Boulder lectures, July 2009

Stochastic thermodynamics

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thanks to:

- F. Berger, J. Mehl, T. Schmiedl and Th. Speck (theory)
- V. Blickle and C. Bechinger (expt's on colloidal particles)
- C. Tietz, S. Schuler and J. Wrachtrup (expt's on single atoms)

Review: U.S., Eur. Phys. J. B, 64 : 423-431, 2008.

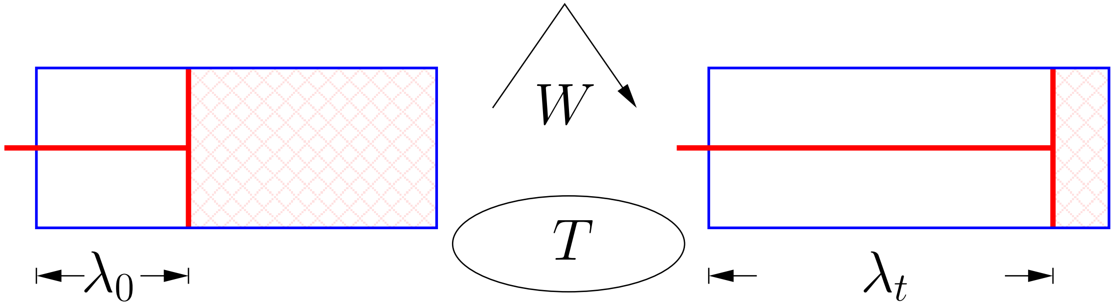
LECTURE I

- Classical vs. stochastic thermodynamics
- First law
- General fluctuation theorem and Jarzynski relation
- Optimization

- Perspective

1820 $\simeq$ 1850	classical thermodynamics	$dW = dU + dQ$ $dS \geq 0$
$\simeq$ 1900	eq stat phys	$p_i = \exp[-(E_i - F)/k_B T]$
1930 $\simeq$ 1960	non-eq: linear response	Onsager Green-Kubo, FDT
$\geq$ 1993	non-eq: beyond linear response stochastic thermodynamics	Fluctuation theorem Jarzynski relation

- Thermodynamics of macroscopic systems [19^{th} cent]



  - First law energy balance:

$$W = \Delta E + Q = \Delta E + T \Delta S_M$$

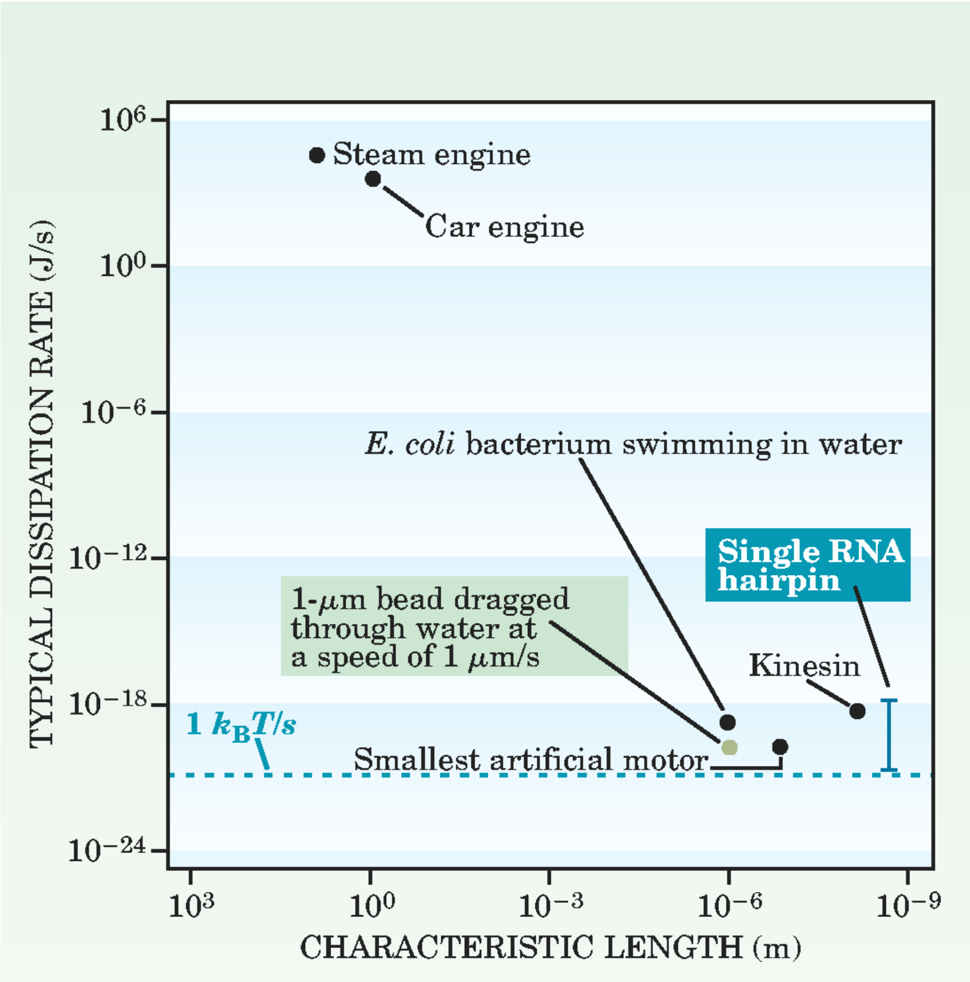
  - Second law:

$$\Delta S_{\text{tot}} \equiv \Delta S + \Delta S_M > 0$$

$$W > \Delta E - T \Delta S \equiv \Delta F$$

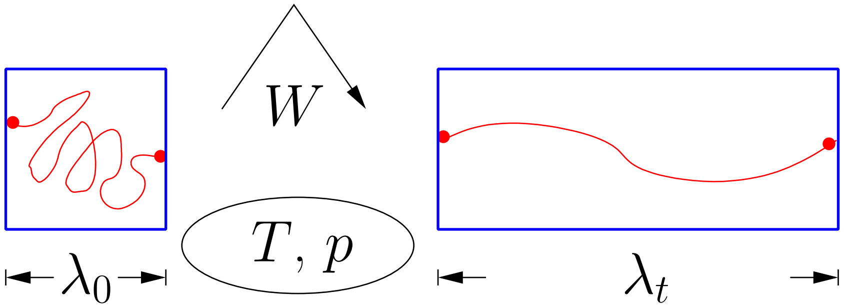
$$W_{\text{diss}} \equiv W - \Delta F > 0$$

