CELEBRATING 50 years of CREATIVE SCIENCE 1962 – 2012

The Institute of Mathematical Sciences

Stochastic Thermodynamics

Plan of the talk

Classical thermodynamics

↓

Jarzynski relation and
Crooks fluctuation theorem

↓

Stochastic dynamics

↓

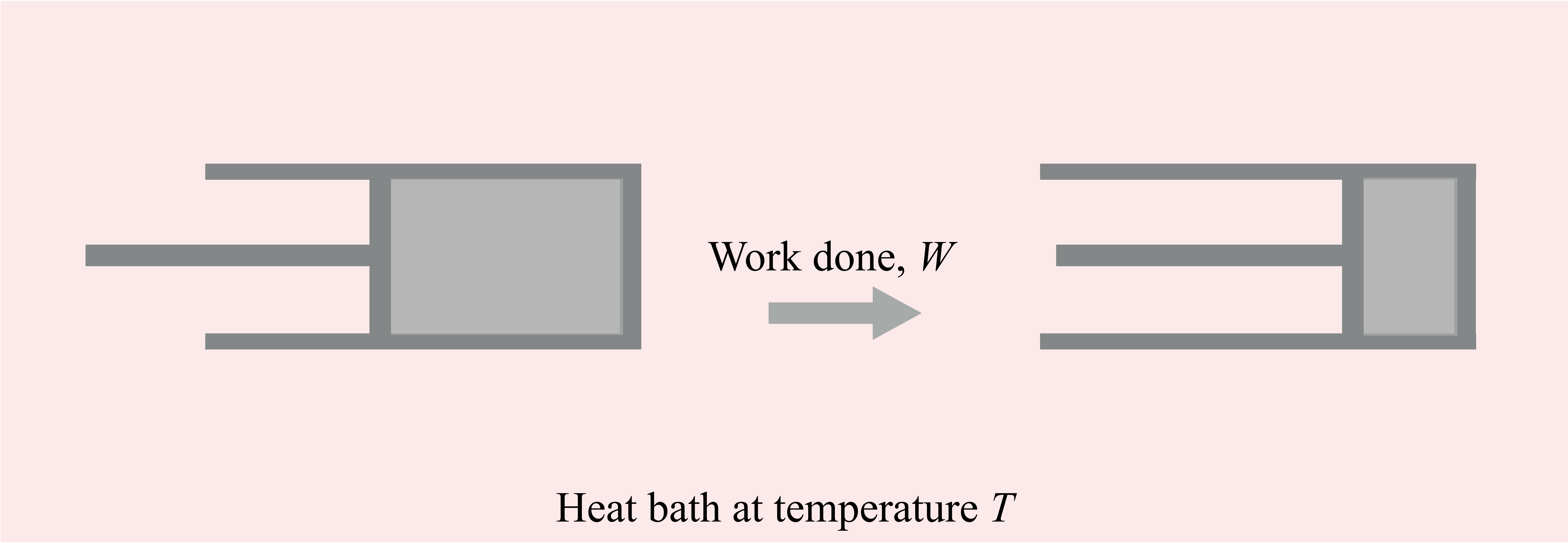
Heat engines

Thermodynamics

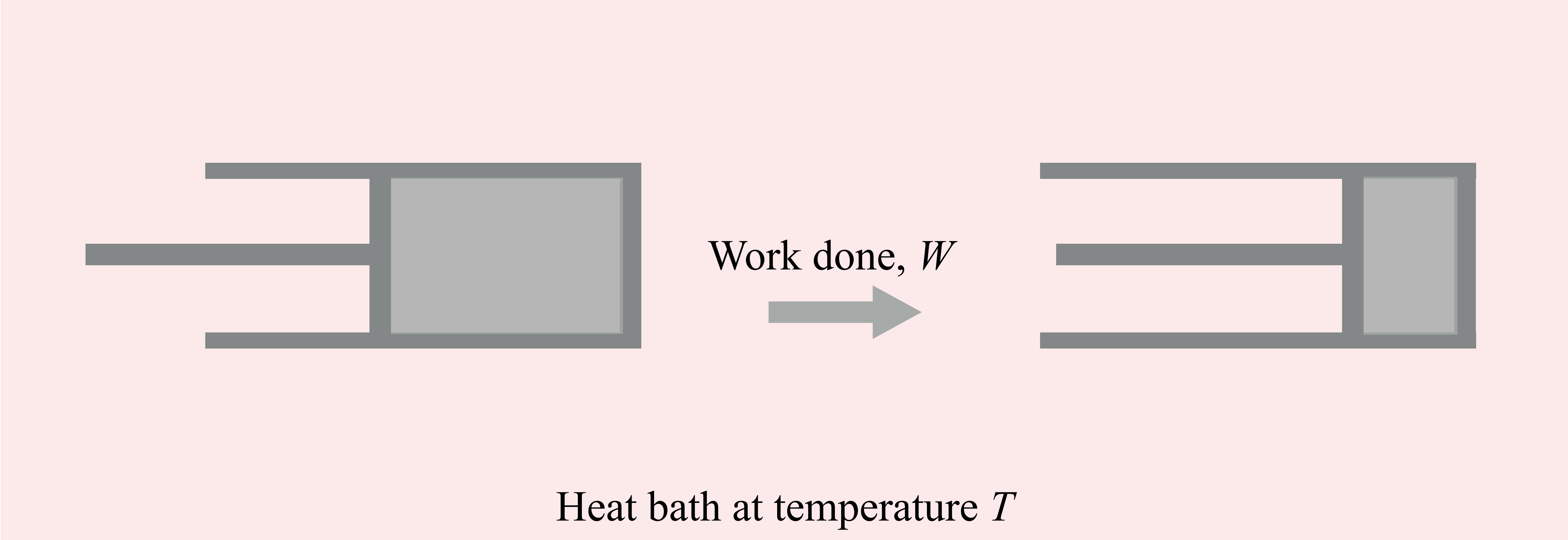
Thermodynamics

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

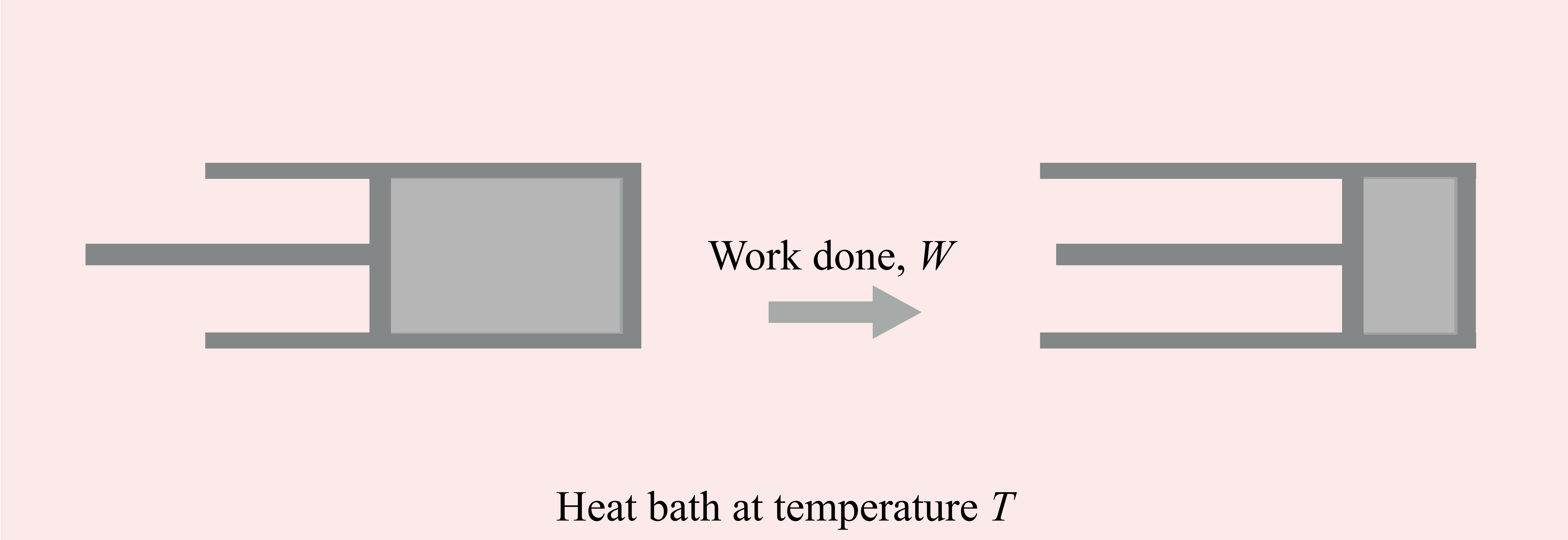


Work done, W
Heat bath at temperature T



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 $Q = T\Delta S_m$



