

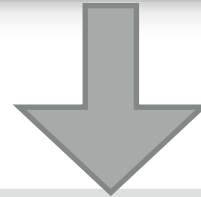


The Institute of Mathematical Sciences

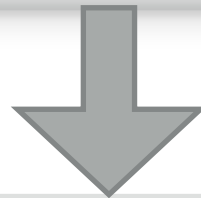
Stochastic Thermodynamics

Plan of the talk

Classical thermodynamics



**Jarzynski relation and
Crooks fluctuation theorem**



Stochastic dynamics

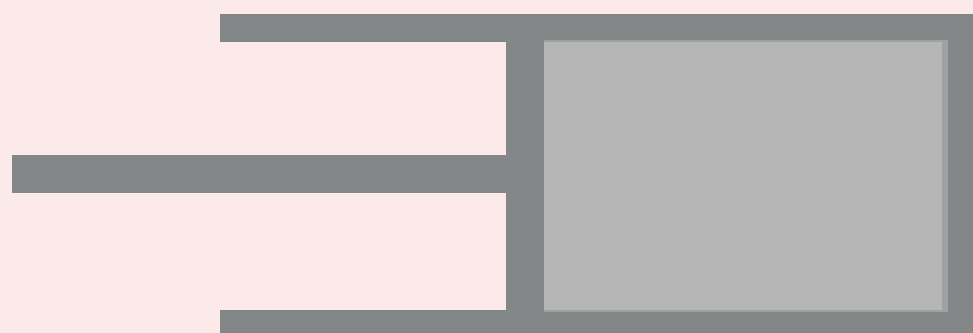


Heat engines

Thermodynamics

Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you anymore.

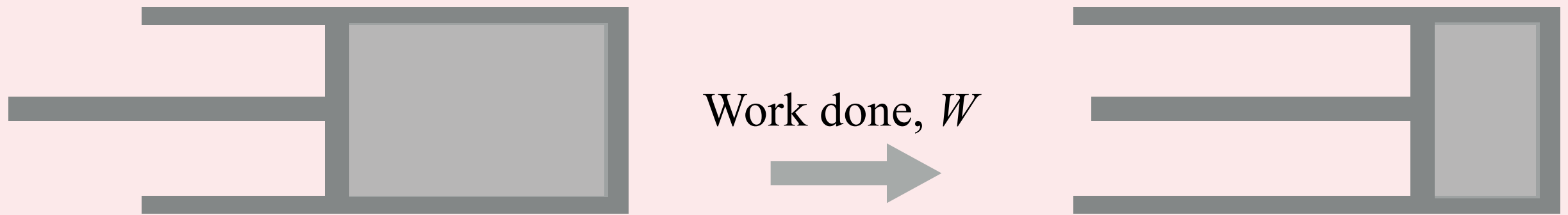
— Arnold Sommerfeld



Work done, W



Heat bath at temperature T



Heat bath at temperature T

First law: $W = \Delta V + Q = \Delta V + T\Delta S$

Work done increases the internal energy of the system, or is dissipated as heat in the medium $Q = T\Delta S_m$

Second law: $\Delta S_{tot} = \Delta S + \Delta S_m \geq 0$

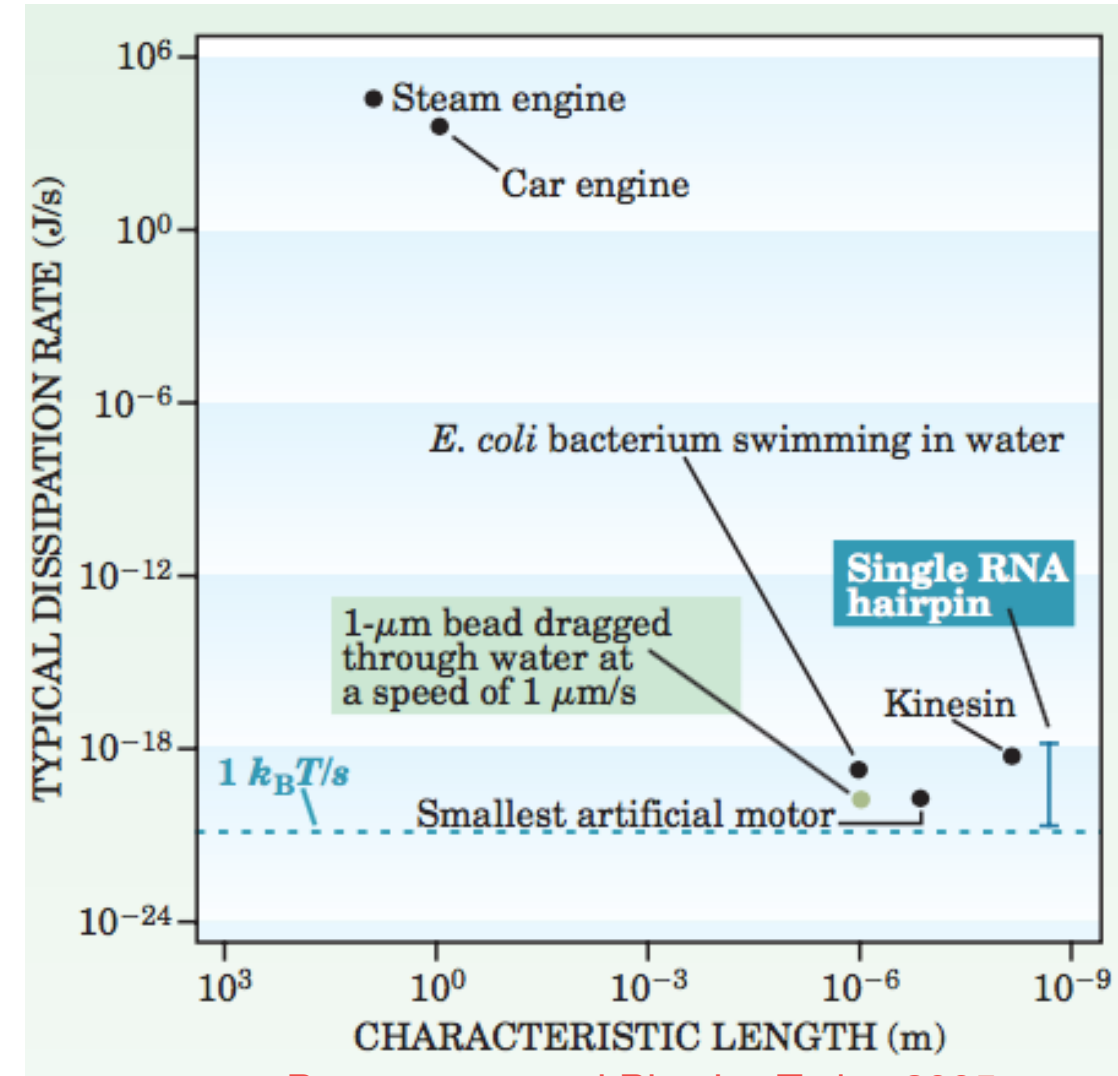
$$W \geq \Delta V - T\Delta S_m \equiv \Delta \mathcal{F}$$