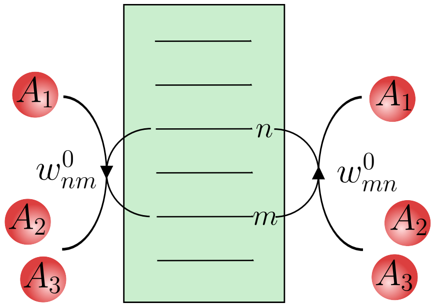
- Macroscopic *vs* mesoscopic *vs* molecular machines



[Bustamante *et al*, Physics Today, July 2005]

- Stochastic thermodynamics for small systems





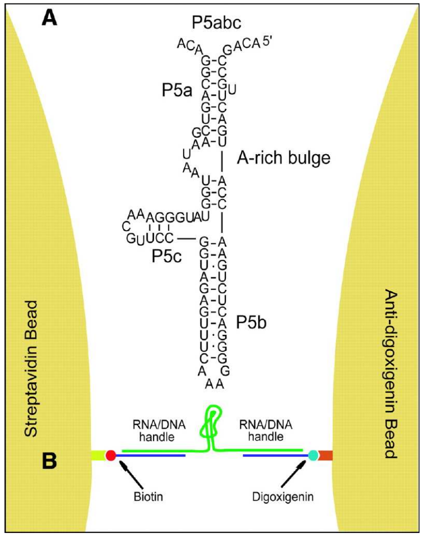
  - First law: how to define work, internal energy and exchanged heat?

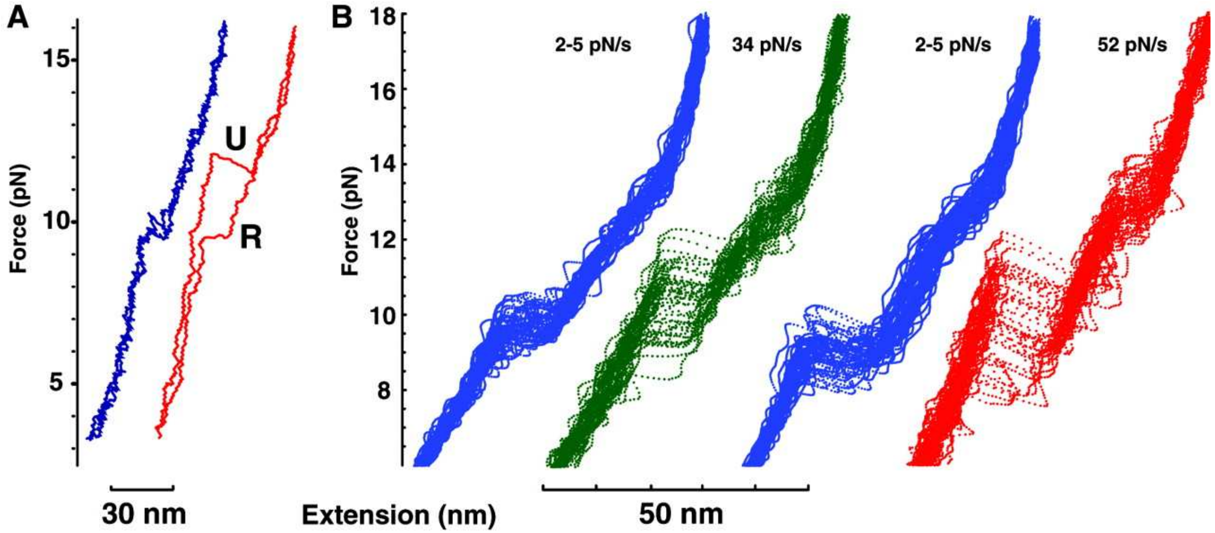
  - fluctuations imply distributions: $p(W; \lambda(\tau))$ ...

  - entropy: distribution as well?

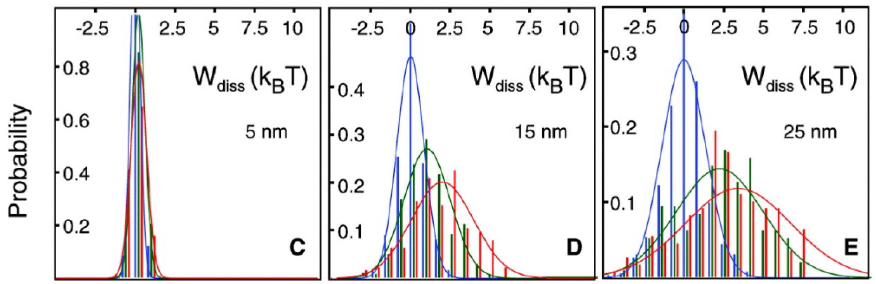
- Nano-world Experiment: Stretching RNA

  [Liphardt et al, Science **296** 1832, 2002.]

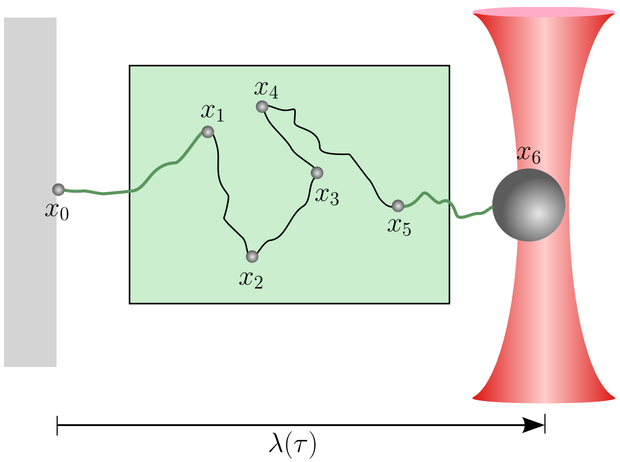




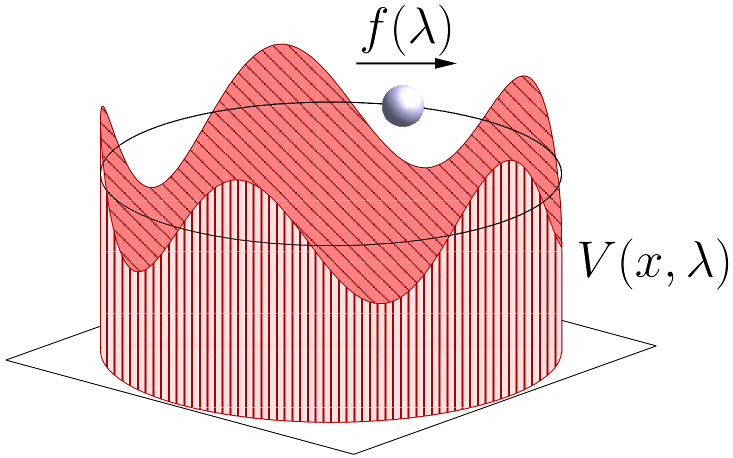
  – distributions of $W_{\rm diss}$:



- Mechanically driven systems

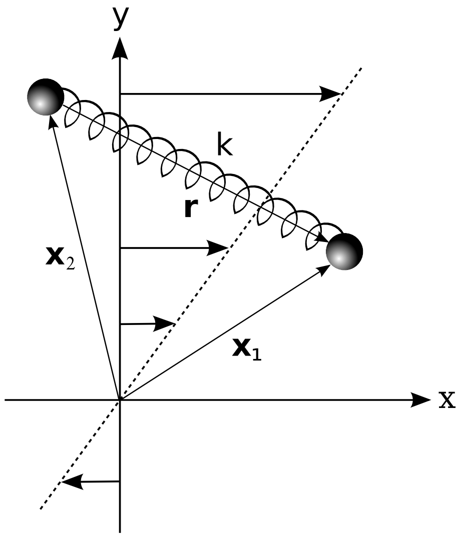


Pulling a biomolecule

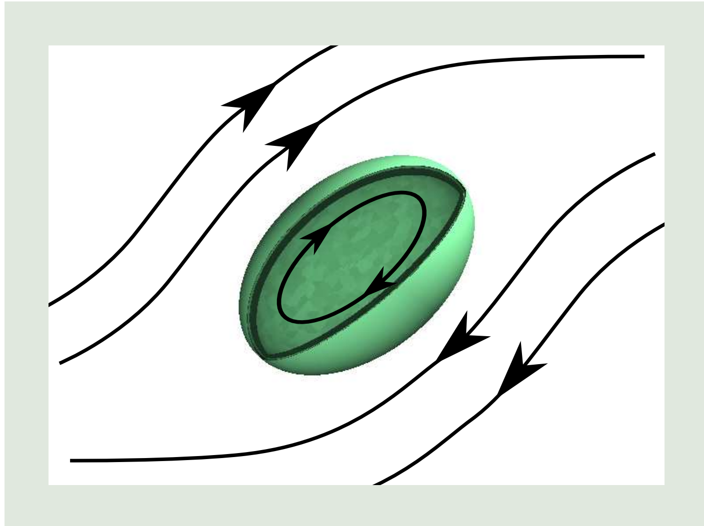


Colloidal partical in a laser trap

- Flow driven systems

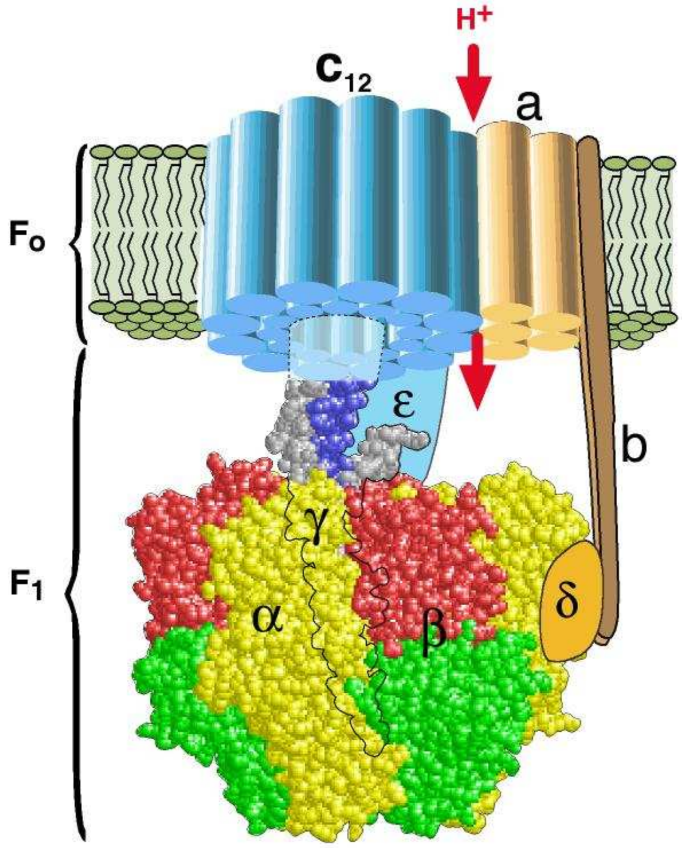


Stretching a polymer (dumbbell)