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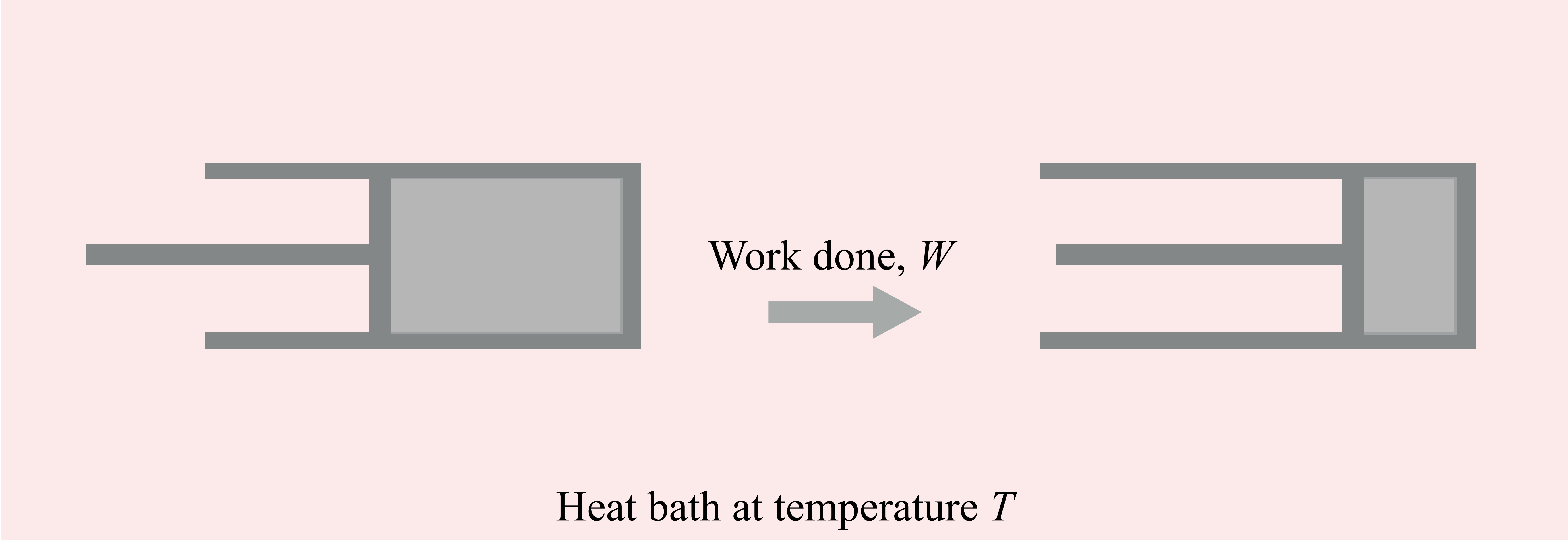

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Second law: $$\Delta S_{tot} = \Delta S + \Delta S_m \geq 0$$

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

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

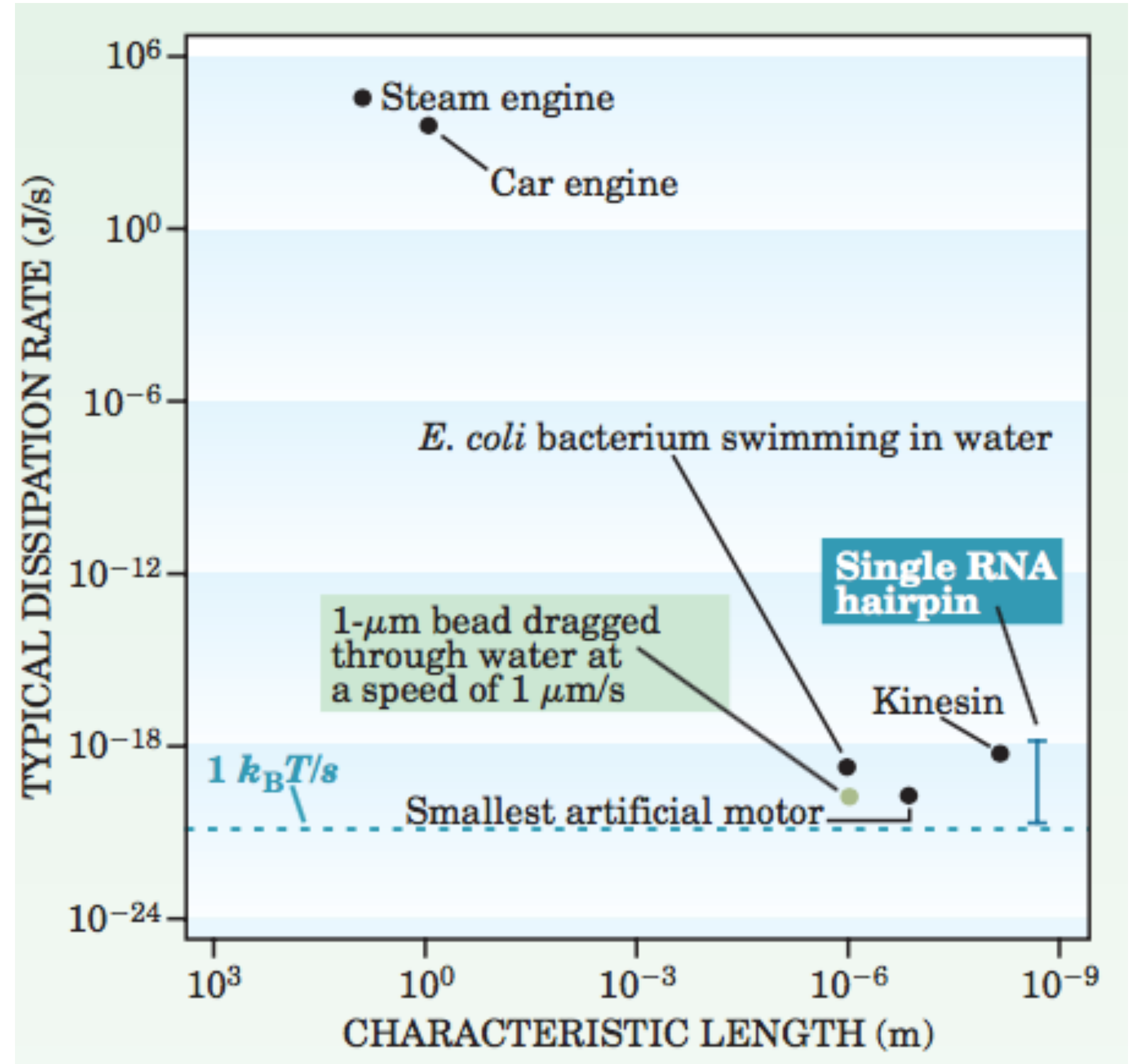
Fluctuation theorems

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

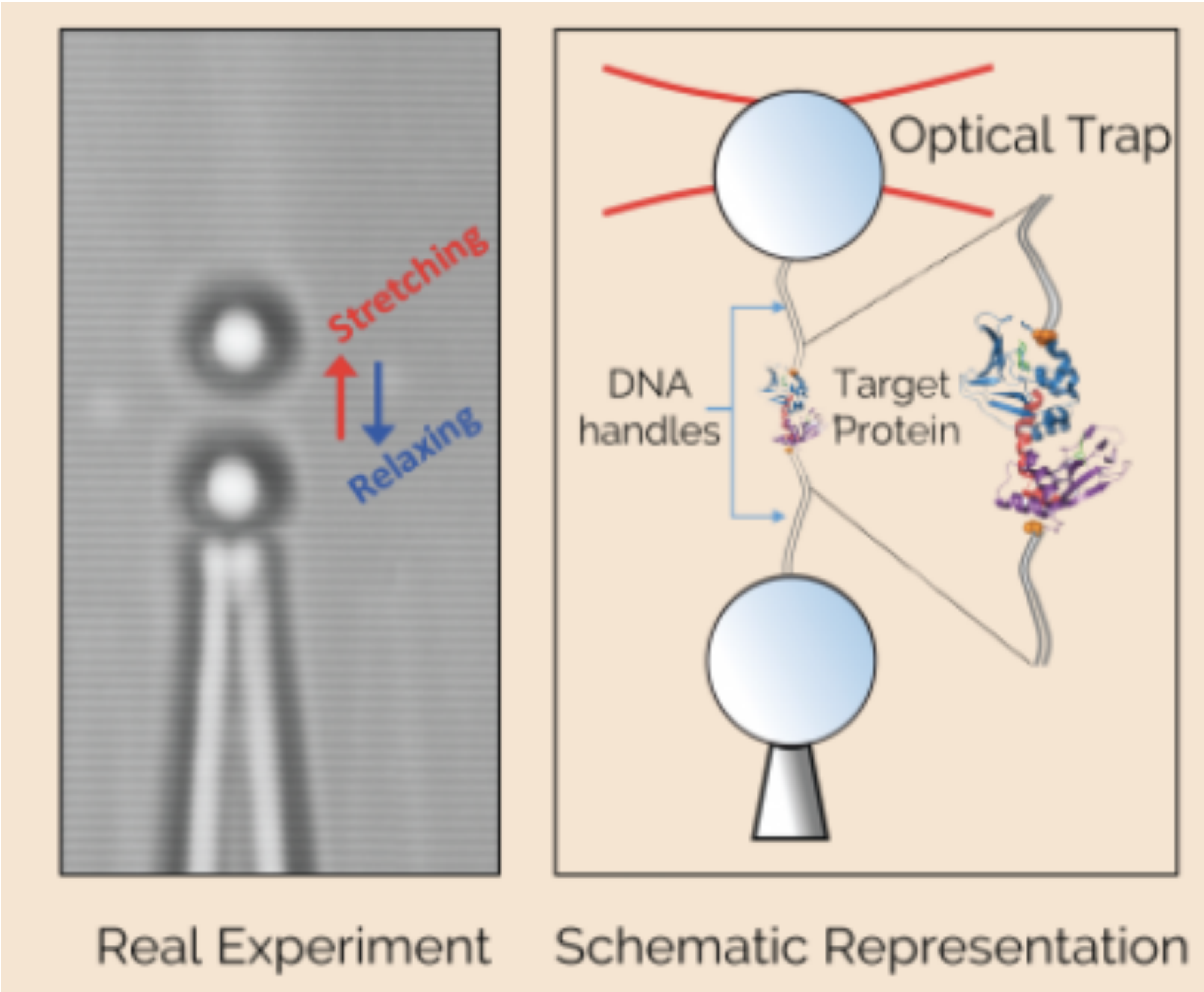
- Stochastic thermodynamics deals with extending concepts from classical thermodynamics to fluctuating trajectories



