Lecture 18

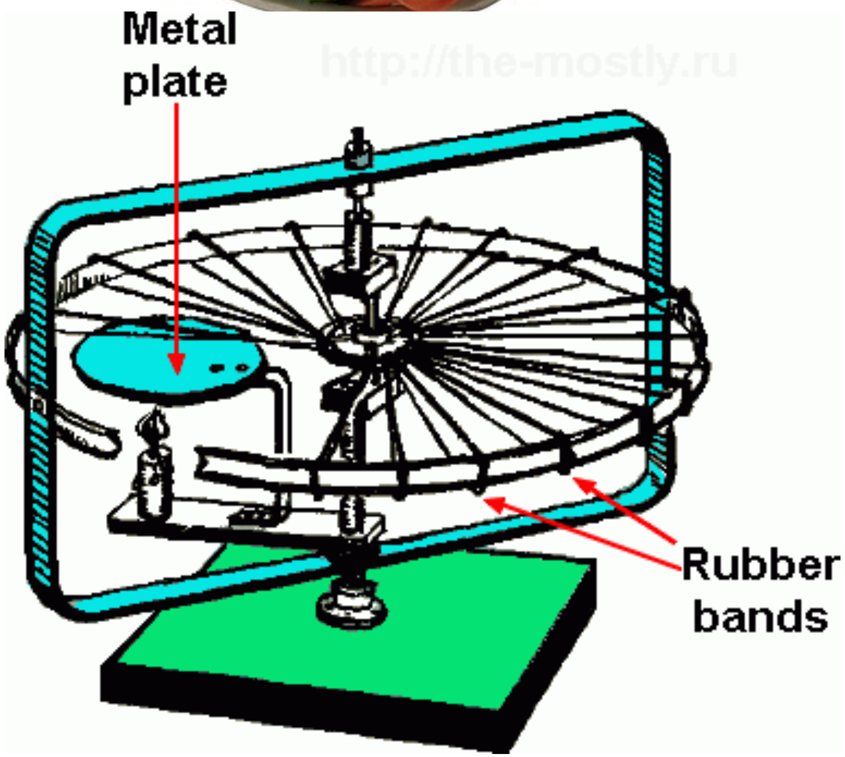
Stretching polymers and proteins

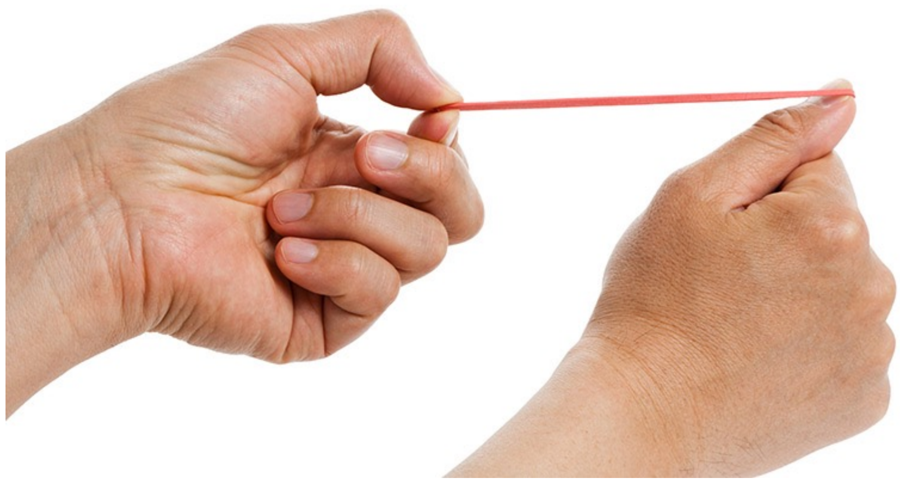
Thermodynamics of rubber bands

Chain molecules tangled up

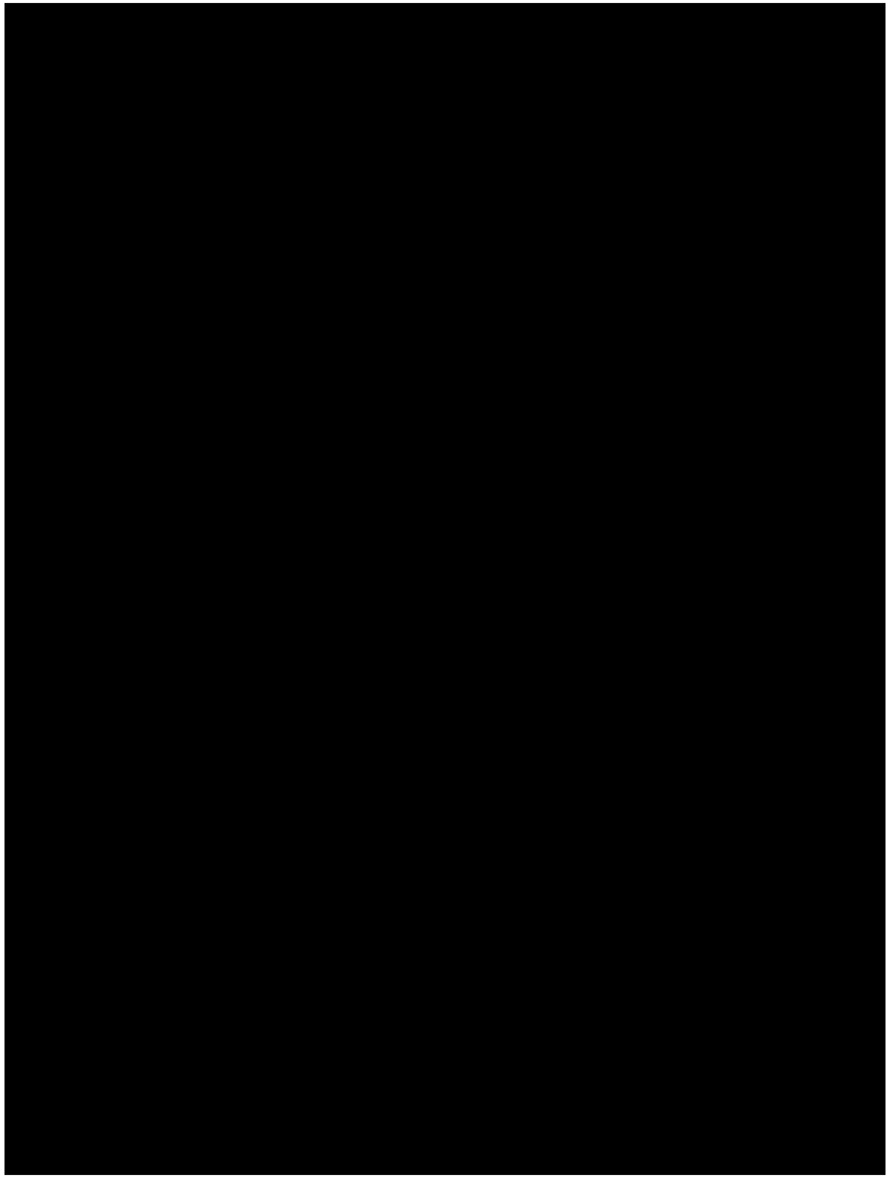