$$W_{\text{diss}} \equiv W - \Delta \mathcal{F} \geq 0$$

Fluctuation theorems

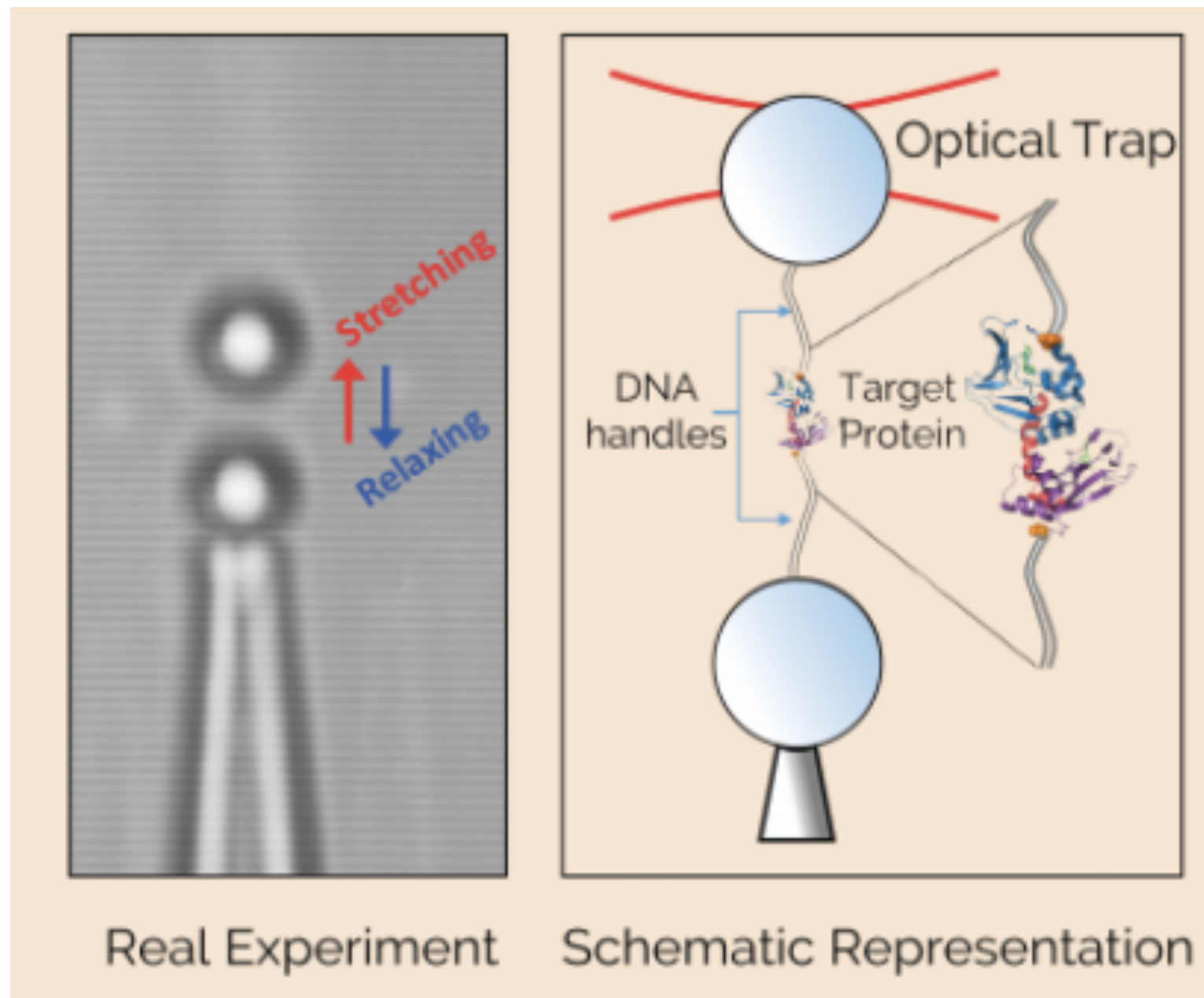
Thermal fluctuations

- The role of thermal fluctuations are important for small systems of energy scale $1-100 k_B T$
- Since the force is fluctuating: W , Q , V will also fluctuate and we will need to determine their probability distributions
- Stochastic thermodynamics deals with extending concepts from classical thermodynamics to fluctuating trajectories
- Examples include Brownian motion of colloidal particles in external potentials. Molecular machines also operate at several $k_B T$. ATP hydrolysis is around $10-20 k_B T$