Bustamante et al Physics Today 2005

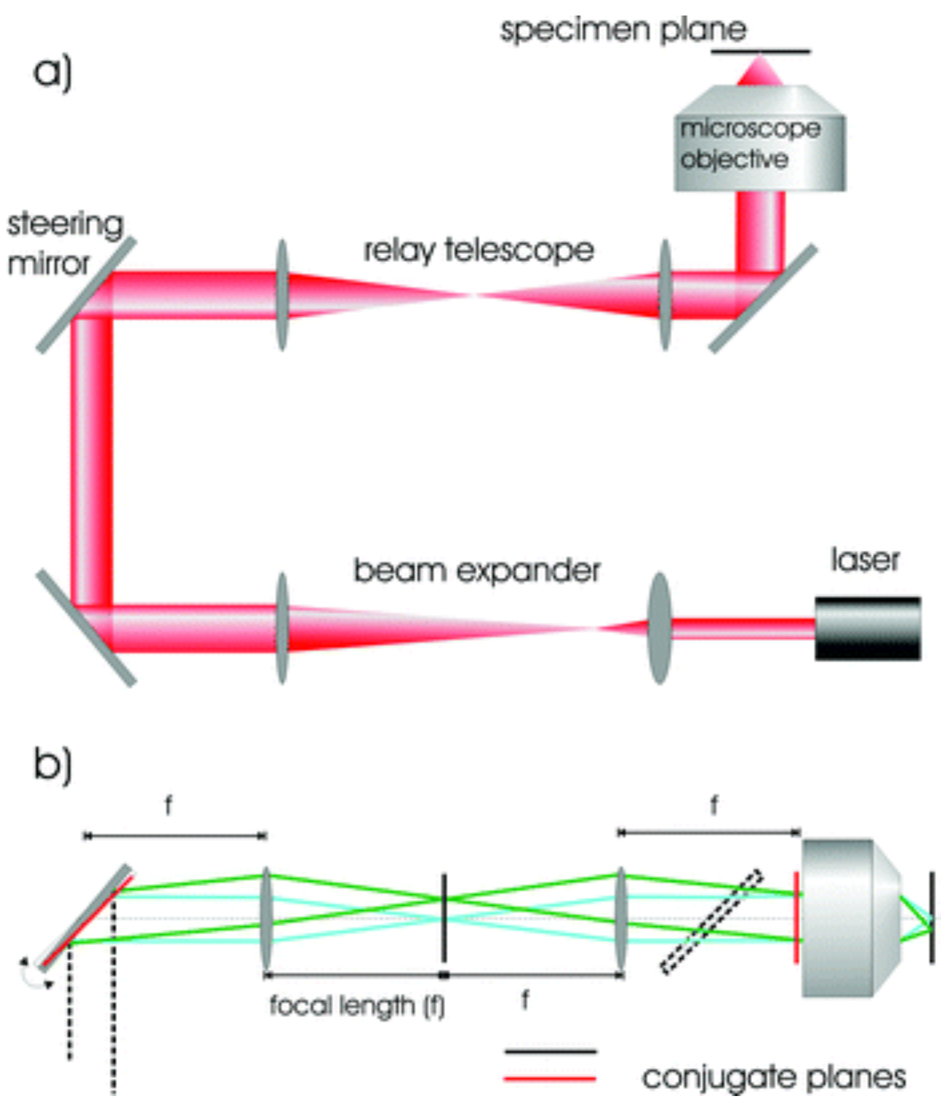
- Examples include Brownian motion of colloidal particles in external potentials. Molecular machines also operate at several $k_B T$. ATP hydrolysis is around 10-20 $k_B T$

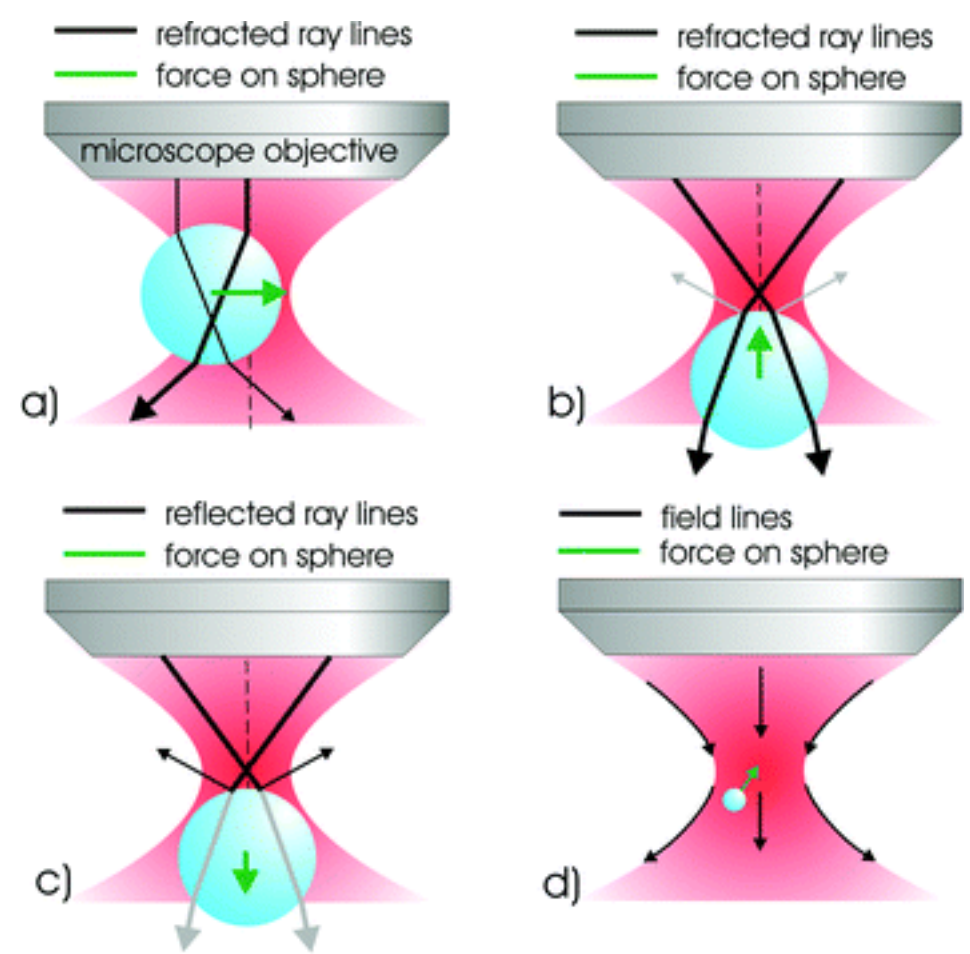
Control parameter



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

Optical Tweezers





Dholakia, Reece, and Gu, Chem Soc Rev 2007

Fluctuation theorems

Fluctuations theorems are the universal properties of the probability distribution $p(\Omega)$ of a concave function Ω.

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A typical relation is of the type

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

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 eqm 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 between an initial (eqm) to a final (noneqm) state.

Jarzynski, PRL 1997

Crooks fluctuation theorem

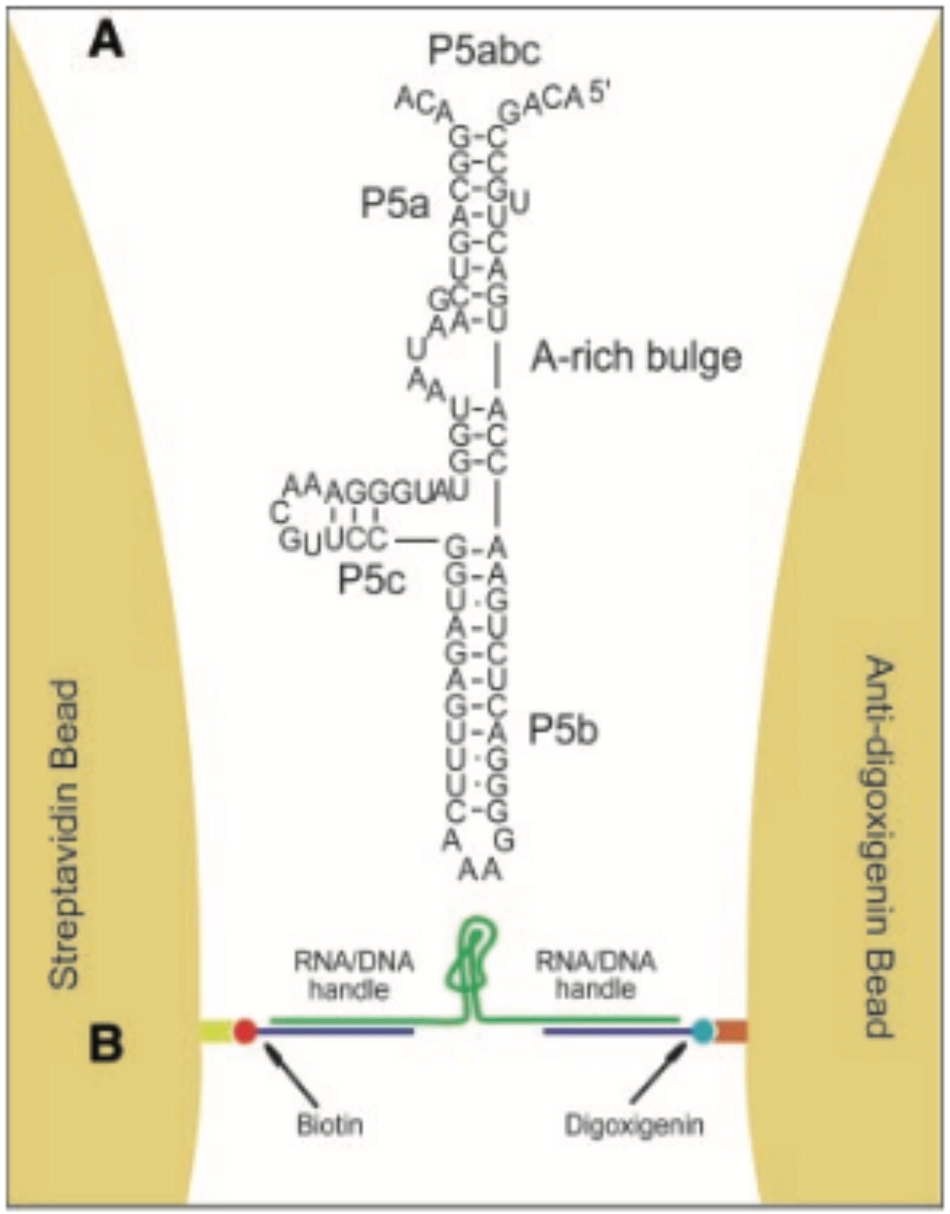
Crooks in 1999, generalized Jarzynski relation. He showed that the ration of probability of work distribution along the forward and the backward path is given as