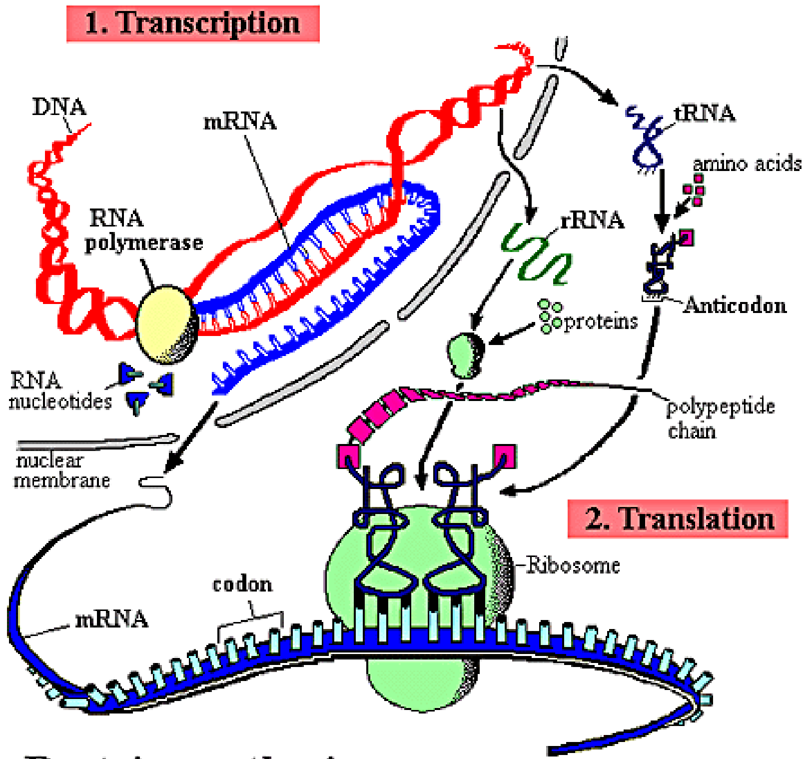


Tank-treading vesicle in shear flow

• (Bio)chemically driven systems



H. Wang and G. Oster (1998). Nature 396:279-282.



Protein synthesis

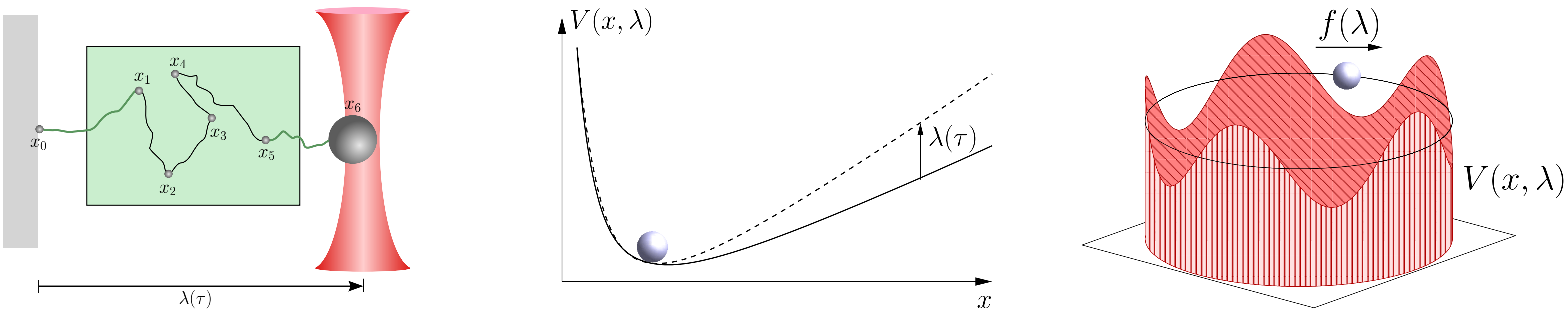
F1-ATPase

- **Stochastic thermodynamics** applies to such systems where
  - non-equilibrium is caused by mechanical or chemical forces
  - ambient solution provides a thermal bath of well-defined T
  - fluctuations are relevant due to small numbers of involved molecules

- Main idea: Energy conservation (1^{st} law) and entropy production (2^{nd} law) along a single stochastic trajectory

- Precursors:
  - notion "stoch th'dyn" by Nicolis, van den Broeck mid '80s (ensemble level)
  - stochastic energetics (1^{st} law) by Sekimoto late '90s
  - work theorem(s): Jarzynski, Crooks late '90s
  - fluct'theorem: Evans, Cohen, Galavotti, Kurchan, Lebowitz & Spohn '90s
  - quantities like stochastic entropy by Crooks, Qian, Gaspard in early '00s
  - ...

- Paradigm for mechanical driving:

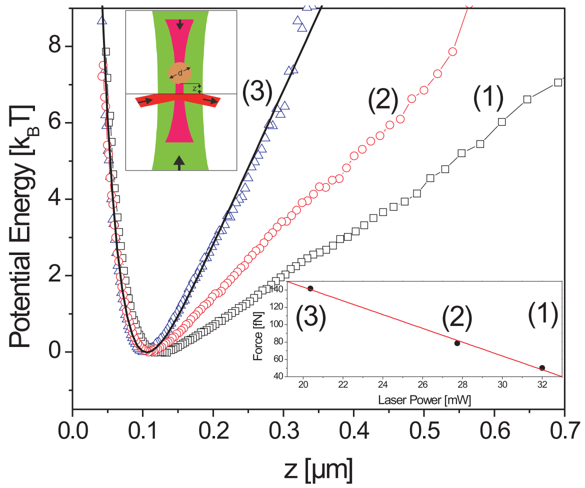


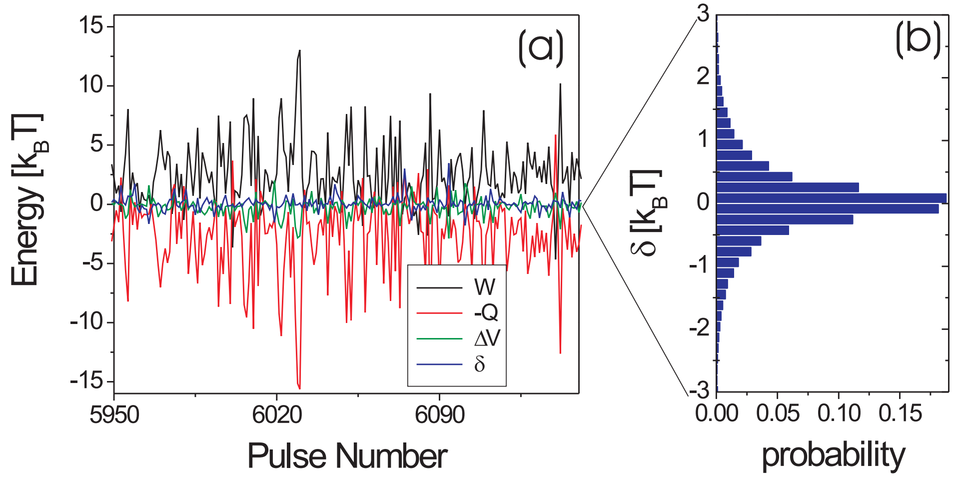
  - Langevin dynamics $\dot{x} = \mu \underbrace{[-V'(x,\lambda) + f(\lambda)]}_{F(x,\lambda)} + \zeta \quad \langle\zeta\zeta\rangle = 2\mu \underbrace{k_B T}_{(\equiv 1)} \delta(\ldots)$
  - external protocol $\lambda(\tau)$

- First law [(Sekimoto, 1997)]: $\boxed{dw = du + dq}$
  - applied work: $dw = \partial_\lambda V(x,\lambda)d\lambda + f(\lambda)dx$
  - internal energy: $du = dV$
  - dissipated heat: $dq = dw - du = F(x,\lambda)dx = T ds_{\text{m}}$