Chain molecules untangling

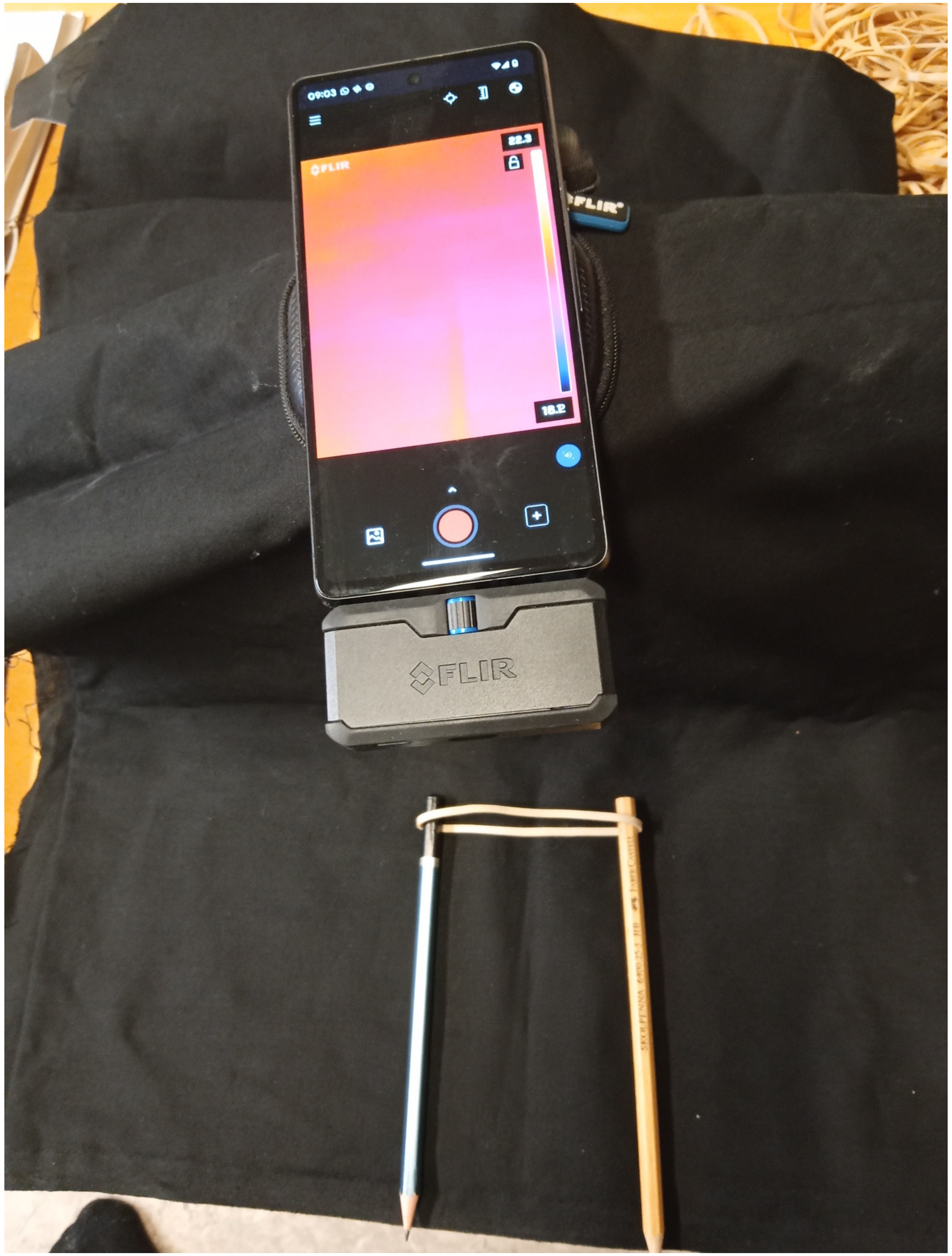
Chain molecules completely untangled



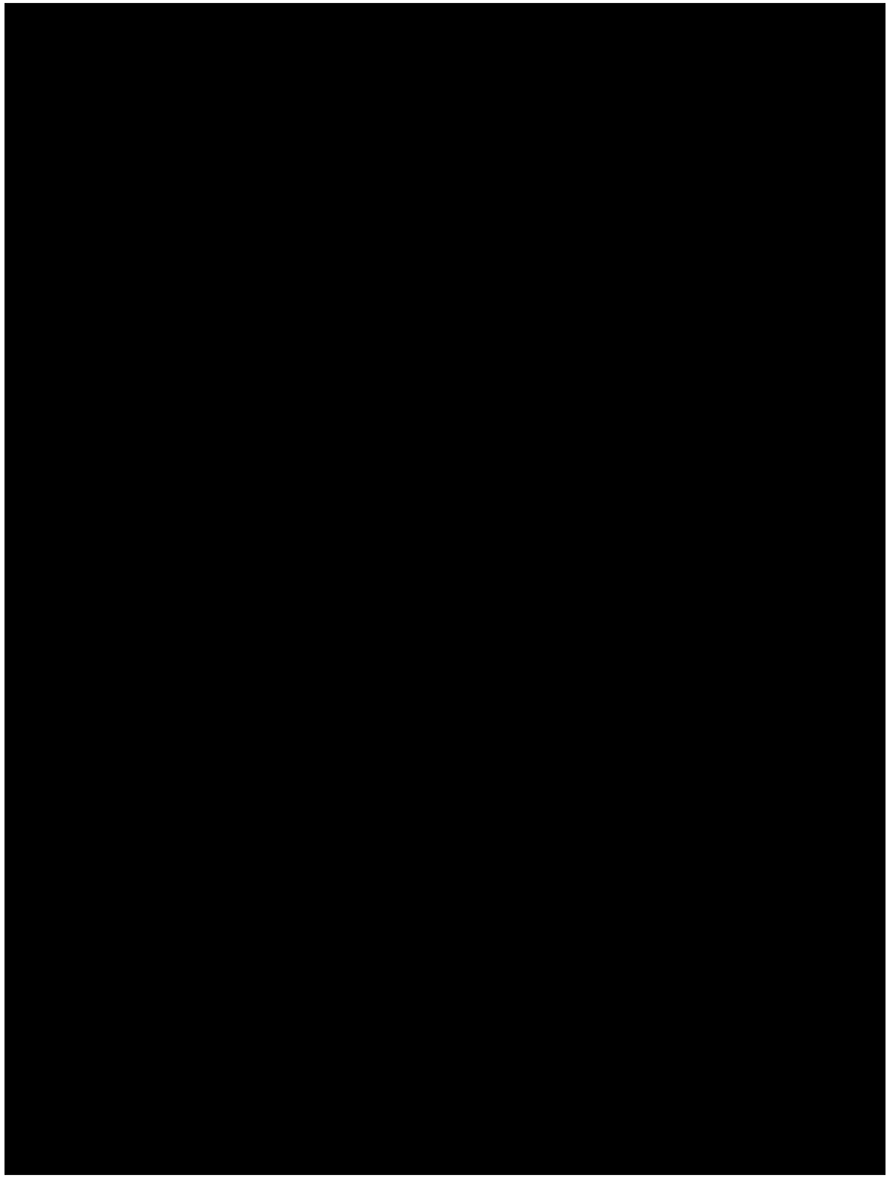


Rubber band thermodynamics with IR camera





Rubber band thermodynamics with IR camera



Observations:

1. when stretched: the rubber band heats above ambient temp.
2. when kept stretched: the rubber band goes to ambient temp.
3. when “unstretched”: the rubber band cools below ambient temp.
4. when left relaxed: the rubber band goes to ambient temp.

Thermodynamics:

- What is the system?
- What variables are of interest?
- Can we make a graph?

Rubber band thermodynamics with IR camera

[redacted]