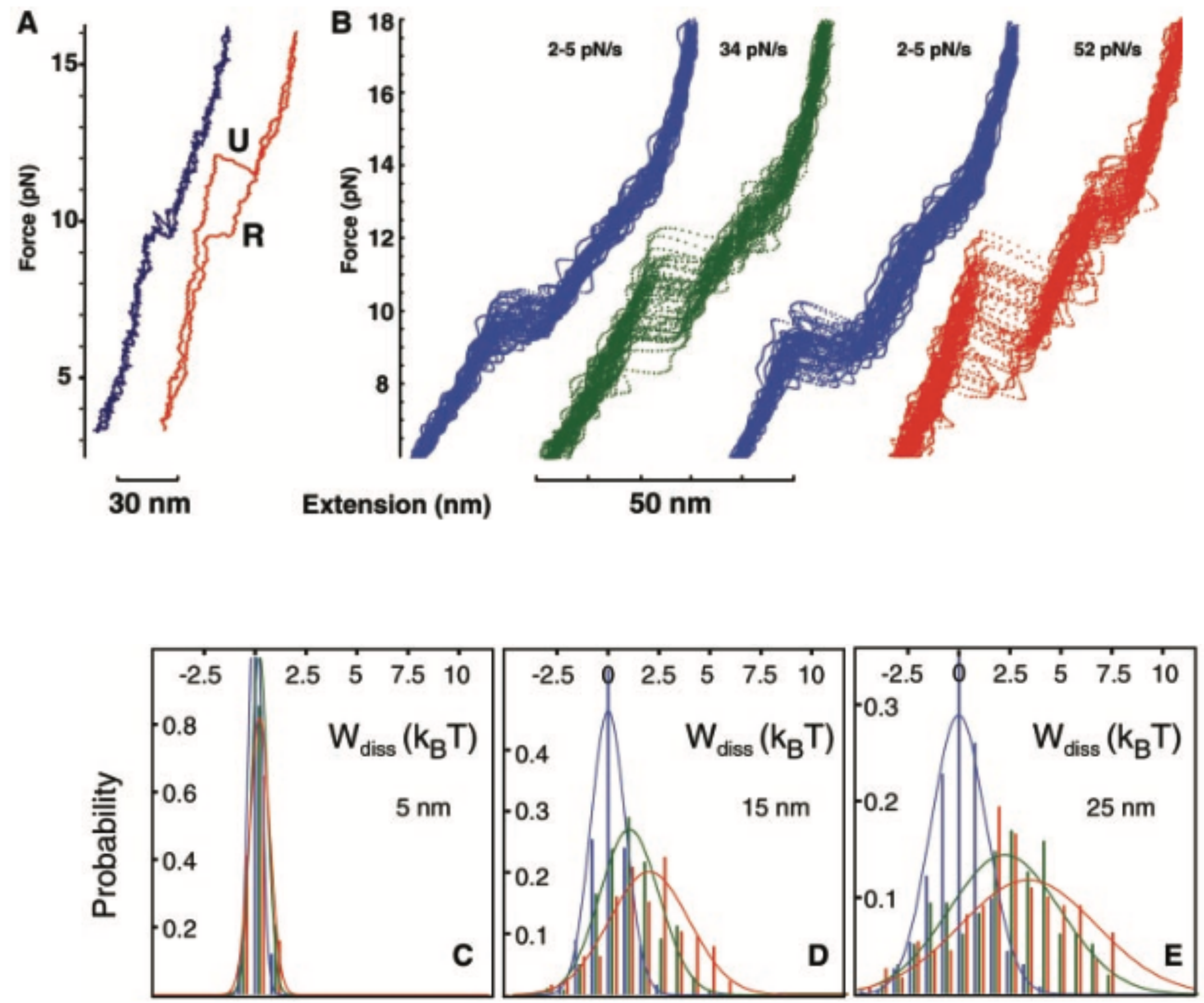
$$\frac{\tilde{p}(-w)}{p(w)} = \exp(-\beta(w - \Delta\mathcal{F}))$$

- 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.

Crooks, PRE 1999

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

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

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

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

First law at single trajectory level

The first law can be identified from the Langevin equation as

$$dw = dV + dq$$

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

Contributions from non-conservative force

Work done at fixed particle position

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Work done at fixed particle position

Plugging above in Langevin equation gives heat dissipated to be

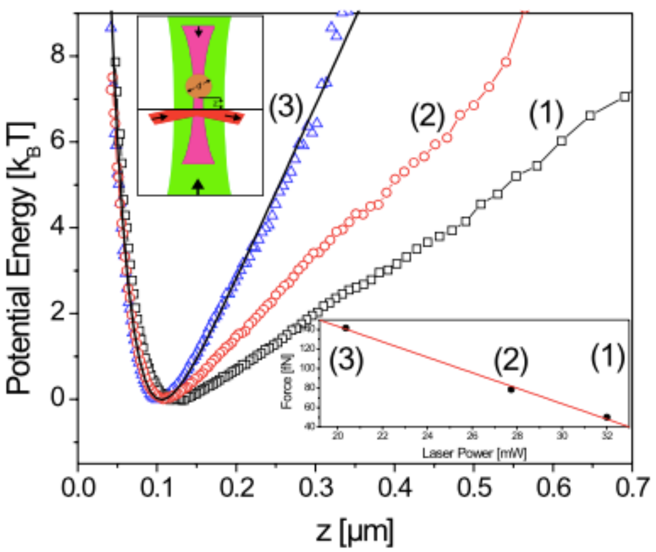
$$dq = dw - dV = F dx = T ds_m$$

Integrating above gives the first law at trajectory level

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

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

Thermodynamics of a colloidal particle



Blickle, Speck, Helden, Seifer and Bechinger PRL 2006

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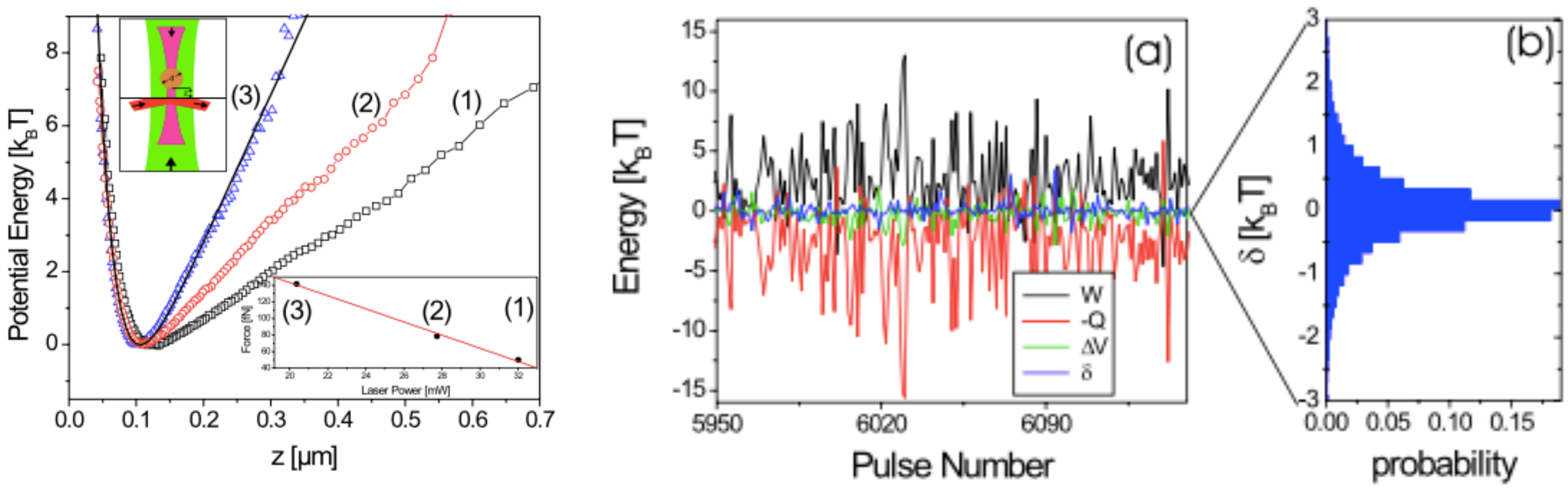

