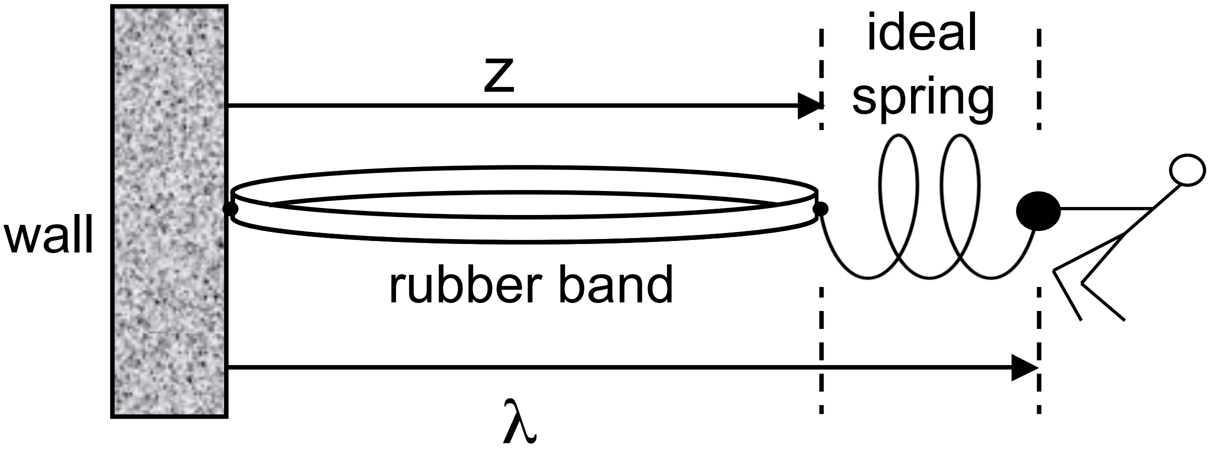
Lecture Notes, C. Jarzynski, University of Maryland
Boulder School for Condensed Matter and Materials Physics, 2009
Nonequilibrium Statistical Mechanics: Fundamental Problems and Applications

Nonequilibrium work relations
I. Macroscopic thermodynamics and the second law

Review of thermodynamic processes

Summarize relevant thermodynamic concepts using pedagogical example - stretching a rubber band - then discuss how these concepts might apply to a microscopic analogue - stretching a single molecule.