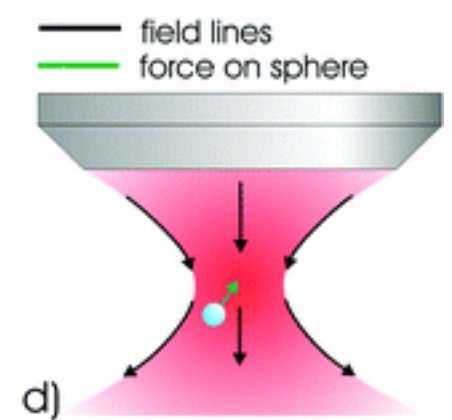
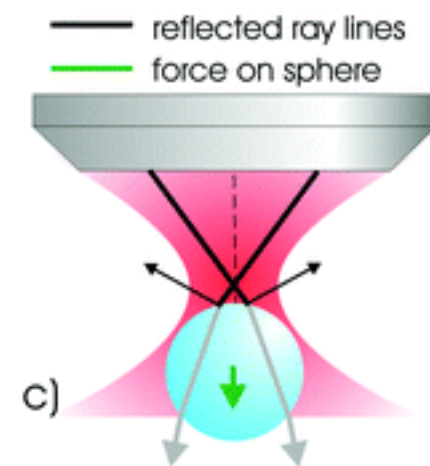
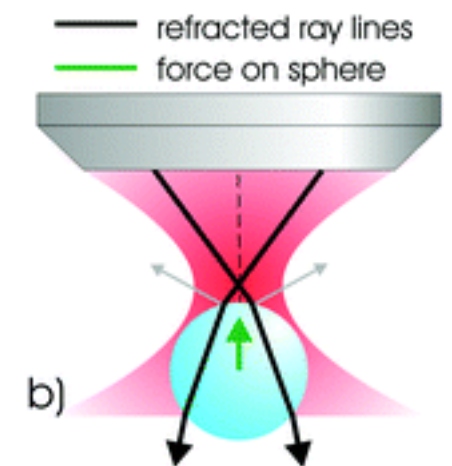
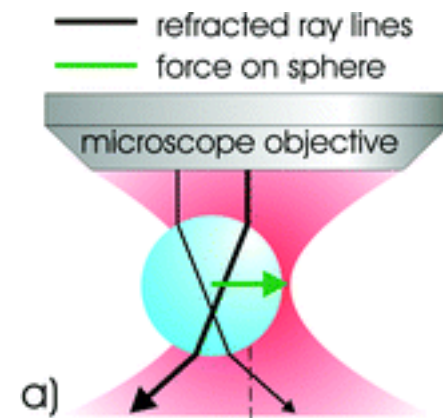
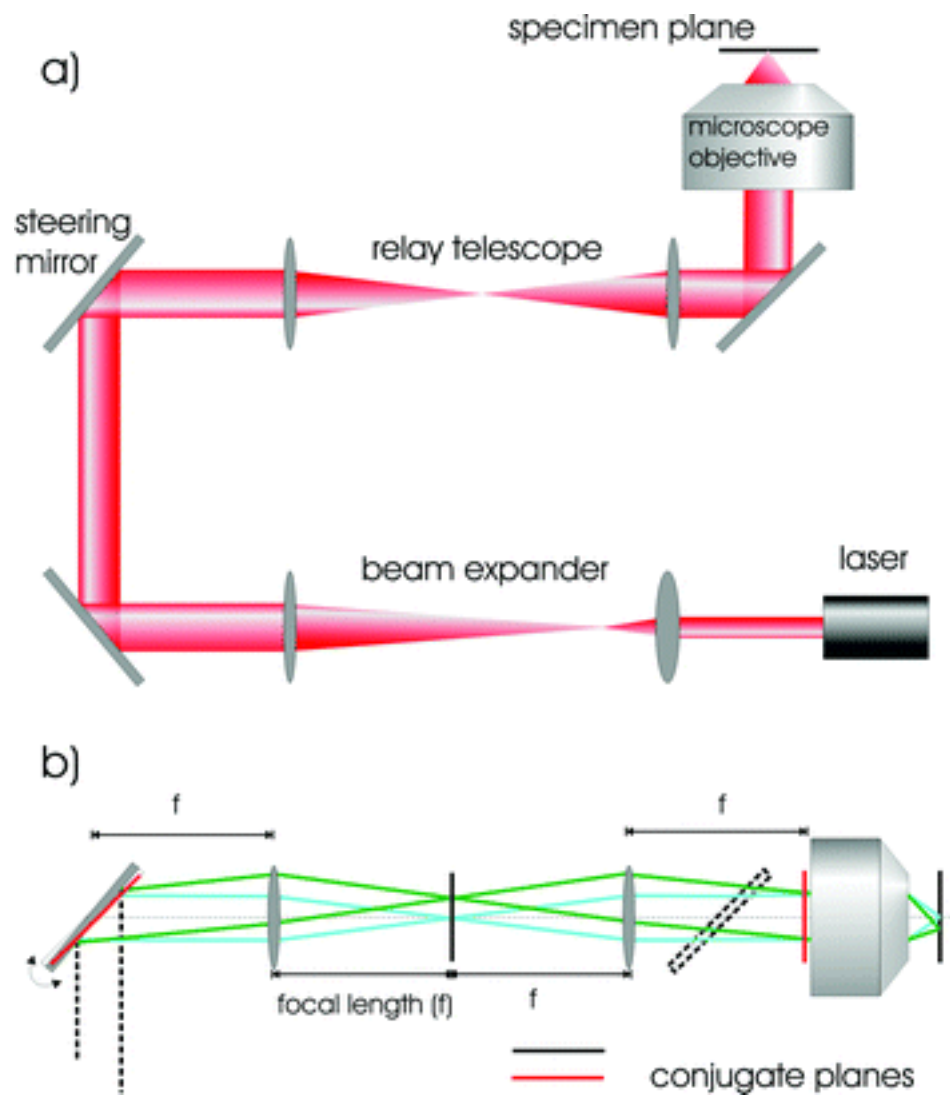
Bustamante et al Physics Today 2005

Control parameter



<http://maillardlab.org/optical-tweezers/>

Optical Tweezers



Fluctuation theorems

Fluctuations theorems describe the behaviour of trajectories under “time-reversal” and give the universal properties of the probability distribution $p(\Omega)$ and $p(-\Omega)$ as a function Ω .

A typical relation is of the type

$$\frac{p(-\Omega)}{p(\Omega)} = e^{-\Omega}$$

Loschmidt's paradox (1876): objection to the statement of second law that entropy always increases. As microscopic laws are time-reversal invariant, Trajectories with decreasing entropy must also be possible.

The fluctuation theorem for entropy explains that such trajectories do exist but become extremely rare for large system sizes.

The Jarzynski relation

In 1997, Jarzynski derived that

$$\langle \exp(-\beta w) \rangle = \exp(-\beta \Delta \mathcal{F})$$

$$\langle \exp(-\beta w_{diss}) \rangle = 1$$

$$\beta = \frac{1}{k_B T}$$

$\Delta \mathcal{F} = \mathcal{F}(\lambda_t) - \mathcal{F}(\lambda_0)$ is the change in free energy to take the system from an initial equilibrium state to some final value. The average indicates infinite number of nonequilibrium experiments. Thus, for a macroscopic system, the dissipated work is positive but trajectories are allowed where dissipated work is ***negative!*** Those trajectories have been called to be transient violations of the second law. It provides a way to find free energy difference.