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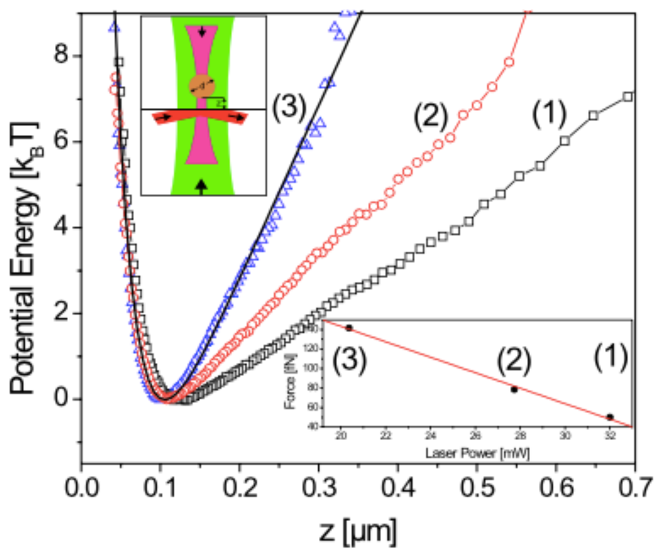

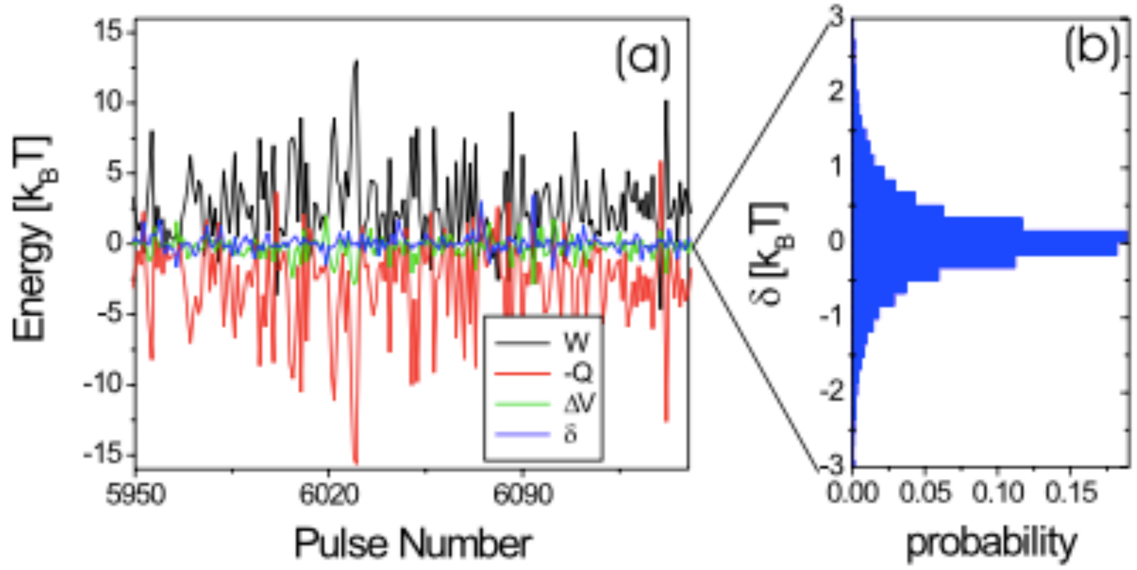

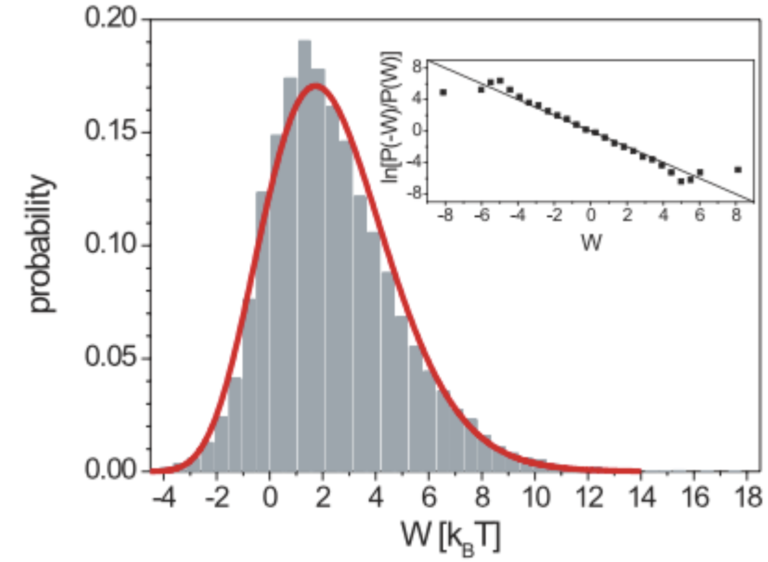

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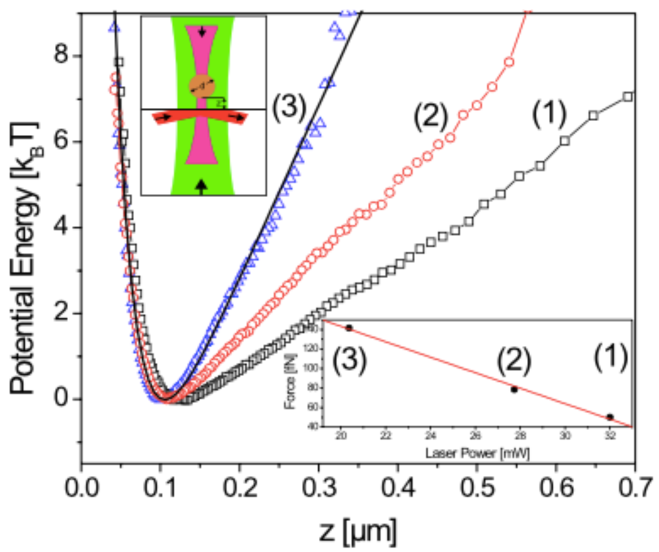

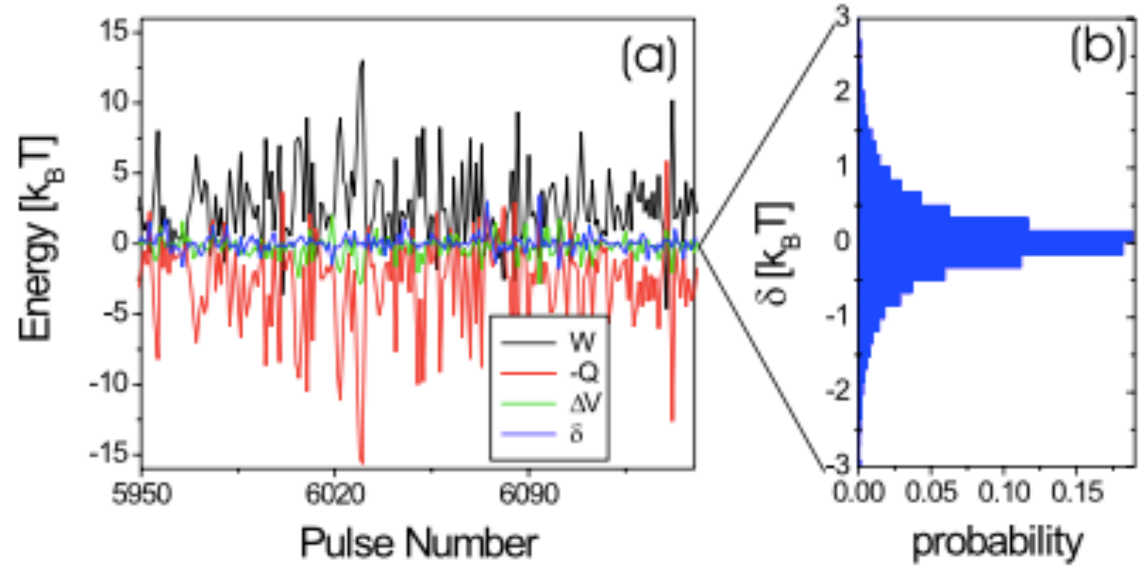

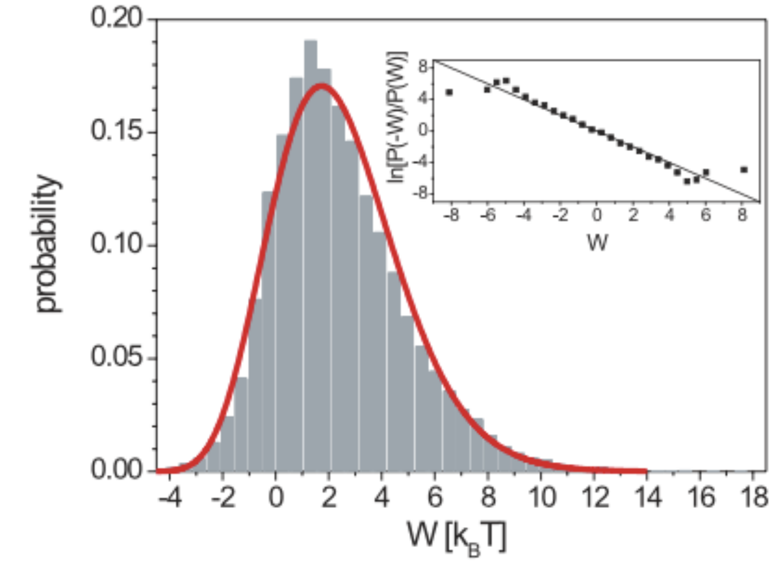

- Charged colloid is repulsed by a wall and is pushed periodically towards it by a laser trap
- The energy, work and heat was measured from the particle trajectory
- They should sum to zero but histogram shows error of the order k_BT.
- The work distribution is non-Gaussian: drive is beyond linear response.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