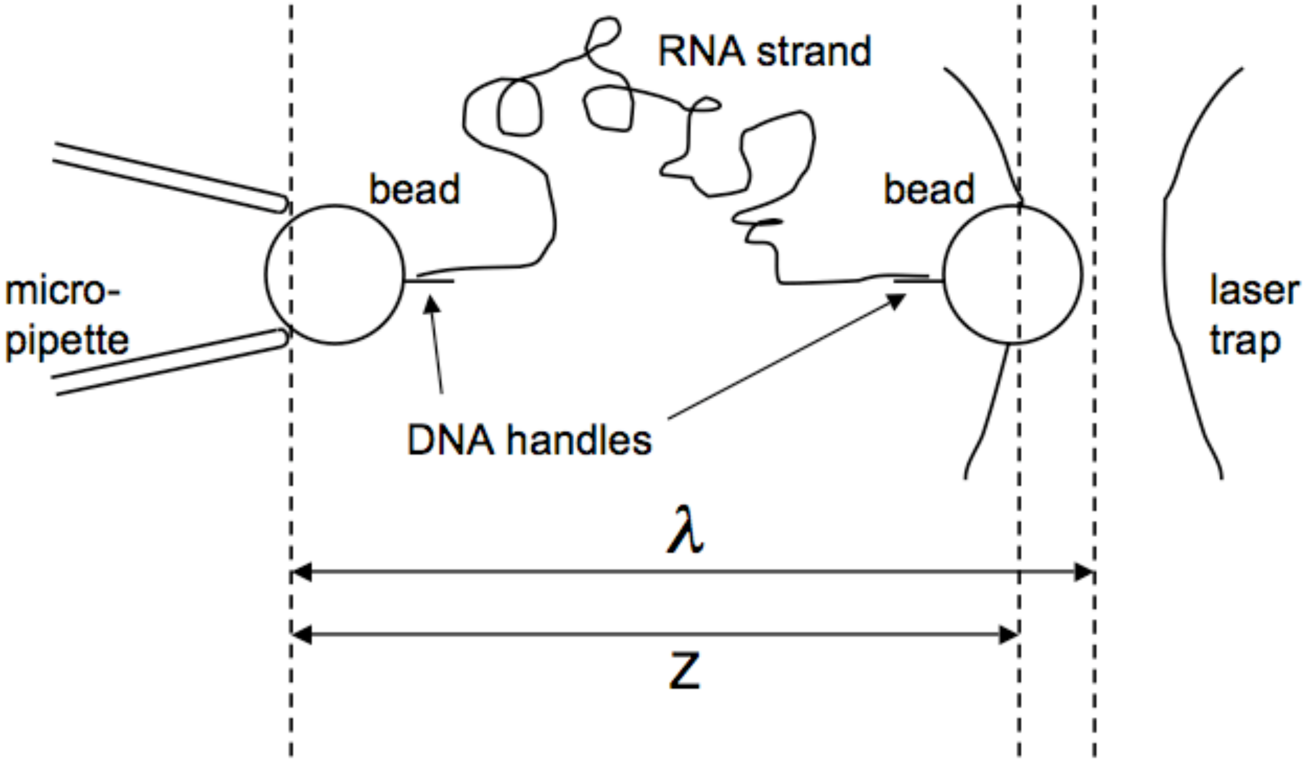


- system of interest = rubber band (+ spring)
- thermal environment = surrounding air ("heat bath", "reservoir")
- work parameter = λ

We act on the system by manipulating the work parameter.

λ fixed → system relaxes to equilibrium state (λ,T).

microscopic analogue: stretching a single molecule



[Lip02]

- system of interest = RNA + beads
- thermal environment = water
- work parameter = λ

(laser trap ~ ideal spring)

alternative approach:
use atomic-force microscopy instead of laser trap [Har07]

Let’s define a *thermodynamic process* to be a sequence of events in which a system of interest evolves from one equilibrium state to another.

- focus on thermodynamic processes in which we act on the system by manipulating a work parameter λ

The first and second laws of thermodynamics make predictions regarding such processes …

First Law of Thermodynamics

$$\Delta U = W + Q$$

This is essentially a statement of energy conservation, but keep in mind that the meaning of the quantities involved depends on how we define our system of interest.

Rubber band example:

1. U = internal energy of rubber band alone

$$W = \int F_{spring} \cdot dz$$

2. U = internal energy of rubber band + ideal spring

$$W = \int F_{spring} \cdot d\lambda$$

Both definitions are acceptable, but we must choose one and stick with it. In these lectures I will use definition 2.

Second Law of Thermodynamics

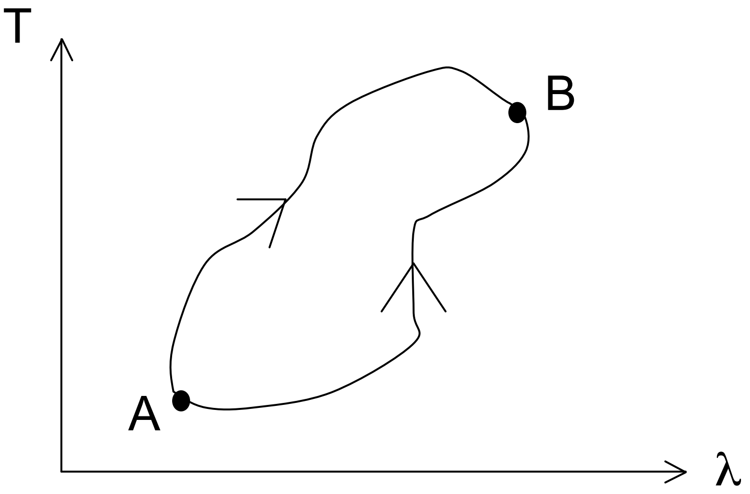
There exists a state function, S (entropy) such that

$$\int_A^B \frac{dQ}{T} \leq \Delta S = S_B - S_A \qquad \textit{(Clausius inequality)}$$

for any thermodynamic process from state A to state B.