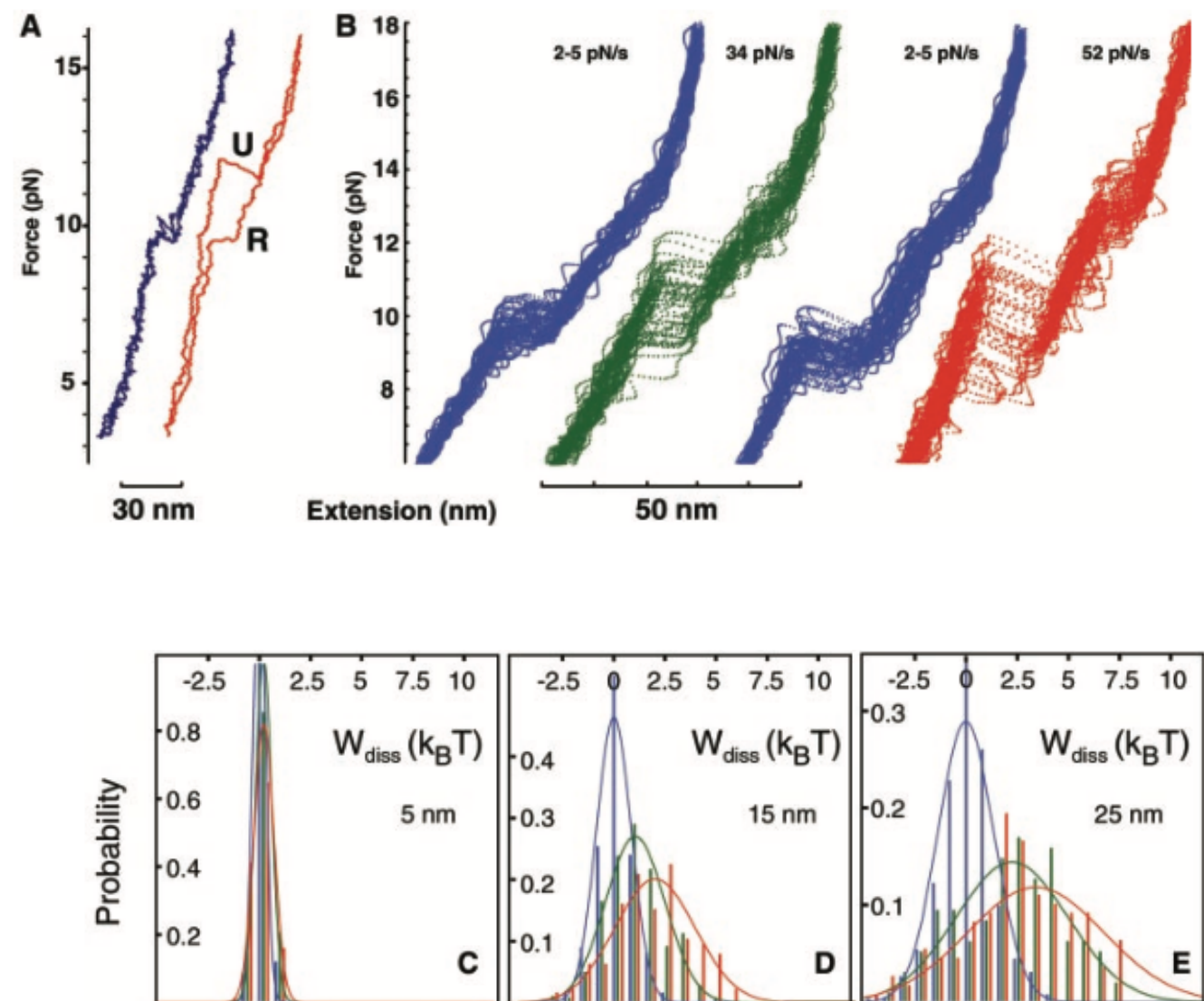
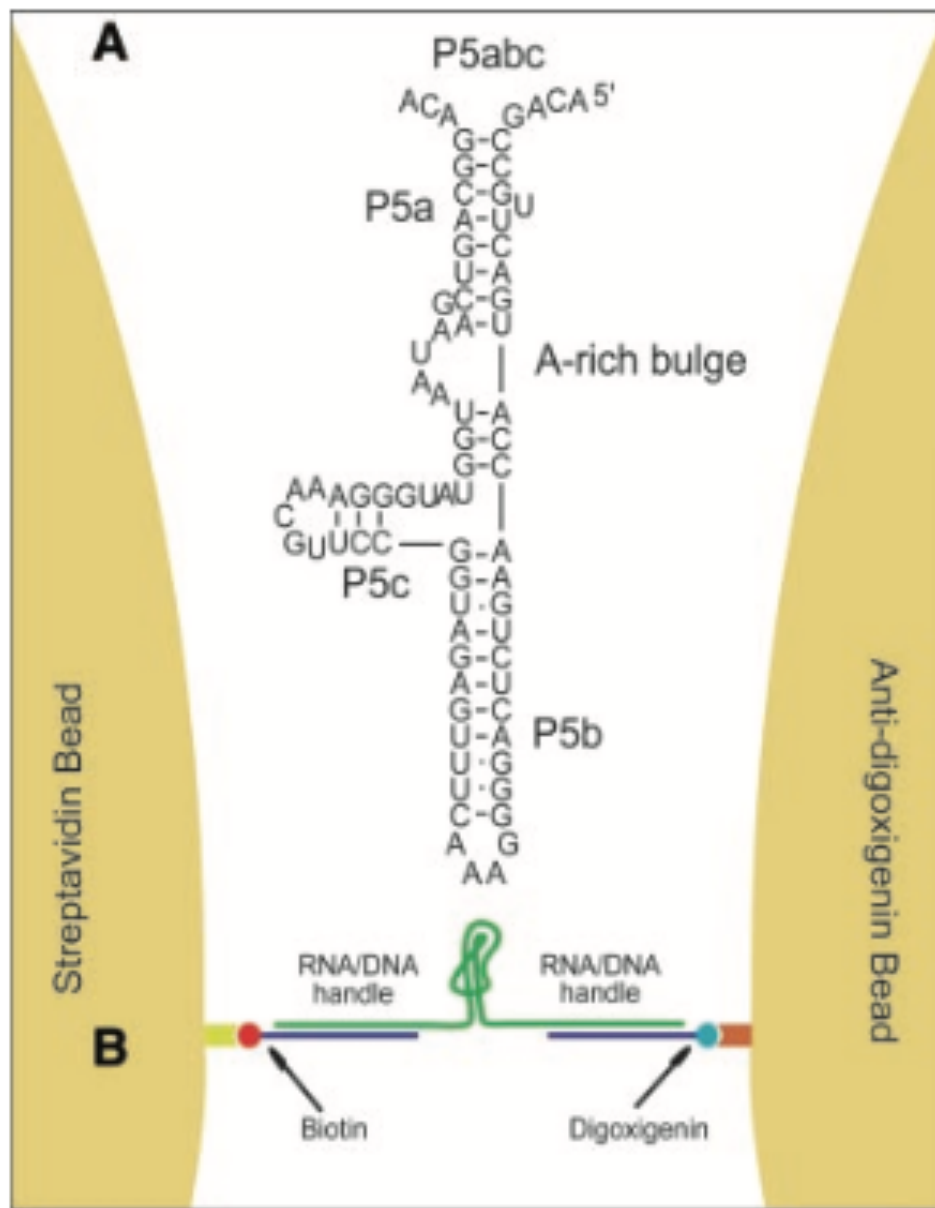
Crooks fluctuation theorem