Blickle, Speck, Helden, Seifer and Bechinger PRL 2006

Path integral representation

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

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

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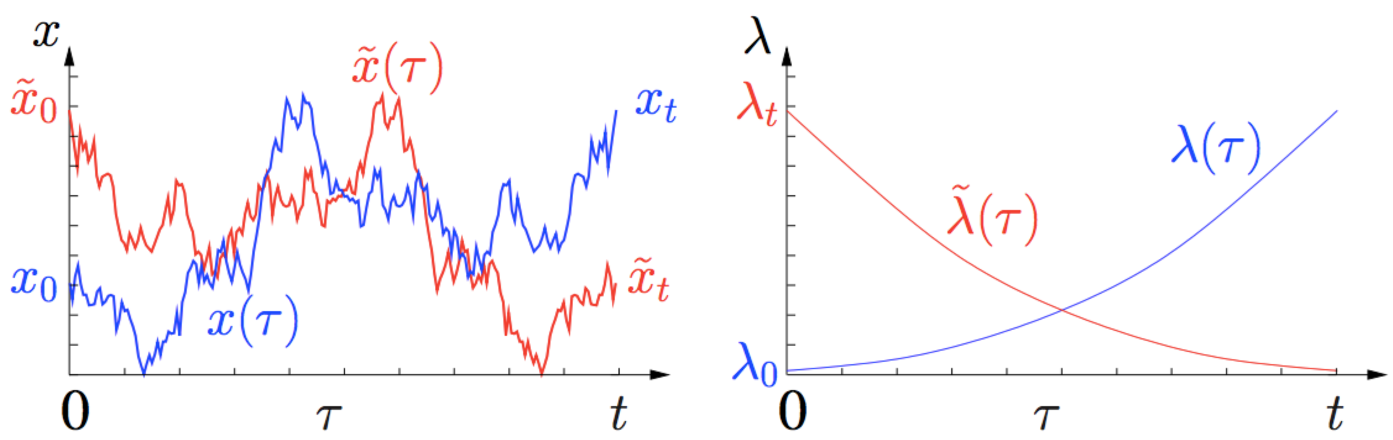

time reversal

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

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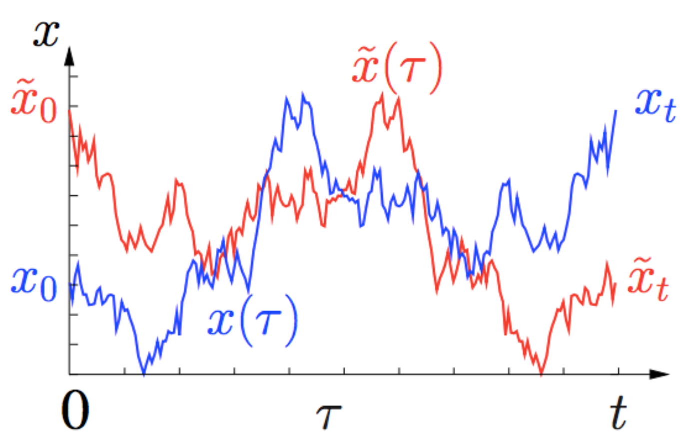

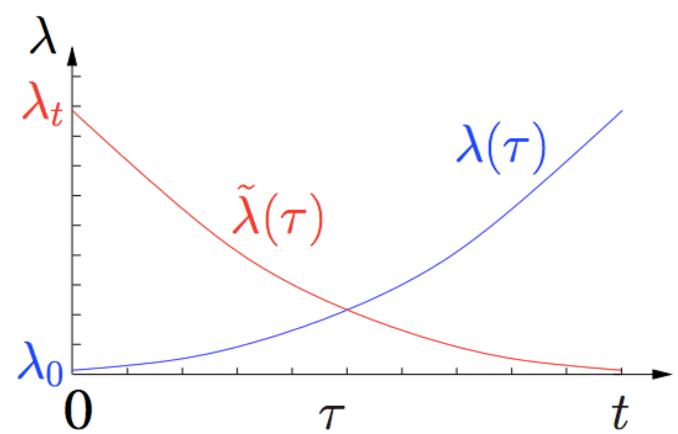

time reversal

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

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

$$\frac{p(x(\tau)|x_0)}{\tilde{p}(\tilde{x}(\tau)|\tilde{x}_0)} = \frac{\exp[-\int_0^t dt\ (\dot{x} - \mu F)^2/4D]}{\exp[-\int_0^t dt\ (\dot{\tilde{x}} - \mu \tilde{F})^2/4D]}$$

$$= \exp\left(\beta \int_0^t d\tau\, \dot{x} F\right) = \exp \Delta s_m$$

Detailed fluctuation theorem

$$1 = \sum_{\tilde{x}(\tau), \tilde{x}_0} \tilde{p}(\tilde{x}(\tau)|\tilde{x}_0) p_1(\tilde{x}_0)$$

Seifert PRL 2005

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Seifert PRL 2005

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$$= \langle \exp[-\Delta s_m]\, p_1(x_t)/p_0 \rangle$$

Seifert PRL 2005

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The above can be rewritten as

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

Seifert PRL 2005

Derivation of Jarzynski relation

From the generalized fluctuation relation we have

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Using these in the fluctuation relation gives Jarzynski relation.

Seifert Rev Prog Phy 2012

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Consider a initial equilibrium distribution of the form

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

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Seifert Rev Prog Phy 2012

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Consider a initial equilibrium distribution of the form

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

We now use the free choice for the last term as

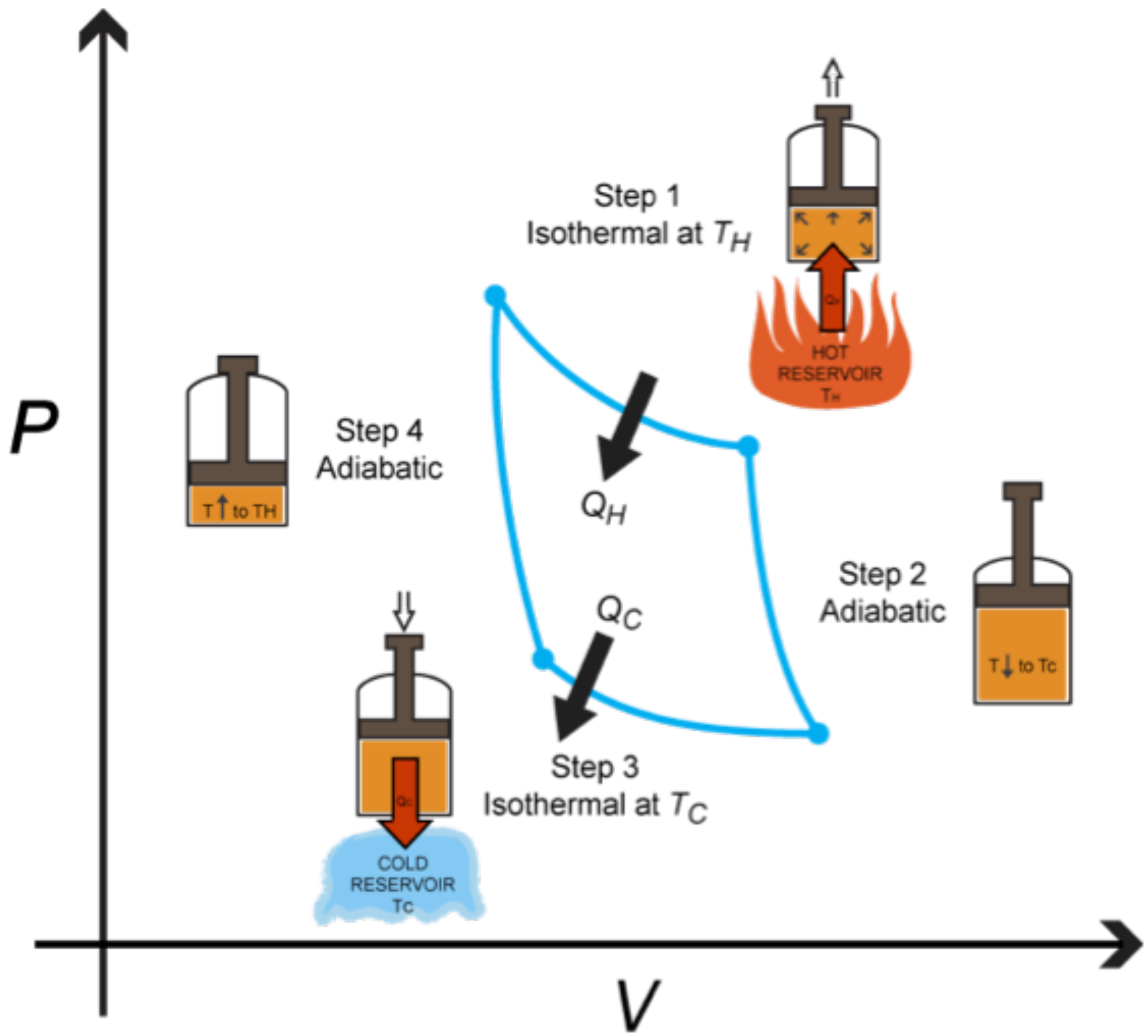
$$p_1(x_t) = \exp[-(V(x_t, \lambda_t) - \mathcal{F}(\lambda_t))]$$

Using these in the fluctuation relation gives Jarzynski relation.