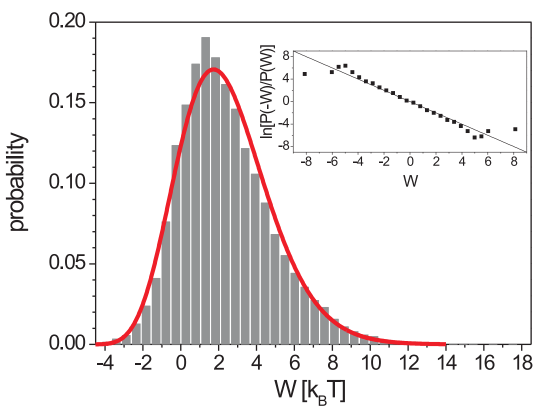
- Experimental illustration: Colloidal particle in $V(x, \lambda(\tau))$

  [V. Blickle, T. Speck, L. Helden, U.S., C. Bechinger, PRL 96, 070603, 2006]





  – work distribution



  – non-Gaussian distribution $\Rightarrow$

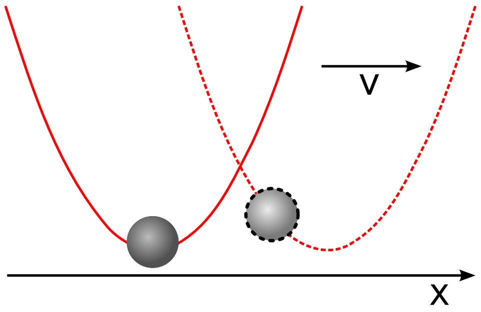
  – Langevin valid beyond lin response

  [T. Speck and U.S., PRE 70, 066112, 2004]

- Role of external flow and frame invariance

  [T. Speck, J. Mehl and U.S., PRL **100** 178302, 2008]

Lab frame

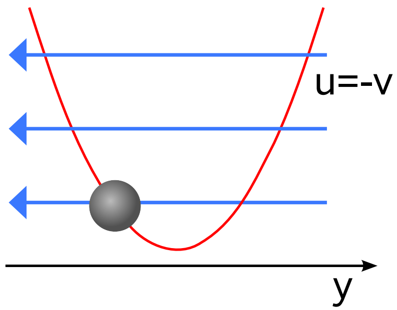


$$V(x,\tau) = k(v\tau - x)^2/2$$

$$\dot{x} = \mu k(v\tau - x) + \zeta$$

$$\dot{w} = \partial_\tau V = kv(v\tau - x(\tau)) \neq 0$$

comoving frame:
$y \equiv x(\tau) - v\tau$



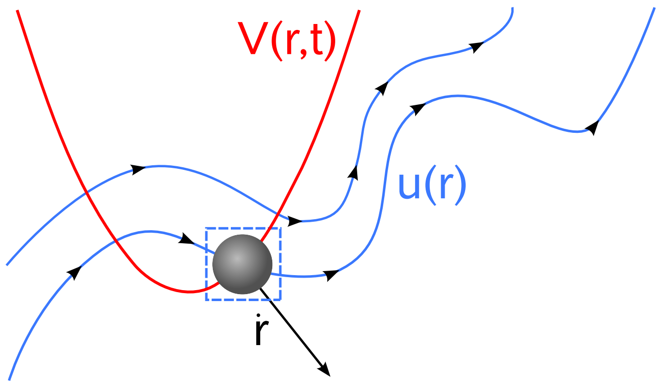
$$V(y) = ky^2/2$$

$$\dot{y} = -\mu k y - v + \zeta$$

$$\dot{w} = \partial_\tau V = 0 \quad ??$$

det balance satisfied: equilibrium ??

- Correct definitions of th'dynamic quantities

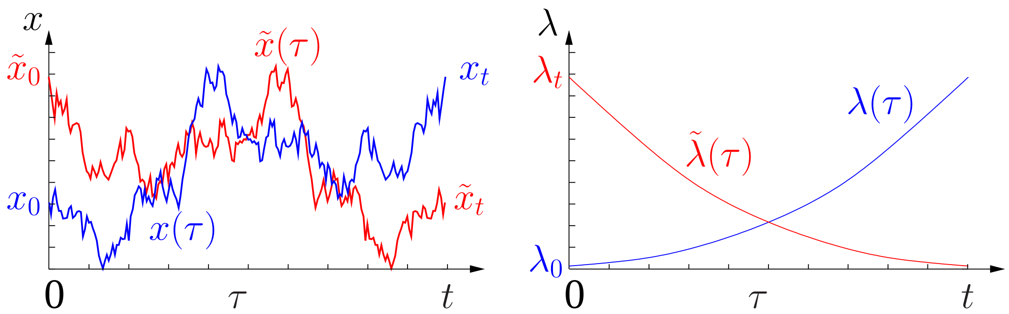


no flow	flow $u(\mathbf{r}) \neq 0$	
$dw = \partial_t V + \mathbf{f} d\mathbf{r}$	$dw \equiv D_t V + \mathbf{f}[d\mathbf{r} - \mathbf{u} dt]$	$(D_t \equiv \partial_t + \mathbf{u}\nabla)$
$dq = (-\nabla V + \mathbf{f}) d\mathbf{r}$	$dq \equiv (-\nabla V + \mathbf{f})(d\mathbf{r} - \mathbf{u} dt)$	

- Path integral representation
  - "Boltzmann factor for a whole trajectory"

$$p[\zeta(\tau)] \sim \exp\ [-\int_0^t d\tau\ \zeta^2(\tau)/4D]$$

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



  - "time reversal" $\tilde{x}(\tau) \equiv x(t-\tau)$ and $\tilde{\lambda}(\tau) \equiv \lambda(t-\tau)$
  - Ratio of forward to reversed path

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

$$= \exp\ \beta \int_0^t d\tau\ \dot{x}F = \exp\ \beta q[x(\tau)] = \exp \Delta s_m$$

- General fluctuation theorem

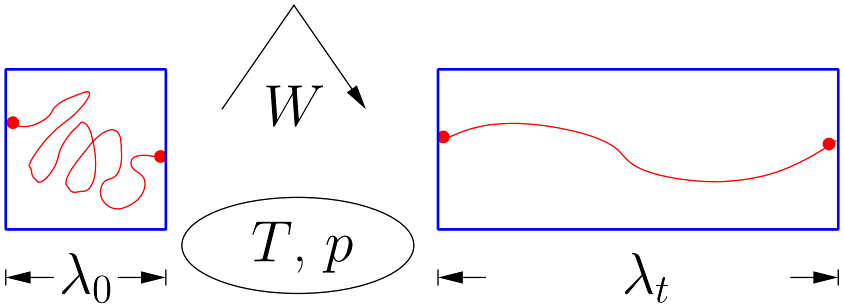
  [U.S., PRL **95**, 040602, 2005; generalizing Jarzynski, Crooks, Maes]

$$
\begin{aligned}
1 &= \sum_{\tilde{x}(\tau),\tilde{x}_0} \tilde{p}[\tilde{x}(\tau)|\tilde{x}_0]\; p_1(\tilde{x}_0) \\
&= \sum_{x(\tau),x_0} p[x(\tau)|x_0]\; p_0(x_0) \frac{\tilde{p}[\tilde{x}(\tau)|\tilde{x}_0]\; p_1(\tilde{x}_0)}{p[x(\tau)|x_0]\; p_0(x_0)} \\
&= \langle \exp[\underbrace{-\beta q[x(\tau)]}_{-\Delta s_{\rm m}} + \ln p_1(x_t)/p_0(x_0)] \rangle
\end{aligned}
$$