Crooks in 1999, generalized Jarzynski relation. He showed that the ratio of probability of work distribution along the forward and the backward path is given as

$$\frac{\tilde{p}(-w)}{p(w)} = \exp(-\beta(w - \Delta\mathcal{F}))$$

- Just like the Jarzynski relation: initial state is at equilibrium while the final state is a non-equilibrium state in both forward and reverse path.
- The Jarzynski relation follows from the above as the probabilities are normalized. Averaging over all the possible states, we get Jarzynski relation from the above.

Experimental verification of Jarzynski relation



Liphardt et al Science 2002

Dynamics

The starting point in nonequilibrium statistical physics is dynamics. This is in contrast to equilibrium where energy plays this role. There exist equivalent but complementary descriptions of stochastic dynamics:

$$\text{Langevin description: } \dot{x} = \mu F(x, \lambda) + \zeta$$

F is a systematic force and thermal noise has zero mean and

$$\langle \zeta(\tau) \zeta(\tau') \rangle = 2k_B T \mu \delta(\tau - \tau')$$

$$\begin{aligned} \text{Fokker-Planck eq: } \partial_t p &= -\partial_x j(x, \tau) \\ &= -\partial_x (\mu F - D \partial_x) p \end{aligned}$$

$$F(x, \lambda) = -\partial_x V(x, \lambda) + f(x, \lambda), \quad D = k_B T \mu$$

First law at single trajectory level

The first law can be identified from the Langevin equation as

$$dw = dV + dq$$

$$dw = \frac{\partial V}{\partial \lambda} \dot{\lambda} d\tau + f dx$$

Work done at fixed particle position

Contributions from non-conservative force

Using above equations, heat dissipated is obtained as

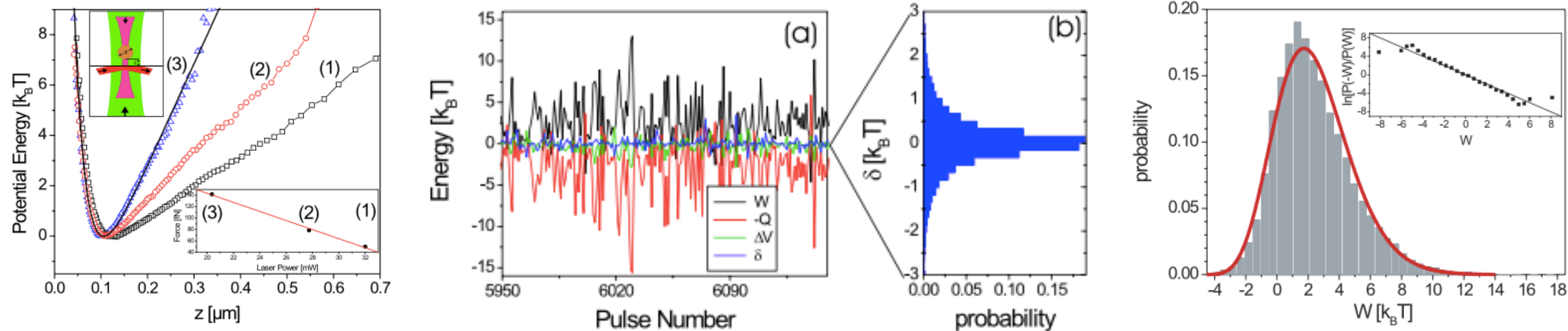
$$dq = dw - dV = F dx = T ds_m$$

Integration of the above form gives the first law at trajectory level

$$w(x(\tau)) = q(x(\tau)) + \Delta V$$

$$w(x(\tau)) = \int_0^t \left(\frac{\partial V}{\partial \lambda} \dot{\lambda} + f \dot{x} \right) d\tau, \quad q(x(\tau)) = \int_0^t F \dot{x} d\tau$$

Thermodynamics of a colloidal particle



- Charged colloid is repulsed by a wall and is pushed periodically towards it by a laser trap
- The energy, work and heat was measured from the particle trajectory
- They should sum to zero but histogram shows error of the order $k_B T$.
- The work distribution is non-Gaussian: drive is beyond linear response. Red curve is theory.