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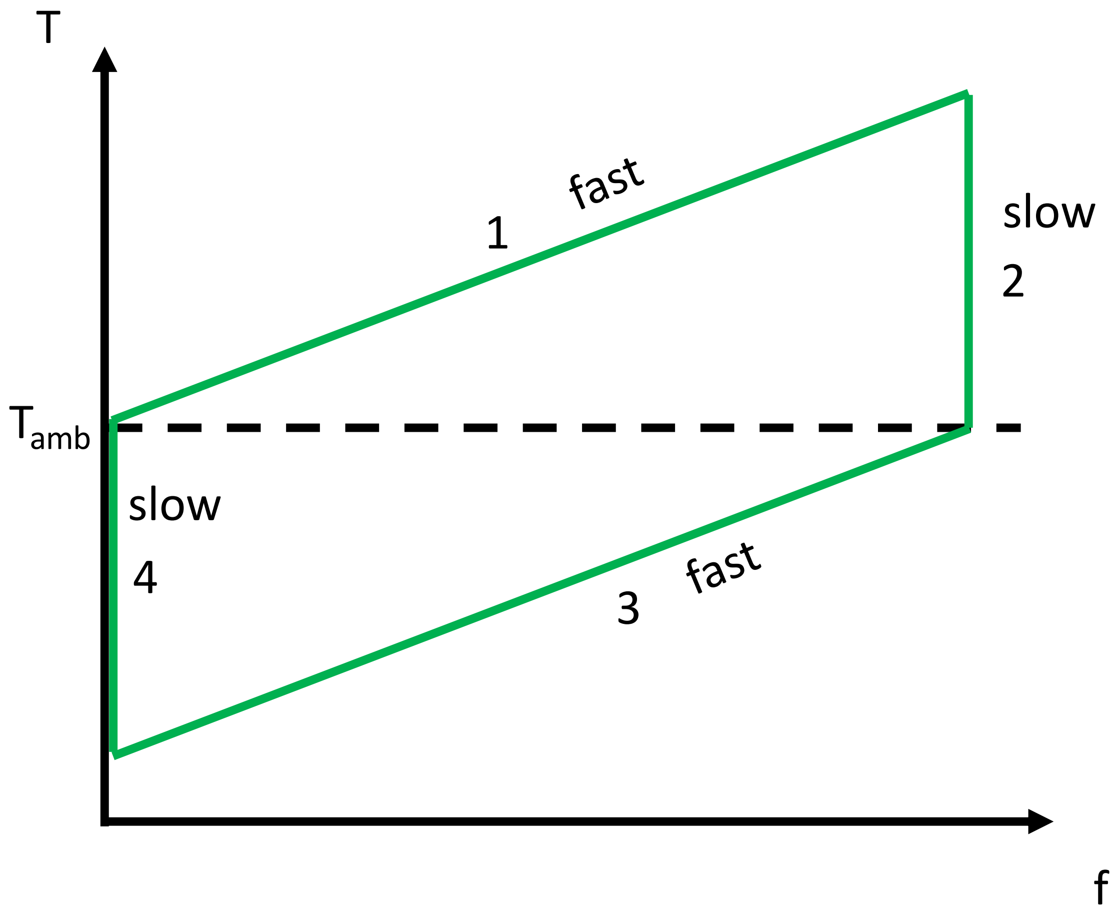
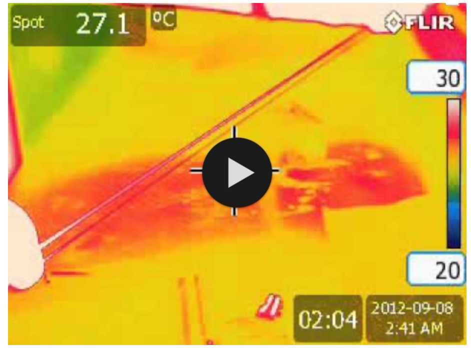


Question: What kind of processes occur during 1, 2, 3 & 4?

Rubber band thermodynamics with IR camera



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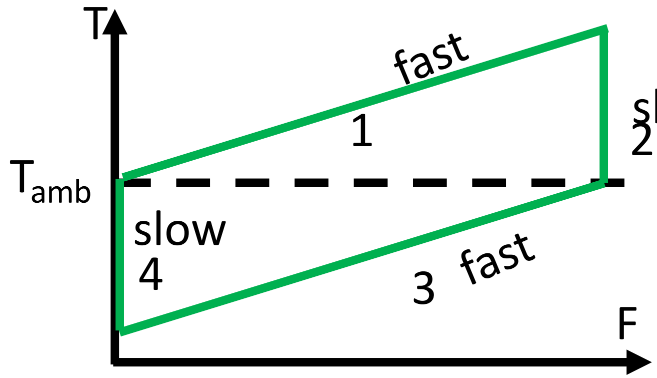

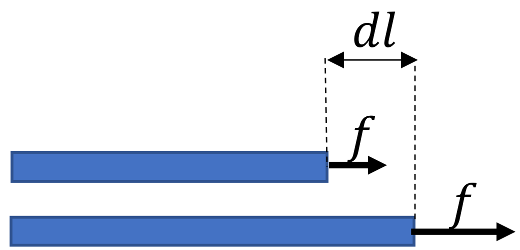

Question: What kind of processes occur during 1, 2, 3 & 4?

1,3:

- $\Delta f \neq 0$ => work W $\neq 0$
- Fast => no time for heat, adiabatic: $Q = 0$

2,4:

- $\Delta f = 0$ => work W $= 0$
- Heating or cooling only: $Q \neq 0$

Do we know some equations for this?

1. $W = -PdV = fdl > 0$
   - f changes→ $W = \int_{l_1}^{l_2} f dl$
   - 1st law: $\Delta U = Q + W$
   - $Q = 0$
   - → $\Delta U = \int_{l_1}^{l_2} f dl > 0$
   - → $\Delta T \propto \Delta U > 0$ (as observed!)