(T = temperature of surroundings
from which heat is absorbed)

- Reversible processes: $\int_A^B \frac{dQ}{T} = S_B - S_A$



- Irreversible processes: $\int_A^B \frac{dQ}{T} < S_B - S_A$

Apply Clausius inequality to stretching a rubber band:

1. Start at λ=A , in equilibrium w/ surrounding air
2. Stretch rapidly, λ : A→B … rubber band heats up
3. Hold λ fixed and allow to cool down

$$\int_A^B \frac{dQ}{T} \leq \Delta S \quad + \quad \text{First Law} \quad \rightarrow \quad W \geq \Delta F$$

(F = U-TS = Helmholtz free energy)

$T = T_{air}$ (constant)

The inequality W≥ΔF is the general statement of the Clausius inequality for processes involving a single thermal reservoir.

Often convenient to separate contributions to W:

$$W = W' - \int P dV + \int \sum_i \mu_i dn_i \geq \Delta F$$

- closed system at constant pressure:

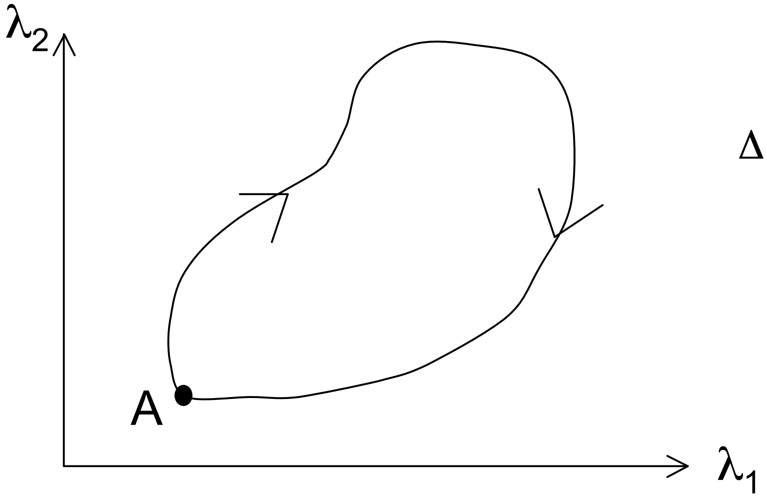
$$W' \geq \Delta F + P\Delta V = \Delta G$$

- fixed volume, open system:

$$W' \geq \Delta F - \sum_i \mu_i \Delta n_i = \Delta \Phi$$

Cyclic processes:

Isothermal* cyclic process :

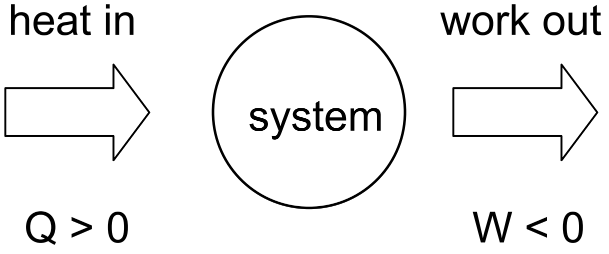


$\Delta F = F_A - F_A = 0$

Clausius inequality : $W_{cyc} \geq 0$ (equivalently, $Q_{cyc} \leq 0$)

No work can be extracted from a cyclic process involving only one thermal reservoir (Kelvin-Planck statement of 2nd law)

… no perpetual motion machines of the second kind:



heat in

system

work out

$Q > 0$

$W < 0$

“no free lunch”

* “isothermal” = only one reservoir is present

Exercise. When a rubber band is stretched rapidly, its temperature increases. Using the Kelvin-Planck statement of the second law, show that this empirical observation implies that a rubber band will contract when heated. You will need to make reasonable assumptions about time scales involving heat exchange and self-equilibration.

“Conjugate” / “forward-reverse” processes.