Path integral representation

$$P(\zeta) \sim \exp\left[-\int_0^t dt \zeta^2 / 4D\right]$$

$$P(x(\tau)|x_0) \sim \exp\left[-\int_0^t dt (\dot{x} - \mu F)^2 / 4D\right]$$

time reversal protocol

$$\tilde{x}(\tau) \equiv x(t - \tau) \quad \tilde{\lambda}(\tau) \equiv \lambda(t - \tau)$$

$$\begin{aligned} \frac{p(x(\tau)|x_0)}{\tilde{p}(\tilde{x}(\tau)|\tilde{x}_0)} &= \frac{\exp\left[-\int_0^t dt (\dot{x} - \mu F)^2 / 4D\right]}{\exp\left[-\int_0^t dt (\dot{\tilde{x}} - \mu \tilde{F})^2 / 4D\right]} \\ &= \exp\left(\beta \int_0^t d\tau \dot{x} F\right) = \exp \Delta s_m \end{aligned}$$

Detailed fluctuation theorem

$$\begin{aligned} 1 &= \sum_{\tilde{x}(\tau), \tilde{x}_0} \tilde{p}(\tilde{x}(\tau) | \tilde{x}_0) p_1(\tilde{x}_0) \\ &= \sum_{\tilde{x}(\tau), \tilde{x}_0} p(x(\tau) | x_0) p_0(x_0) \frac{\tilde{p}(\tilde{x}(\tau) | \tilde{x}_0) p_1(\tilde{x}_0)}{p(x(\tau) | x_0) p_0(x_0)} \\ &= \langle \exp[-\Delta s_m] p_1(x_t) / p_0 \rangle \end{aligned}$$

The above can be rewritten as

$$\langle \exp[-(w - \Delta V)/T] p_1(x_t) / p_0 \rangle = 1$$

Derivation of Jarzynski relation

From the generalized fluctuation relation we have

$$\langle \exp[-(w - \Delta V)/T] p_1(x_t)/p_0 \rangle = 1$$

Consider a initial equilibrium distribution of the form

$$p_0 = \exp[-(V(x_0, \lambda_0) - \mathcal{F}(\lambda_0))]$$

Use the free choice for the last term to complete the derivation

$$p_1(x_t) = \exp[-(V(x_t, \lambda_t) - \mathcal{F}(\lambda_t))]$$

Heat engines

The Carnot engine

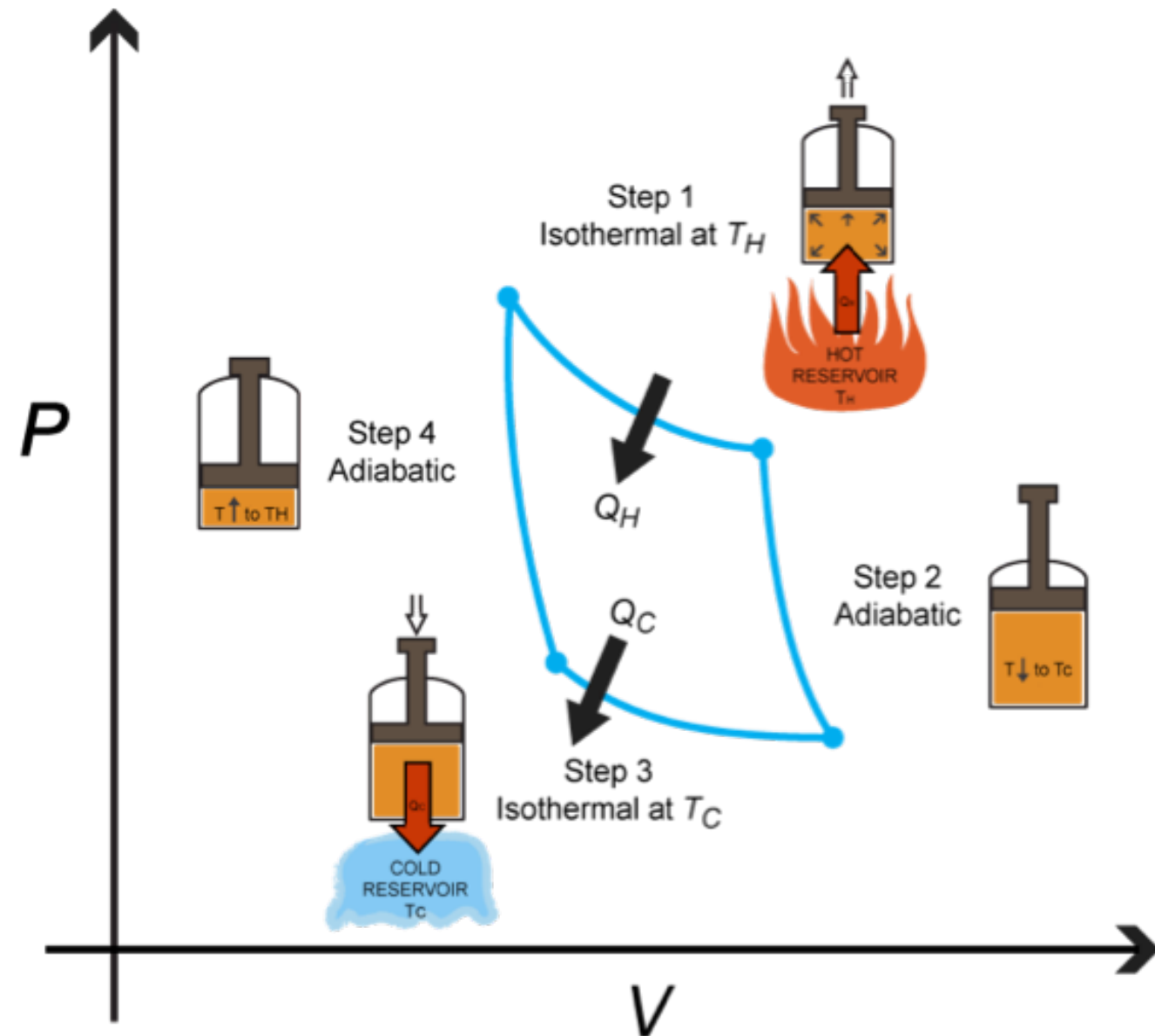
$$\text{Efficiency, } \eta_C = \frac{W}{Q_H} = 1 - \frac{T_c}{T_h}$$

Carnot (1824) showed that the most efficient cycle for a heat engine. But it has a zero power as the process is quasi-static, infinitely slow operation.

