Onsager Lecture, Kanpur Jan 2010

Stochastic Thermodynamics:

Theory and Experiments

Udo Seifert

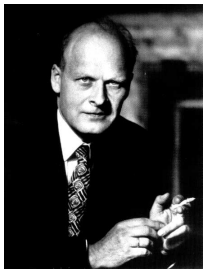
II. Institut für Theoretische Physik, Universität Stuttgart

Acknowledgments:

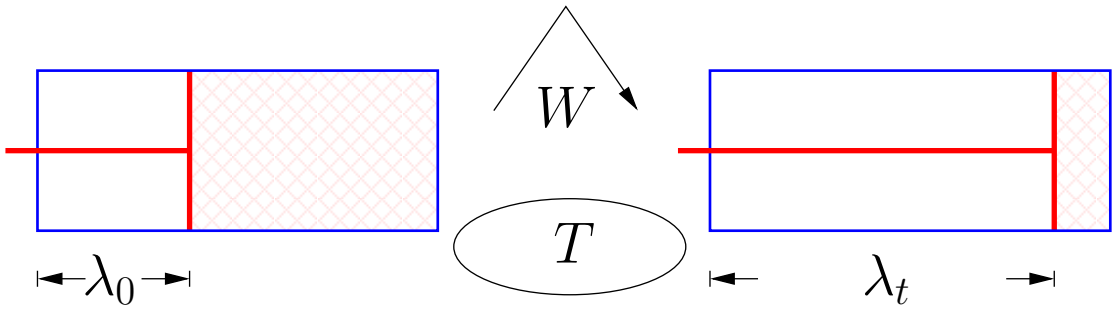
- F. Berger, J. Mehl, T. Schmiedl and Th. Speck (Theory)
- V. Blickle and C. Bechinger (Colloids)
- C. Tietz, S. Schuler and J. Wrachtrup (Single molecules)

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

- 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	 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:

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

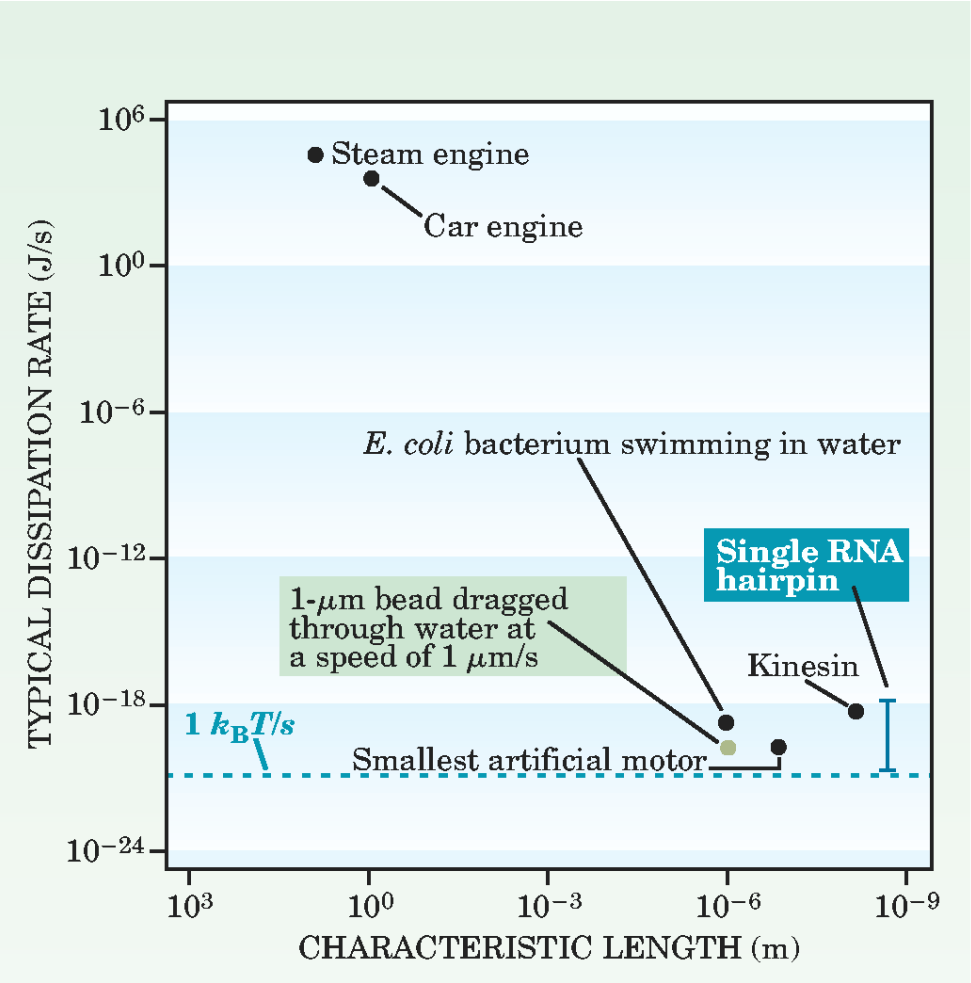
  - Second law:

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

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

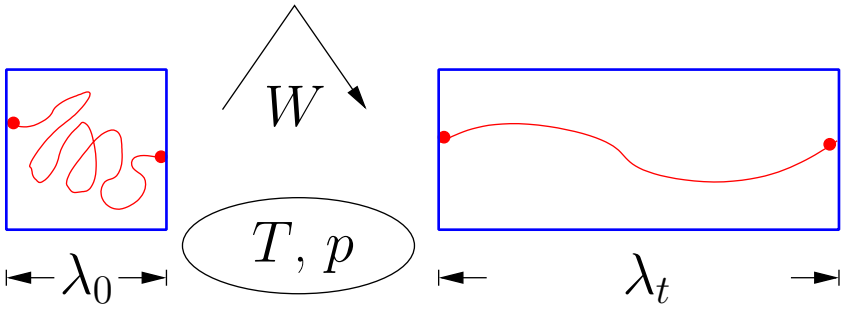
$$W_{\text{diss}} \equiv W - \Delta F > 0$$

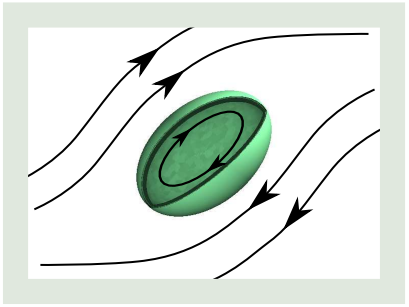
- Macroscopic *vs* mesoscopic *vs* molecular machines

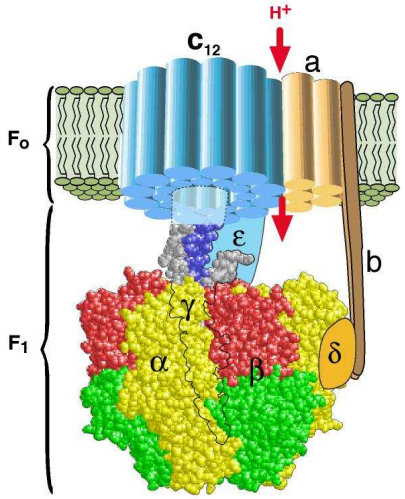


[Bustamante *et al*, Physics Today, July 2005]

- Stochastic thermodynamics for small systems







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

driving: mechanical hydrodynamical (bio)chemical

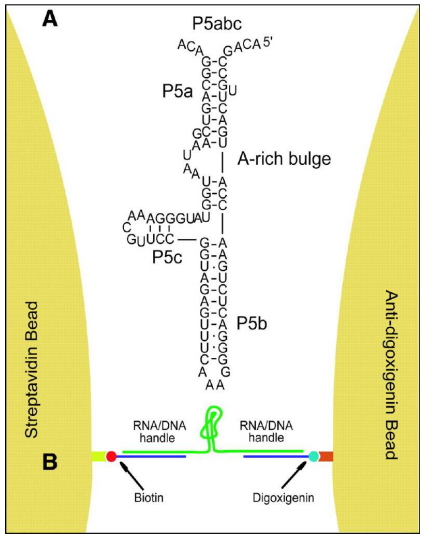
– First law: how to define work, internal energy and exchanged heat?