Seifert Rev Prog Phy 2012

Heat engines

The Carnot engine

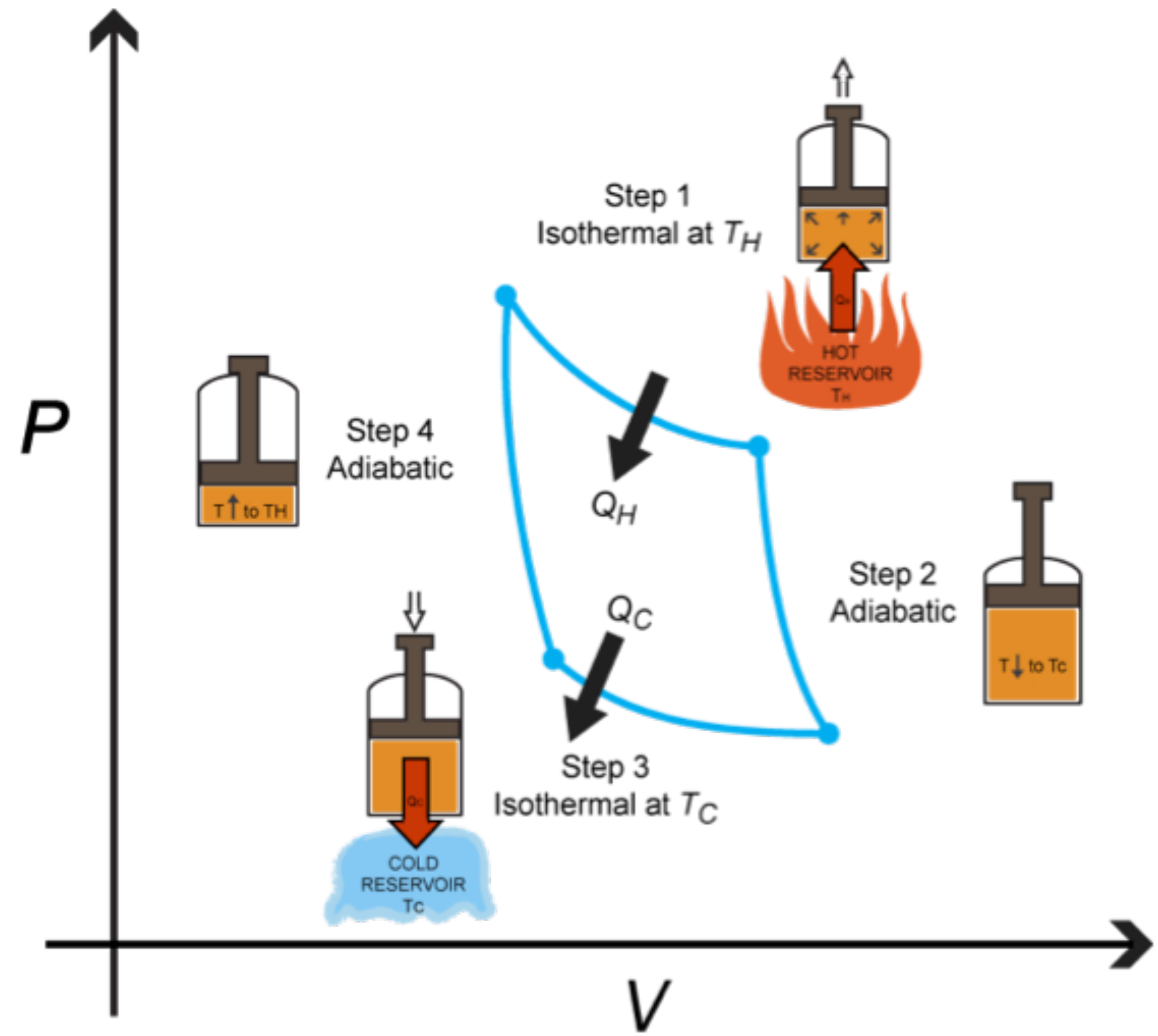


https://www.shmoop.com/thermodynamics/carnot-cycle.html

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.



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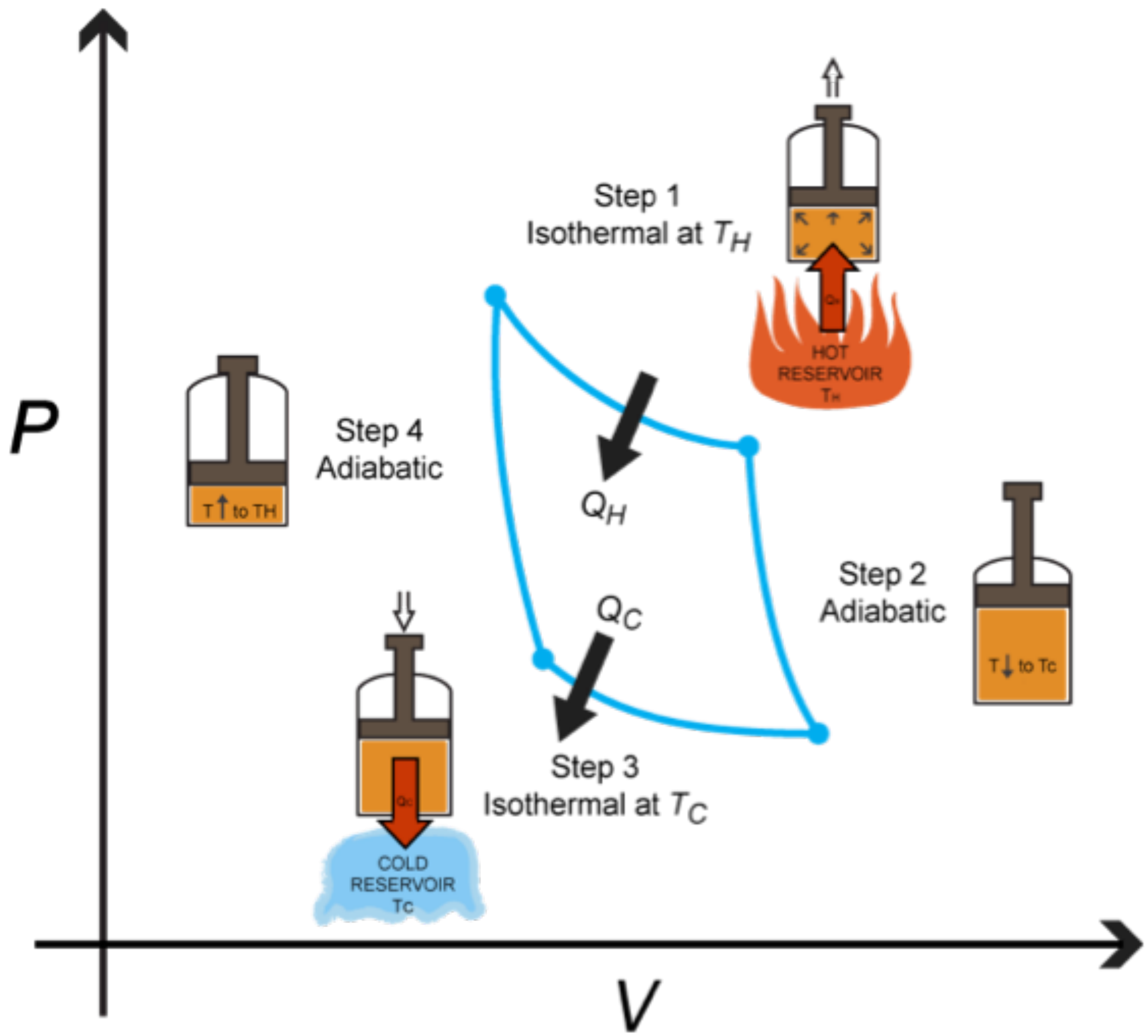
Curzon and Ahlborn (1975) showed the efficienct at maximum power is