Curzon and Ahlborn (1975) showed the efficiency at maximum power is

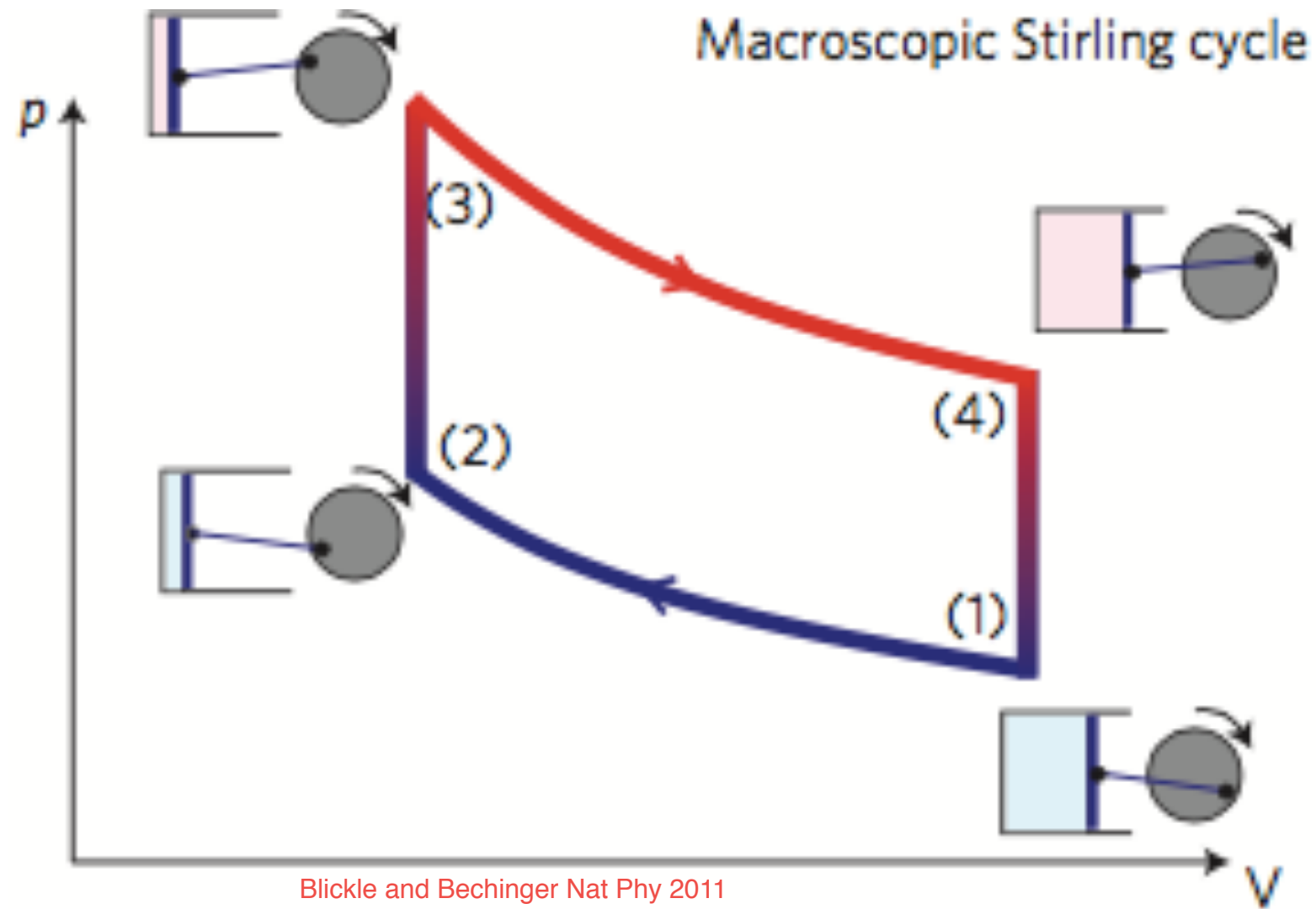
$$\eta^* = 1 - \sqrt{\frac{T_c}{T_h}}$$

Here, a constant time ratio between the adiabatic and isothermal steps is taken.



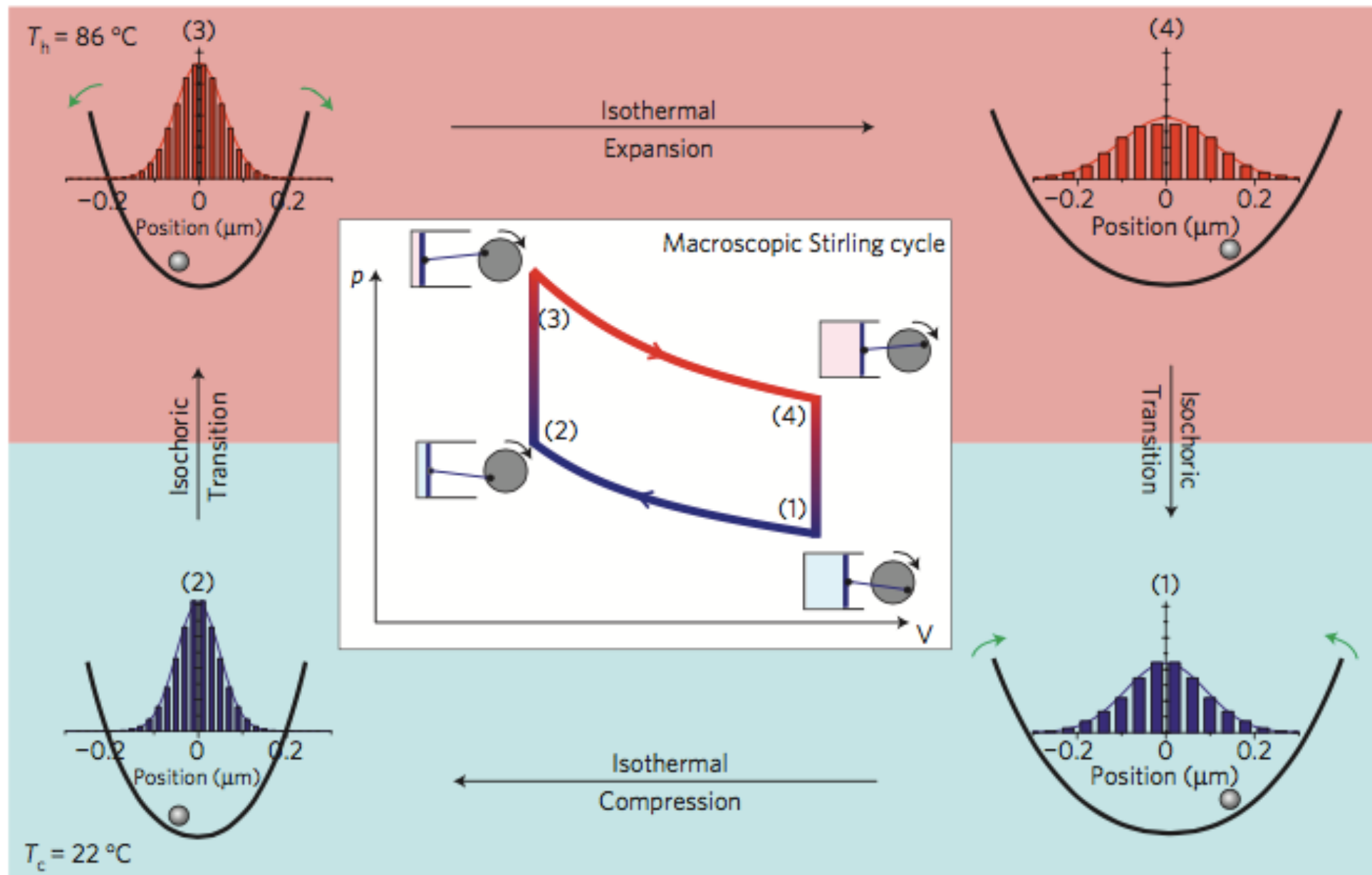
<https://www.shmoop.com/thermodynamics/carnot-cycle.html>