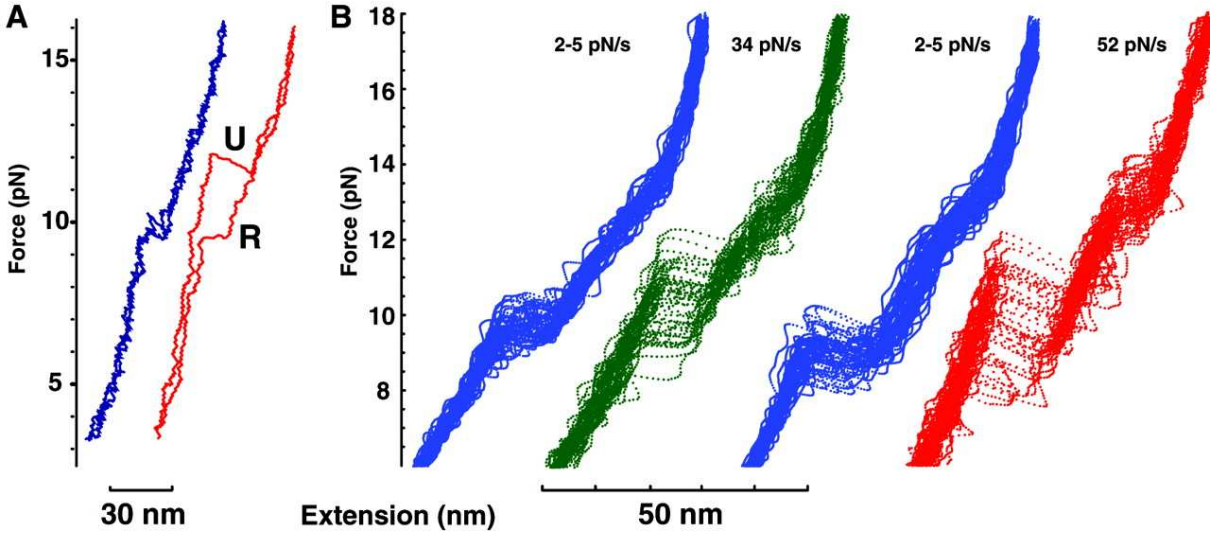
– fluctuations imply distributions: $p(W; \lambda(\tau))$ ...

– entropy: distribution as well?

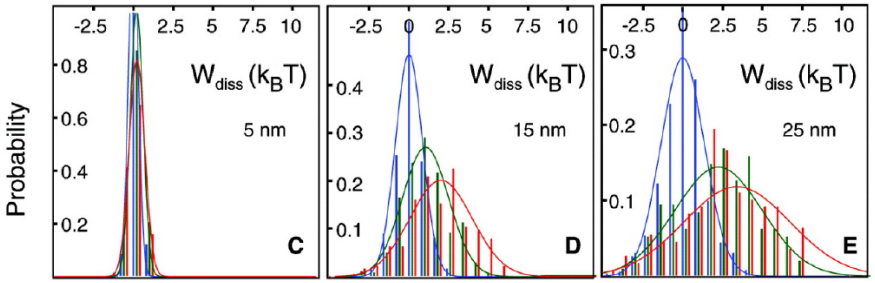
- Nano-world Experiment: Stretching RNA

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





– distributions of W_{diss}:

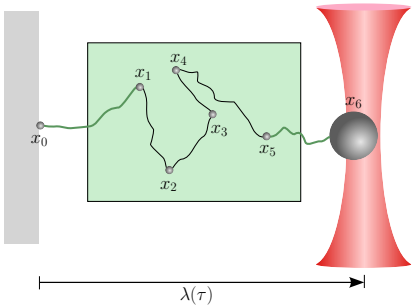


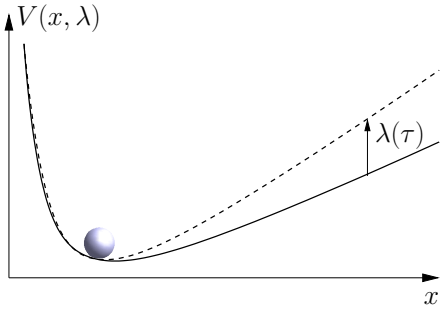
- **Stochastic thermodynamics** applies to such systems where
  - non-equilibrium is caused by mechanical or chemical forces
  - ambient solution provides a thermal bath of well-defined T
  - fluctuations are relevant due to small numbers of involved molecules

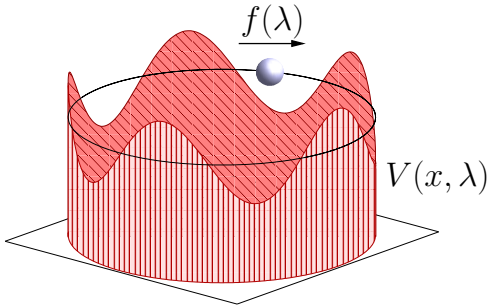
- Main idea: Energy conservation (1^{st} law) and entropy production (2^{nd} law) along an individual stochastic trajectory

- 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:





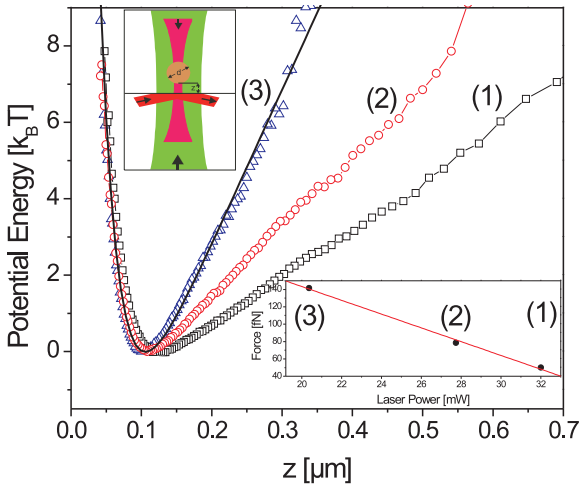


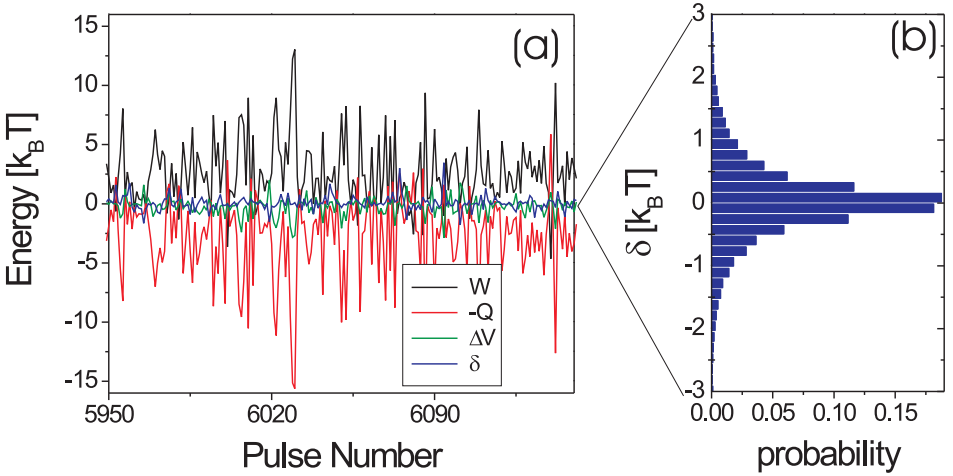
  - Langevin dynamics $\dot{x} = \mu \underbrace{[-V'(x,\lambda) + f(\lambda)]}_{F(x,\lambda)} + \zeta \qquad \langle \zeta\zeta \rangle = 2\mu \underbrace{k_B T}_{(\equiv 1)}$
  - external protocol $\lambda(\tau)$