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

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



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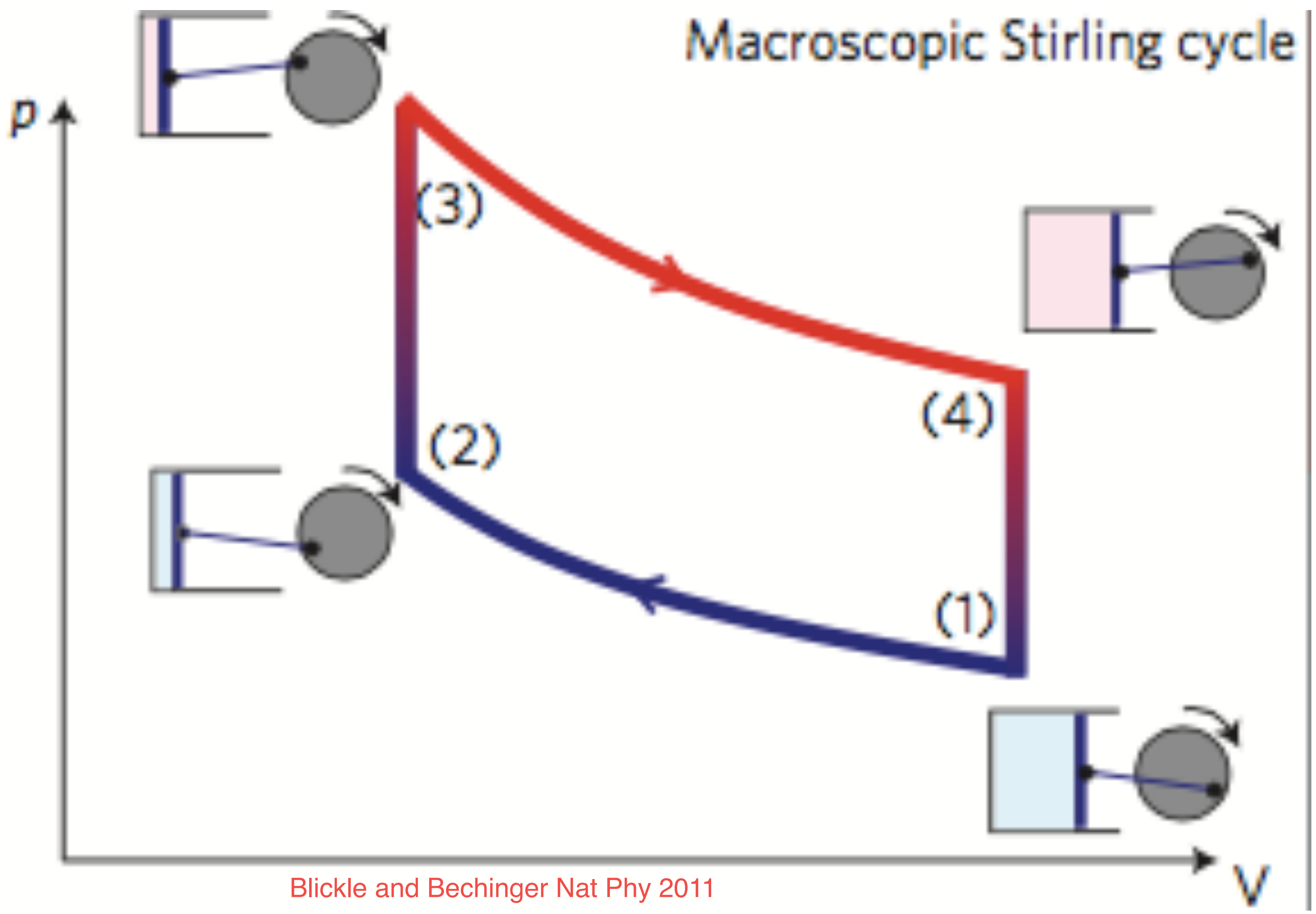
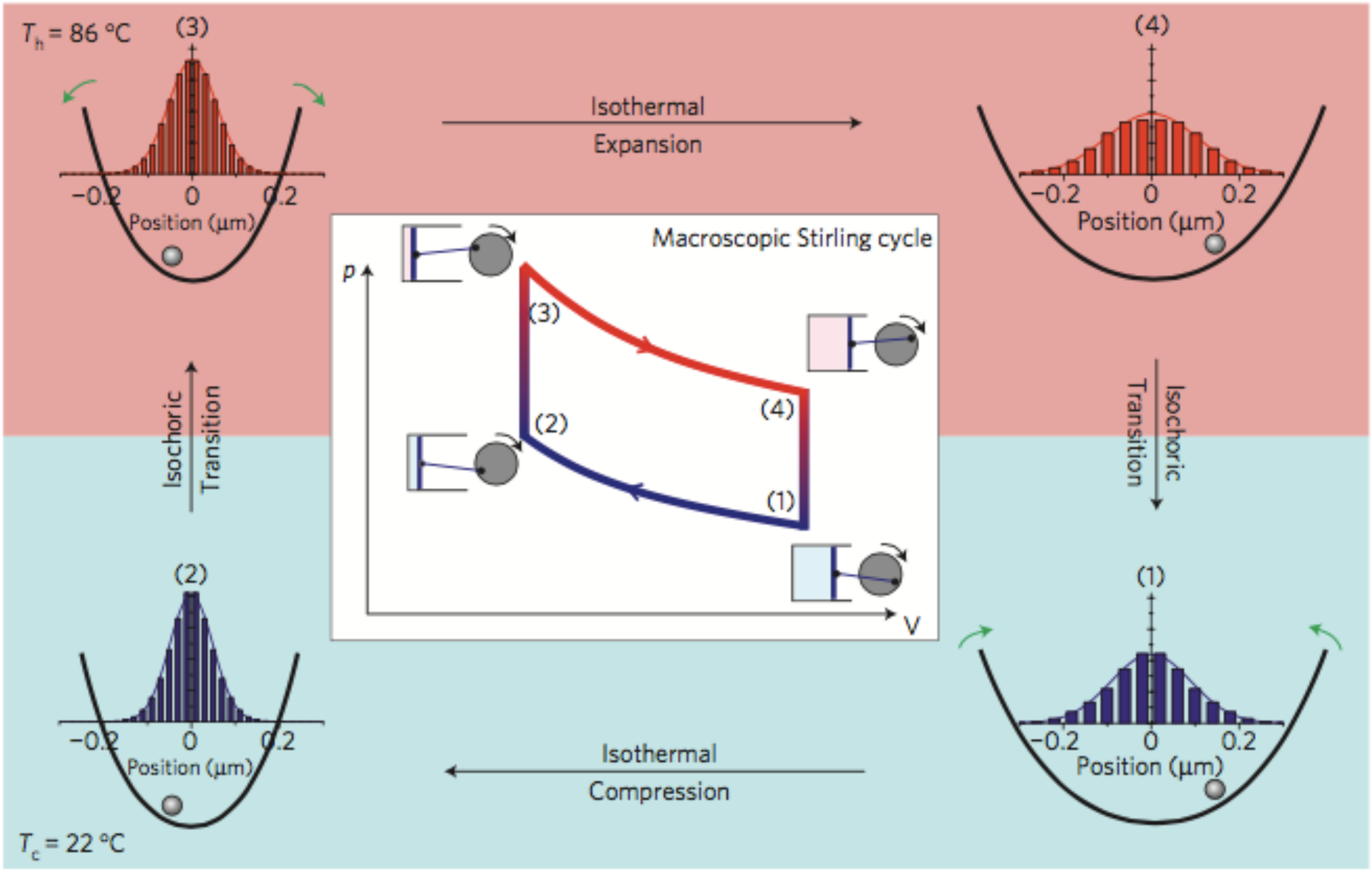
The Stirling engine



Blickle and Bechinger Nat Phy 2011

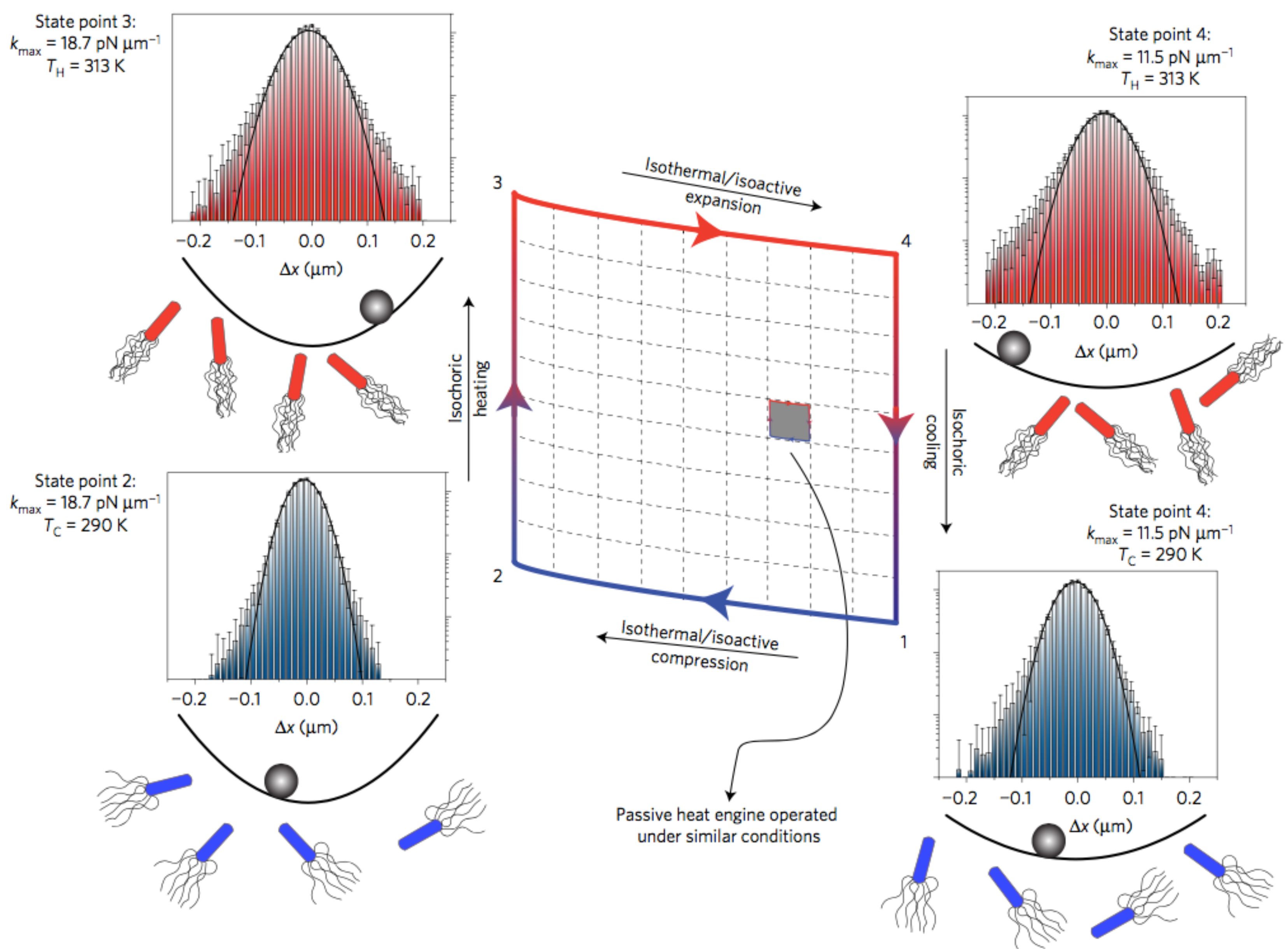
Efficiency of Stirling's engines is same as the Carnot's engine.

Micrometer sized heat engine



Blickle and Bechinger, Nat Phy 2011

Micrometer sized heat engine in Bacterial bath



Krishnamurthy, Ghosh, Chatterji, Ganapathy and Sood, Nat Phy 2016

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 !

Entropy production

Heat dissipated to the environment is identified as

$$\Delta s_m[x(t)] \equiv q[x(\tau)]/T$$

Trajectory dependent entropy

$$s(\tau) = -\ln p(x(\tau), t)$$