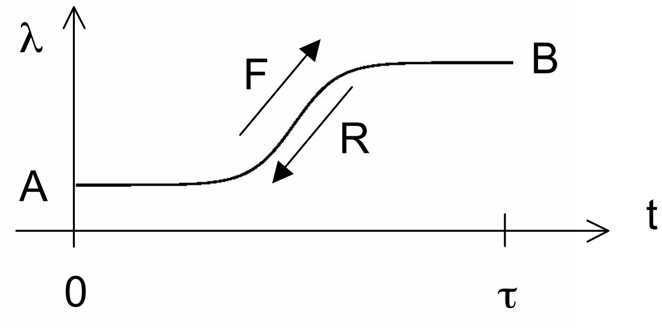
We’ll often consider a pair of processes:

Forward process , λ : A→B (then relax to equilibrium)
Reverse process , λ : B←A (then relax to equilibrium)

with

$$\lambda_t^R = \lambda_{\tau-t}^F$$

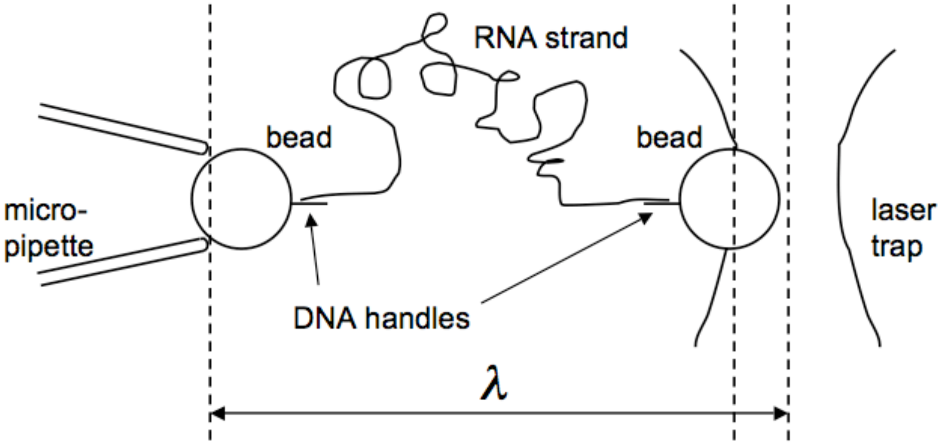
where τ is the duration of the process, e.g.:



$$W_F \geq F_B - F_A$$
$$W_R \geq F_A - F_B \quad \longrightarrow \quad -W_R \leq \Delta F \leq W_F$$

cycle : A→B→A … $W_{cyc} = W_F + W_R \geq 0$

How might these results apply to thermodynamic processes involving microscopic systems?



1. Start at λ=A , in equilibrium w/ water

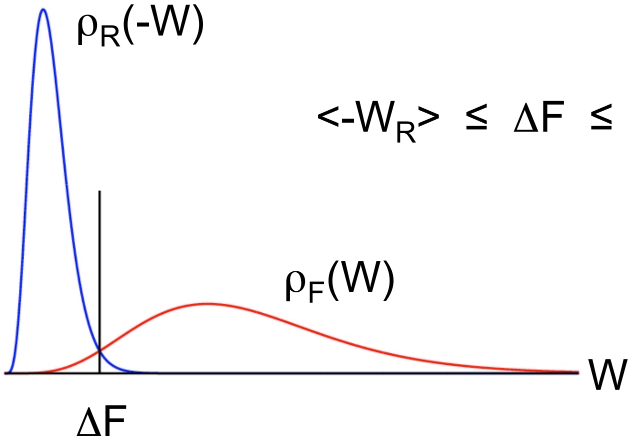
forward {
2. Stretch rapidly, $\lambda : A \rightarrow B$
3. Hold λ fixed and allow to re-equilibrate

reverse {
4. "Unstretch" rapidly, $\lambda : A \leftarrow B$
5. Hold λ fixed and allow to re-equilibrate

6. *Repeat*

thermal fluctuations of microscopic degrees of freedom
→ statistical fluctuations in W !

extrapolating the 2nd law to the microscopic scale, we expect:



$$\langle -W_R \rangle \leq \Delta F \leq \langle W_F \rangle$$