  – for arbitrary initial condition $p_0(x)$

  – for arbitrary (normalized) function $p_1(x_t)$

- Jarzynski relation (PRL, 1997)



2^{nd} law:
$\langle W \rangle_{|\lambda(\tau)} \geq \Delta F \equiv F(\lambda_t)) - F(\lambda_0)$

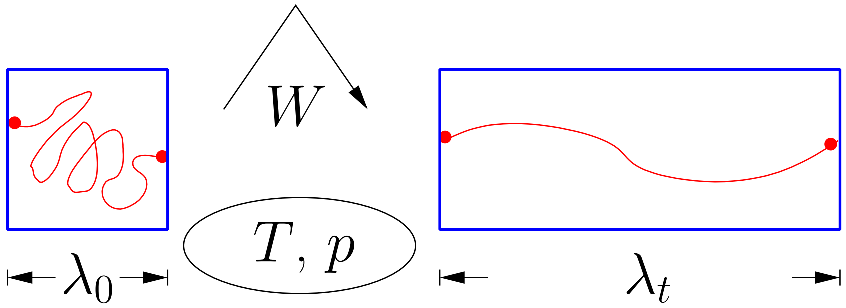
– $\boxed{\langle \exp[-W] \rangle = \exp[-\Delta F]}$ $\quad (k_B T = 1)$

– Short proof: $1 = \langle \exp[\underbrace{-q[x(\tau)]}_{-\Delta s_m} + \ln p_1(x_t)/p_0(x_0)] \rangle$

  * $p_0(x_0) \equiv \exp[-(V(x_0, \lambda_0) - F(\lambda_0)]$
  * $p_1(x_t) \equiv \exp[-(V(x_t, \lambda_t) - F(\lambda_t)]$

– within stochastic dynamics an identity!

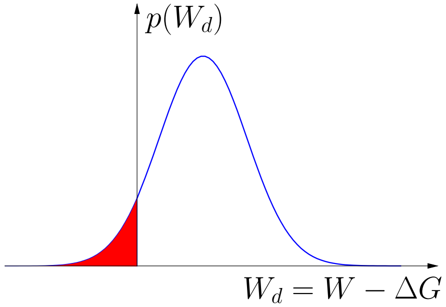
- Jarzynski (cont'd) $(k_B T = 1)$

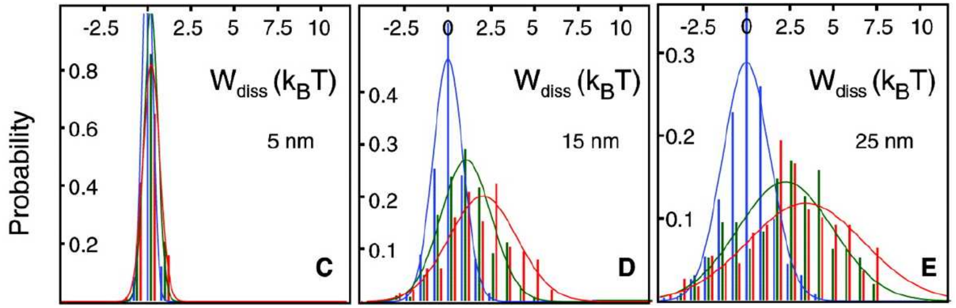


  - $\boxed{\langle e^{-W} \rangle_{|\lambda(\tau)} \stackrel{!}{=} e^{-\Delta F}}$
  - start with initial thermal distribution
  - valid for any protocol $\lambda(\tau)$
  - valid beyond linear response
  - allows to extract free energy differences from non-eq data
  - "implies" a variant of the second law
    $\langle e^x \rangle \geq e^{\langle x \rangle} \quad \Rightarrow \quad \langle W \rangle \geq \Delta F$

- Dissipated work $W_d \equiv W - \Delta G$

  – $\langle \exp[-W_d] \rangle \equiv \int_{-\infty}^{+\infty} dW_d \, p(W_d) \exp[-W_d] = 1$





  – red events "violate the second law" (??)

  – Special case: Gaussian distribution

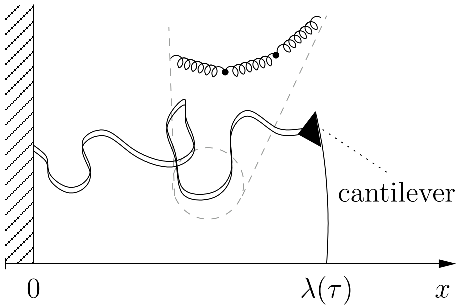
$$p(W_d) \sim \exp[-(W_d - \langle W_d \rangle)^2 / 2\sigma^2] \qquad \text{with} \qquad \langle W_d \rangle = \sigma^2/2$$

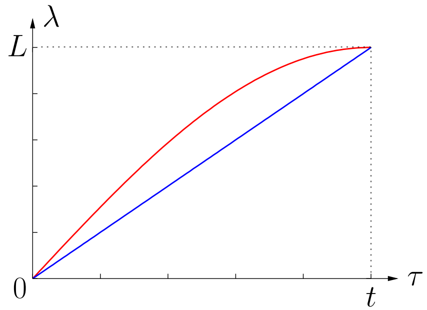
    * scenario 1: slow driving of any process

      [T. Speck and U.S., Phys. Rev E **70**, 066112, 2004]

- Scenario 2: linear equations of motion and arbitrary driving

  Ex: Stretching of Rouse polymer [T.S. and U.S., EPJ B 43, 521, 2005]



