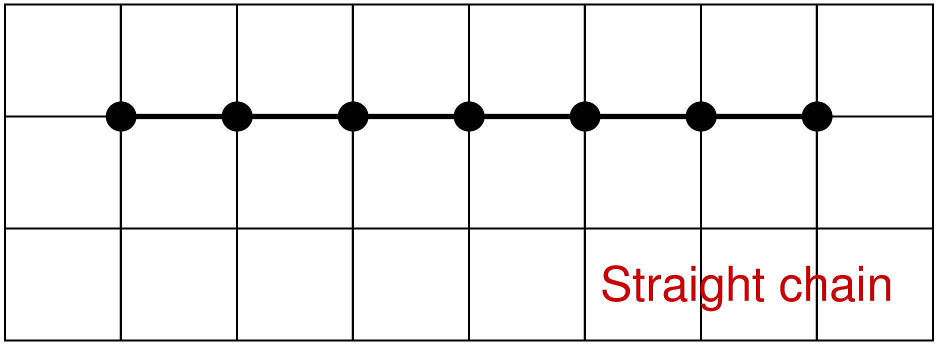


Notes

Polymer: microscopic model

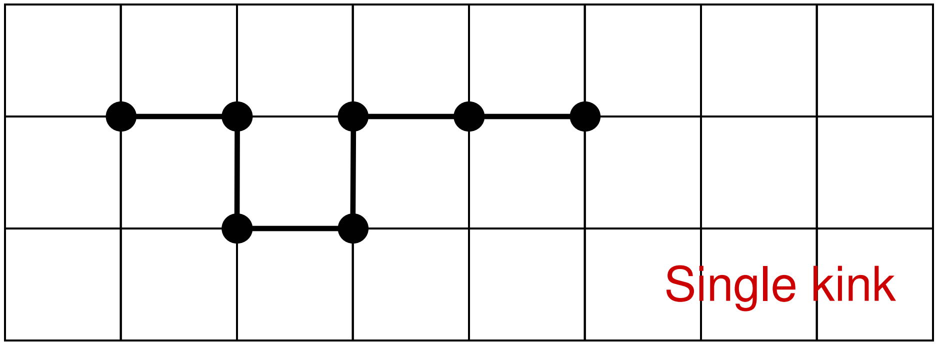
L = 6

Single microstate



L = 4

Number of microstates (assuming monomers cannot occupy the same volume):
8+6+4+2 = 20



These states have the same energy

The number of microstates rises dramatically with decreasing length, so the entropy increases with decreasing length. State with L = 0 has the highest entropy.

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Let us check that the fundamental relation we derived indeed satisfies the Euler equation:

$$\frac{1}{T} = \frac{cL_0}{U} \qquad -\frac{\Gamma}{T} = -cB\frac{(L-L_0)}{L_0} \qquad \Longrightarrow \qquad S = \frac{1}{T}U - \frac{\Gamma}{T}(L-L_0) - \frac{\mu}{T}L_0$$

(for simplicity we assume that unit length of the rubber band is one mole)

Note that is it important to keep the chemical potential term in the Euler equation even though we are not changing the mole number of rubber in this problem. You get a wrong answer if you set the chemical potential to zero!

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Euler equation $$S = \frac{1}{T}U - \frac{\Gamma}{T}(L - L_0) - \frac{\mu}{T}L_0$$

To obtain the value of μ/T, we can use the Gibbs-Duhem relation:

$$Ud\left(\frac{1}{T}\right) - (L - L_0)d\left(\frac{\Gamma}{T}\right) - L_0 d\left(\frac{\mu}{T}\right) = 0$$

Dividing by L_0 and using the equations of state: $$\frac{1}{T} = \frac{cL_0}{U} \qquad -\frac{\Gamma}{T} = -cB\frac{(L - L_0)}{L_0}$$

$$cUd\left(\frac{1}{U}\right) - \frac{cB(L - L_0)}{L_0^2}d(L - L_0) = d\left(\frac{\mu}{T}\right)$$

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$$cUd\left(\frac{1}{U}\right)-\frac{cB\left(L-L_0\right)}{L_0^2}d\left(L-L_0\right)=d\left(\frac{\mu}{T}\right)$$

$$\Downarrow$$

$$-cd\ln\left(U\right)-\frac{cB}{2L_0^2}d\left(L-L_0\right)^2=d\left(\frac{\mu}{T}\right)$$

Integrating, we obtain: $$-c\ln\left(U\right)-\frac{cB}{2L_0^2}\left(L-L_0\right)^2+const=\frac{\mu}{T}$$

So, the chemical potential of a rubber band is not zero!

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Substituting T, Γ and μ into the Euler equation: $S = \frac{1}{T}U - \frac{\Gamma}{T}(L - L_0) - \frac{\mu}{T}L_0$

$$\frac{1}{T} = \frac{cL_0}{U} \qquad -\frac{\Gamma}{T} = -cB\frac{(L - L_0)}{L_0} \qquad \frac{\mu}{T} = -c\ln(U) - \frac{cB}{2L_0^2}(L - L_0)^2 + const$$

We obtain: $S = \frac{cL_0}{U}U - \frac{cB}{L_0}(L - L_0)^2 + cL_0\ln(U) + \frac{cB}{2L_0}(L - L_0)^2 - const$

$S = cL_0\ln(U) - \frac{cB}{2L_0}(L - L_0)^2 - const$ This expression is identical to the one we obtained by integrating the differential of dS.

Notes