- 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: $dq = dw - du = F(x,\lambda) dx = T ds_{\mathsf{m}}$

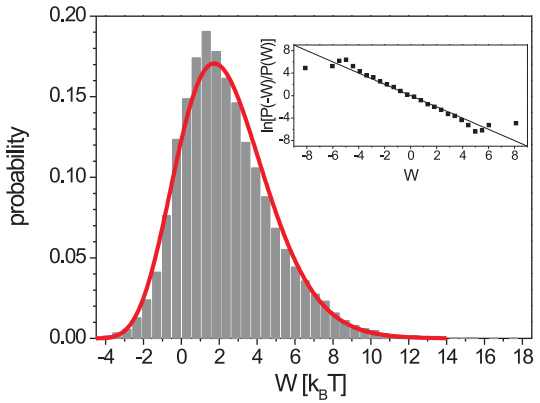
- Experimental illustration: Colloidal particle in $V(x, \lambda(\tau))$

[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]

- Stochastic entropy [U.S., PRL 95, 040602, 2005]

  - Fokker-Planck equation
    $\partial_\tau p(x,\tau) = -\partial_x j(x,\tau) = -\partial_x \left(\mu F(x,\lambda) - D\partial_x\right) p(x,\tau) \quad [D = \mu k_B T]$

  - Common non-eq **ensemble** entropy $\quad [k_B \equiv 1]$
    $S(\tau) \equiv -\int dx \; p(x,\tau) \ln p(x,\tau)$

  - Stochastic entropy for an **individual trajectory** $x(\tau)$
    $s(\tau) \equiv -\ln p(x(\tau),\tau) \quad$ with $\langle s(\tau)\rangle = S(\tau)$

  - $\Delta s_{\rm tot} \equiv \Delta s_{\rm m} + \Delta s$

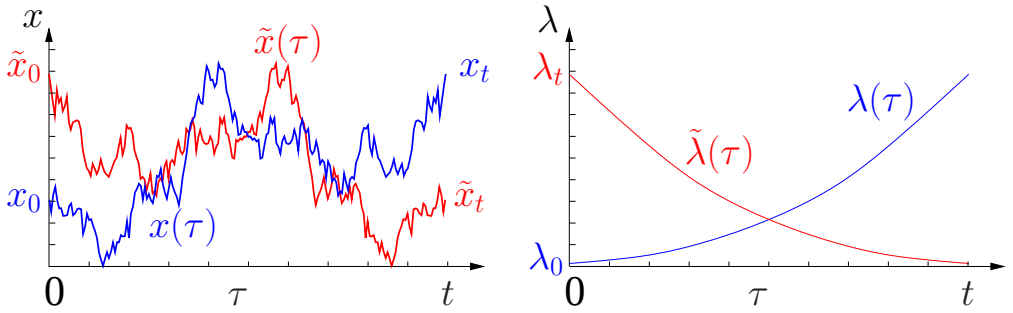
  - $\boxed{\langle \exp[-\Delta s_{\rm tot}]\rangle = 1} \Rightarrow \boxed{\langle \Delta s_{\rm tot}\rangle \geq 0}$

    * integral fluctuation theorem for total entropy production
    * arbitrary initial state, driving, length of trajectory

- Path integral representation (cf. Onsager & Machlup, 1953)
  - "Boltzmann factor for a whole trajectory"

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

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



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

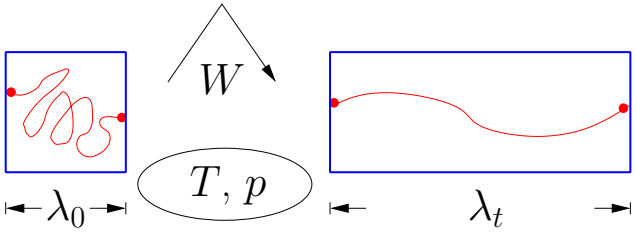
$$\frac{p[x(\tau)|x_0]}{\tilde{p}[\tilde{x}(\tau)|\tilde{x}_0]} = \frac{\exp\left[-\int_0^t d\tau\ (\dot{x}-\mu F)^2/4D\right]}{\exp\left[-\int_0^t d\tau\ (\dot{\tilde{x}}-\mu \tilde{F})^2/4D\right]}$$