Rubber band thermodynamics with IR camera

Observations:

1. when stretched the rubber band heats above ambient temp.
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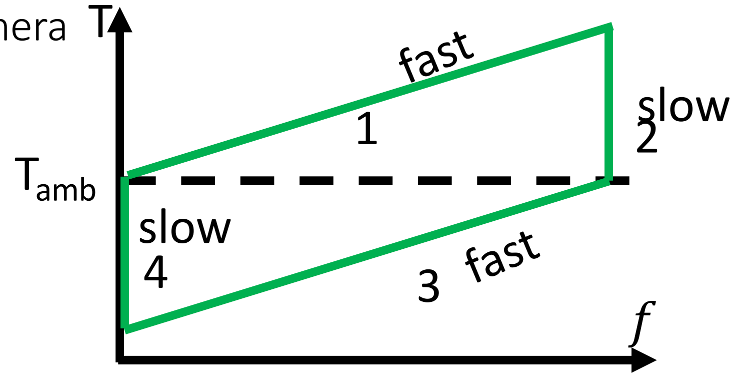
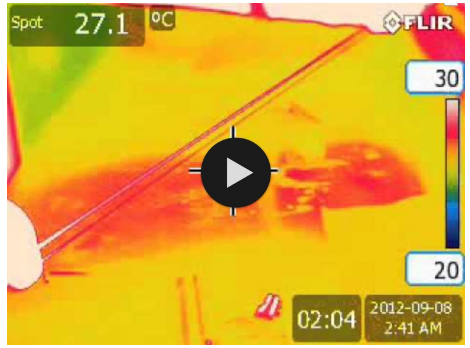
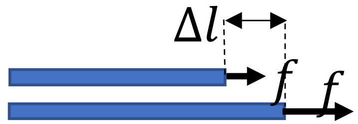






Question: What kind of processes occur during 1, 2, 3 & 4?

1,3: • $\Delta F \neq 0$ => work W $\neq 0$ • Fast => no time for heat, adiabatic: $Q = 0$	2,4: • $\Delta F = 0$ => work W $= 0$ • Heating or cooling only: $Q \neq 0$

First analysis:

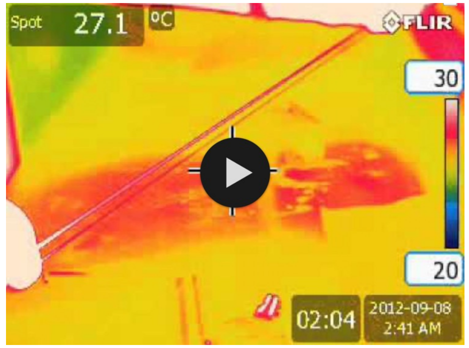
1. $W = -PdV = fdl > 0$
   - f changes➔ $W = \int_{l_1}^{l_2} fdl$
   - 1st law: $\Delta U = Q + W$
   - $Q = 0$
   - ➔ $\Delta U = \int_{l_1}^{l_2} fdl > 0$
   - ➔ $\Delta T \propto \Delta U > 0$ (as observed)
   - $Q = \int_{S_1}^{S_2} TdS = 0$ ➔ $S_2 < S_1$
2. Cooling: $Q = TdS < 0$

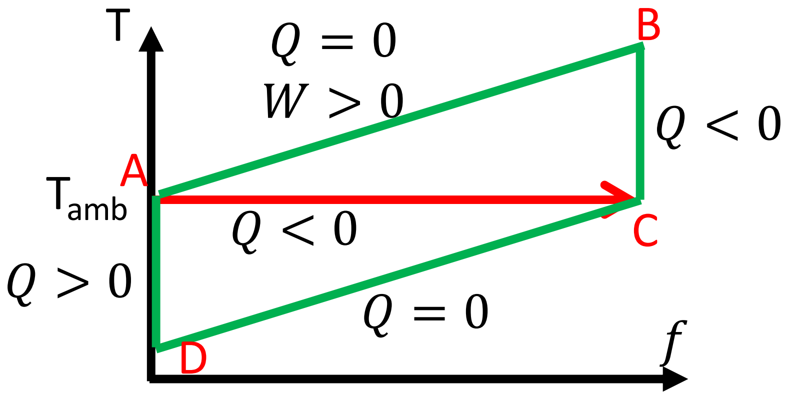
First analysis:

3. Let go of rubber band: $W = 0$
   - $Q = 0$, but $Q \neq TdS$
   - ➔ $\Delta U = Q + W = 0$
   - ➔ $\Delta T \propto \Delta U = 0$ (NOT as observed)
   - *Oops!*
4. Heating: $Q = TdS > 0$

Let's try again!