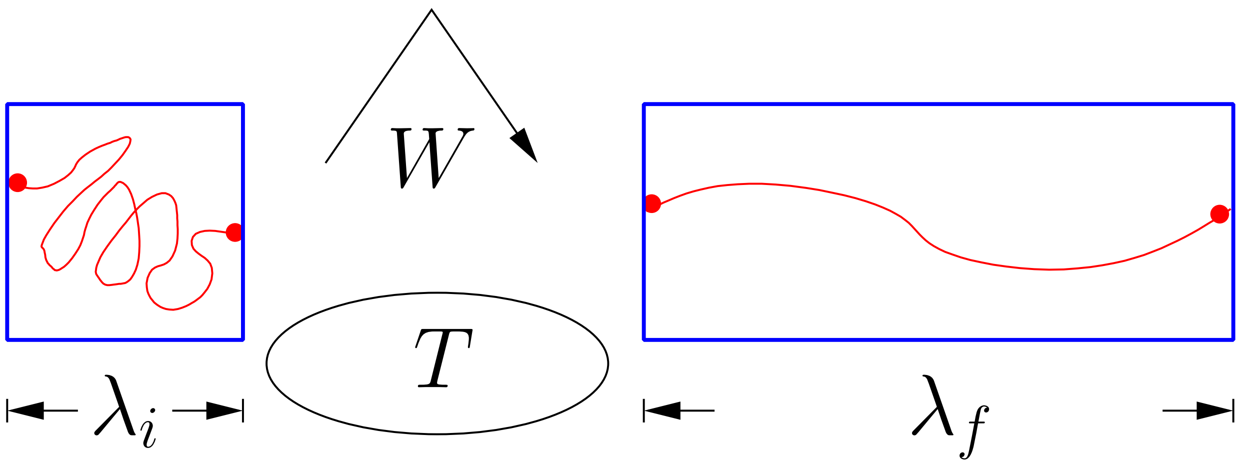


  – different protocols

    * linear: $\lambda(\tau) = \tau L/t \quad \Rightarrow \quad \langle W_d \rangle = (N\gamma/3)L^2/t$
    * periodic: $\lambda(\tau) = L \sin \pi\tau/2t \quad \Rightarrow \langle W_d \rangle = [\pi^2/8](N\gamma/3)L^2/t$

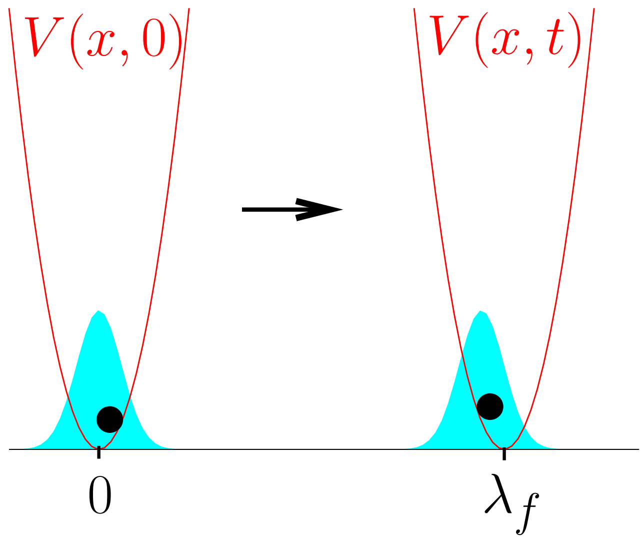
- Optimal finite-time processes in stochastic thermodynamics

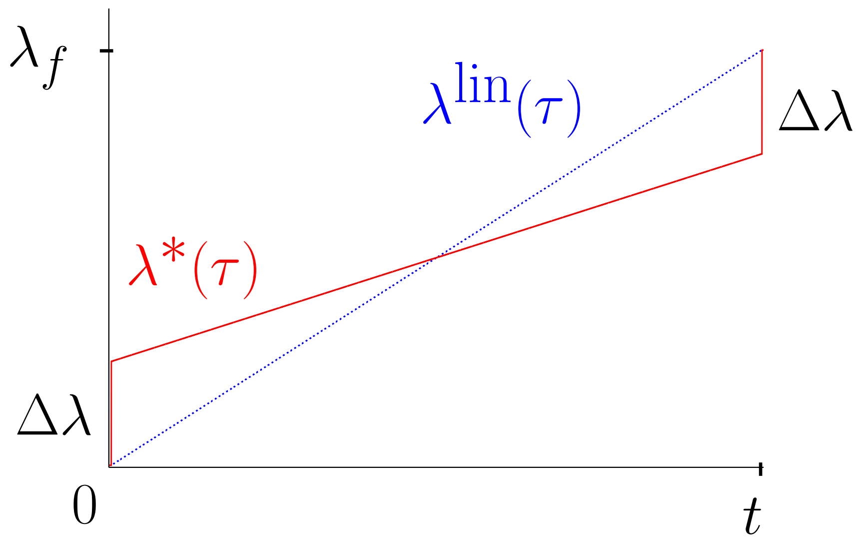
  [T. Schmiedl and U.S., PRL 98, 108301, 2007]



  – optimal protocol $\lambda^*(\tau)$ minimizes $\langle W \rangle$ for given λ_i, λ_f and finite t

- Ex 1: Moving a laser trap $V(x, \lambda) = (x - \lambda(\tau))^2/2$

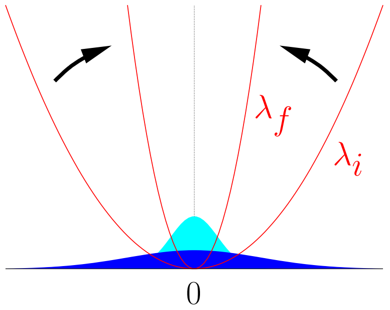


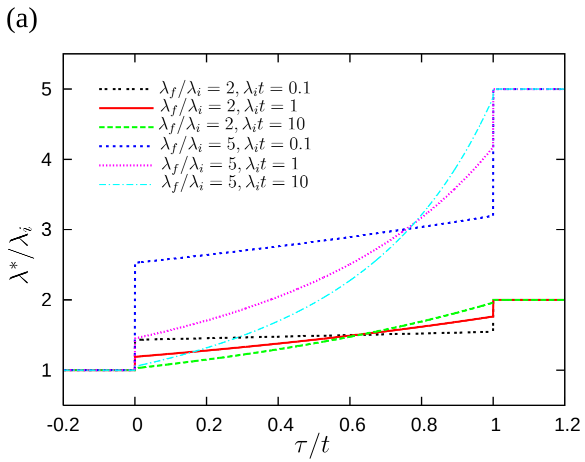


  - $\lambda^*(\tau)$ requires jumps at beginning and end $\qquad \Delta\lambda = \lambda_f/(t+2)$