The Stirling engine



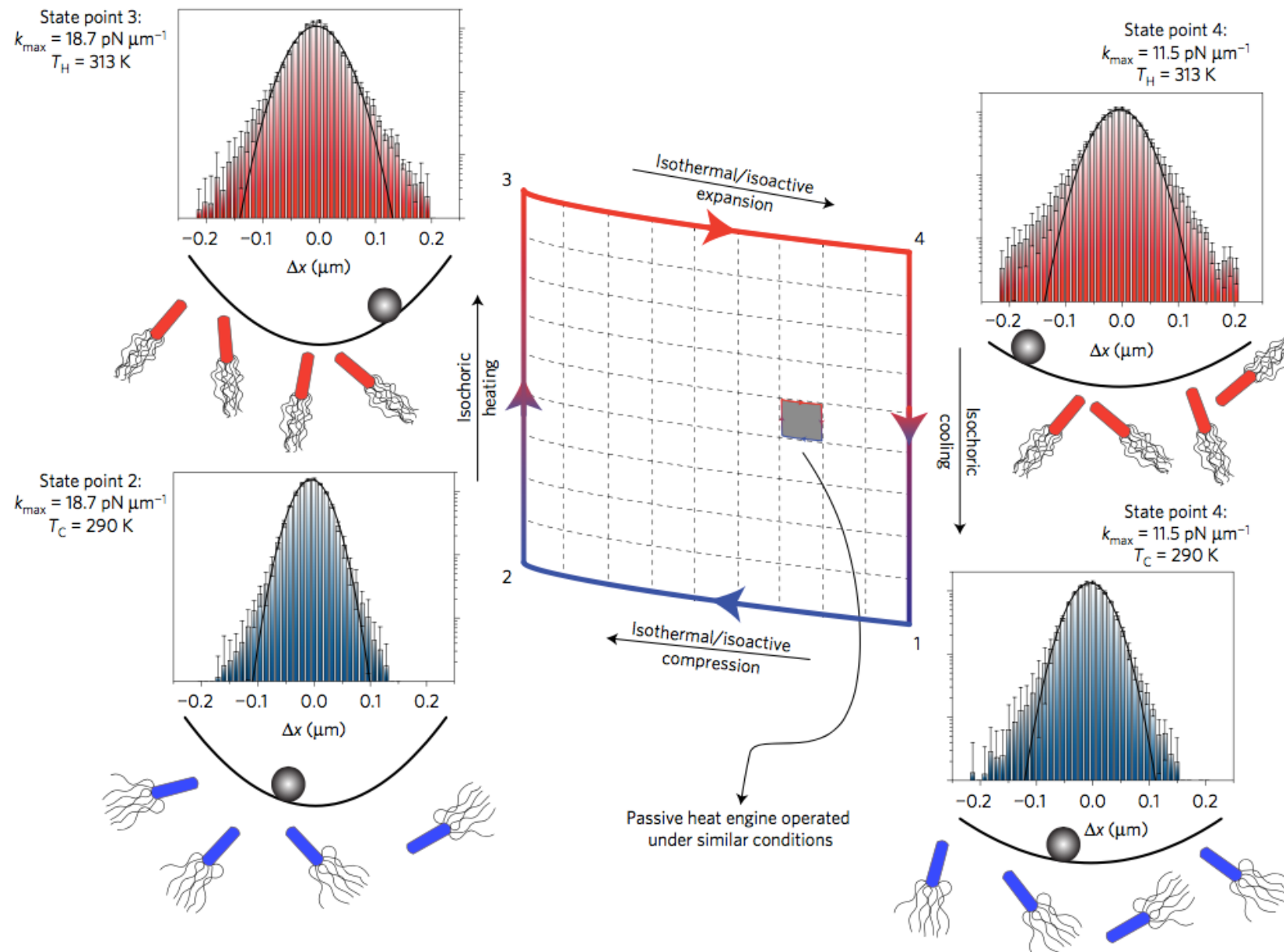
Efficiency of Stirling's engines is same as the Carnot's engine.

Micrometer sized heat engine



Blickle and Bechinger, Nat Phy 2011

Micrometer sized heat engine in Bacterial bath



Summary

- Fluctuations are crucial for small systems
- Fluctuation theorems: analytical relations for non-equilibrium system
- Stochastic thermodynamics: notions like work, heat and entropy of classical thermodynamics extended to microscopic systems
- Dynamics is obtained by Langevin and Fokker-Planck descriptions
- The distributions functions of the mesoscopic quantities can be of the non-Gaussian form

Thank You !