Try again!





C-D: Adiabatic, $Q = 0$

D-A: Quasistatic, $Q = T\Delta S > 0$

=>A-C: Quasistatic, $Q = T\Delta S < 0$

$\Rightarrow$ A-C:

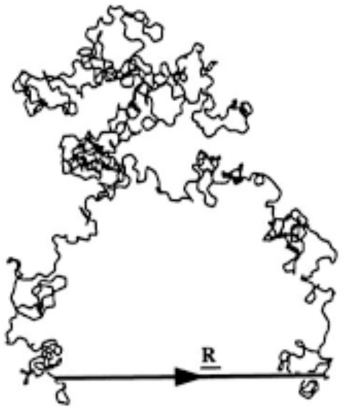
- $\Rightarrow \Delta S < 0$
- $\Rightarrow$ stretching reduces entropy
- $\Rightarrow \frac{\partial S}{\partial l} < 0$

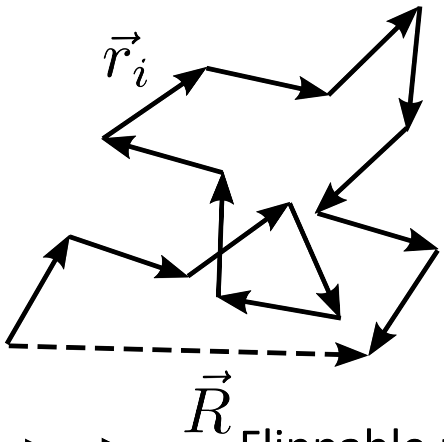
Total differential	$dS = \left(\frac{\partial S}{\partial U}\right)_l dU + \left(\frac{\partial S}{\partial l}\right)_U dl$
Thermodynamic identity	$dU = TdS + f dl$
Find $\frac{\partial S}{\partial l}$	$dS = \frac{1}{T} dU - \frac{f}{T} dl$
Identify	$\left(\frac{\partial S}{\partial l}\right)_U = -\frac{f}{T}$
Observation:	$\frac{f}{T} > 0$!!

Why does entropy decrease when rubber is stretched?
Answer outside thermodynamics => go microscopic!

Next: microscopic model of rubber band.

Microscopic model of rubber band

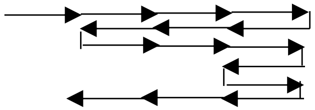




Polymers curling up:

RW / freely jointed chain: $\boldsymbol{R}^2 = \left(\sum \boldsymbol{r}_i\right)^2 = \mathrm{N}|r|^2$

1D:



Flippable monomers pointing left: N_L

Flippable monomers pointing right: N_R

Flippable monomers total $\mathrm{N} = N_L + N_R$

Two-state model:

Micro state: (1,1,1,1,-1,-1,-1,1,1,1,-1,1,-1,-1,-1) = (1,1,1,1,0,0,0,1,1,1,0,1,0,0,0)

=$\{s_i\}$

Macro state (length change) $\Delta L = l \sum s_i = l(N_R - N_L) = l(N - 2N_R)$

Multiplicity $\Omega(N, N_R) = \frac{N!}{N_R!(N-N_R)!}$

Entropy $S = k \ln \Omega$

Analysis of experiment: $\left(\frac{\partial S}{\partial \Delta L}\right)_U = -\frac{f}{T}$

Problem 3.34: $\Delta l \ll Nl$ $f = \frac{kT}{Nl^2} \Delta L = c\Delta L$

$\Rightarrow$ Hook's law with spring constant c.

What happens to f when you heat the rubber?
Describe an experiment.