  - gain $\qquad 1 \geq W^*(t)/W^{lin}(t) \geq 0.88$

- Ex 2: Stiffening trap $V(x, \lambda) = \lambda(\tau) x^2/2$





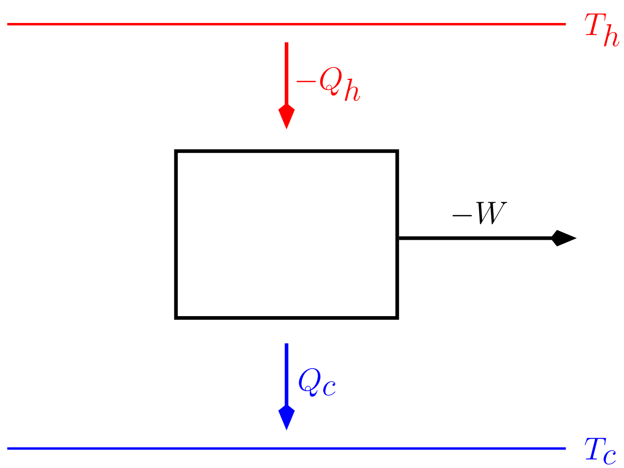
  - jumps are generic

  - should help to improve convergence of $\langle \exp(-W) \rangle$

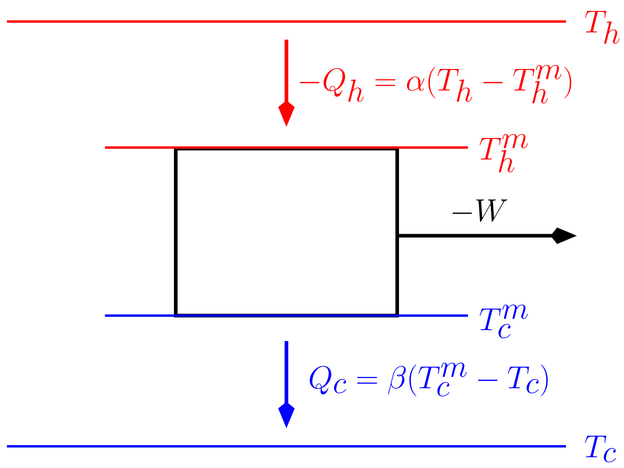
  - generalization: underdamped dynamics $\Rightarrow$ delta-peaks

    [A. Gomez-Marin, T.Schmiedl , U.S., J. Chem. Phys., 129 : 024114, 2008]

- Heat engines at maximal power
  - Carnot (1824)



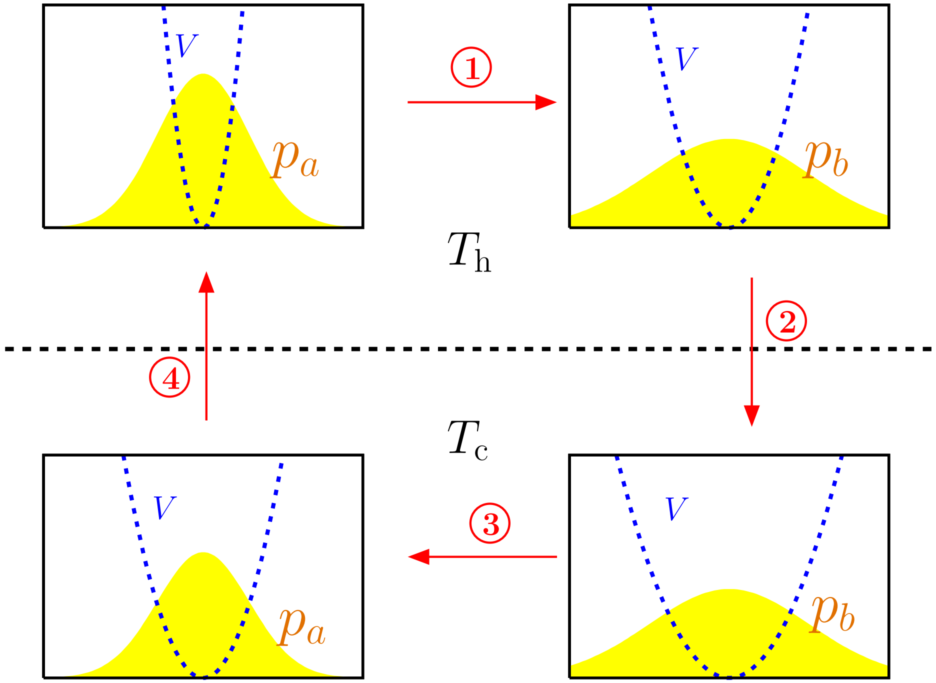
  - $\eta_c \equiv 1 - T_c/T_h$
    but zero power
  - Curzon-Ahlborn (1975)

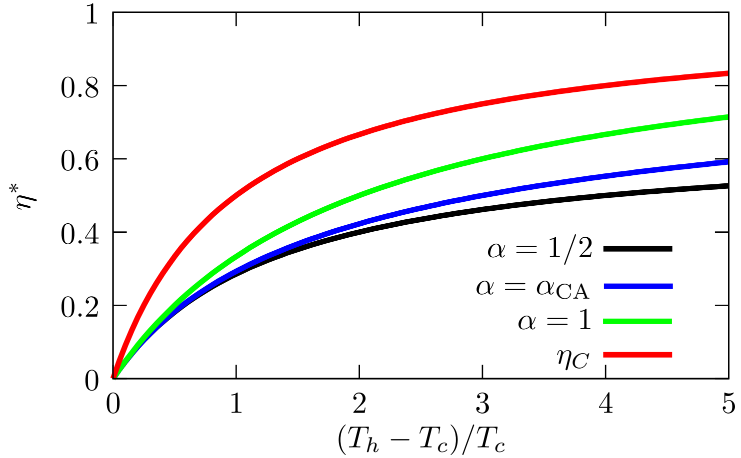


  - efficiency at maximum power
    $\eta_{ca} \equiv 1 - \sqrt{T_c/T_h}$
  - recent claims for universality(?)
  - what about fluctuations?

- Brownian heat engine at maximal power

[T. Schmiedl and U.S., EPL **81**, 20003, (2008)]





– $\eta^* = \frac{\eta_c}{2-\alpha\eta_c}$ with $\alpha = 1/2$ for temp-independent mobility

– Curzon-Ahlborn neither universal nor a bound

- Optimizing potentials for temperature ratchets

  [F. Berger, T. Schmiedl, U.S., PRE **79**, 031118, 2009]