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

- General integral fluctuation theorem

$$\boxed{1 = \langle \exp[\underbrace{-q[x(\tau)]}_{-\Delta s_{\mathrm{m}}} + \ln p_1(x_t)/p_0(x_0)] \rangle}$$ for any (normalized) $p_1(x_t)$

- Jarzynski relation (1997)



2^{nd} law:

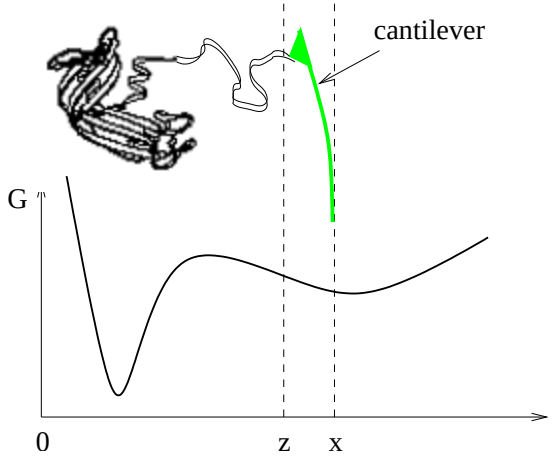
$\langle W \rangle_{|\lambda(\tau)} \geq \Delta F \equiv F(\lambda_t)) - F(\lambda_0)$

– $\boxed{\langle \exp[-W] \rangle = \exp[-\Delta F]}$ or $\boxed{\langle \exp[-W_d] \rangle = 1}$

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

- Probing energy profiles by periodic loading

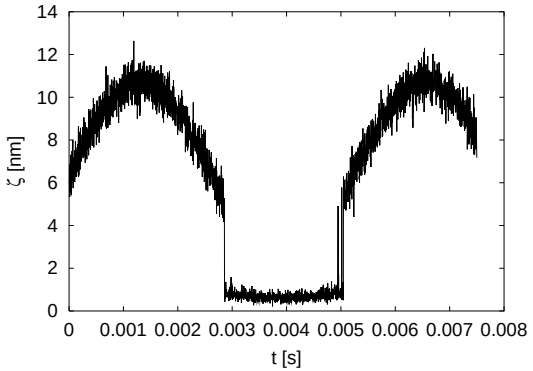
  [O. Braun, A. Hanke and U.S., PRL 93, 158105, 2004]



  - $V(z,\tau) = G(z) + (k/2)(\lambda(\tau) - z)^2$

  - Simulation using a Langevin equation

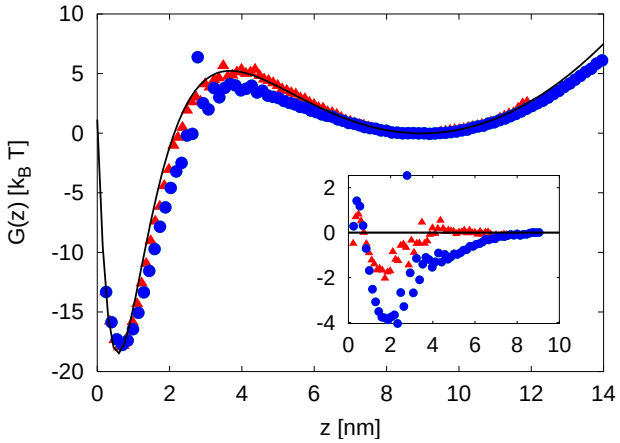
$$\dot{z} = \mu(-dV/dz) + \zeta$$



- Reconstruction of energy profile by z-resolved Jarzynski relation

$$p_1(z) = \delta(z(t) - z) \quad \Rightarrow \quad e^{-G(z)} = \langle \delta[z - z(t)] e^{-W(t)} \rangle \quad e^{(k/2)(z-\lambda(\tau))^2}$$

[cf. Hummer & Szabo, PNAS, 2001]

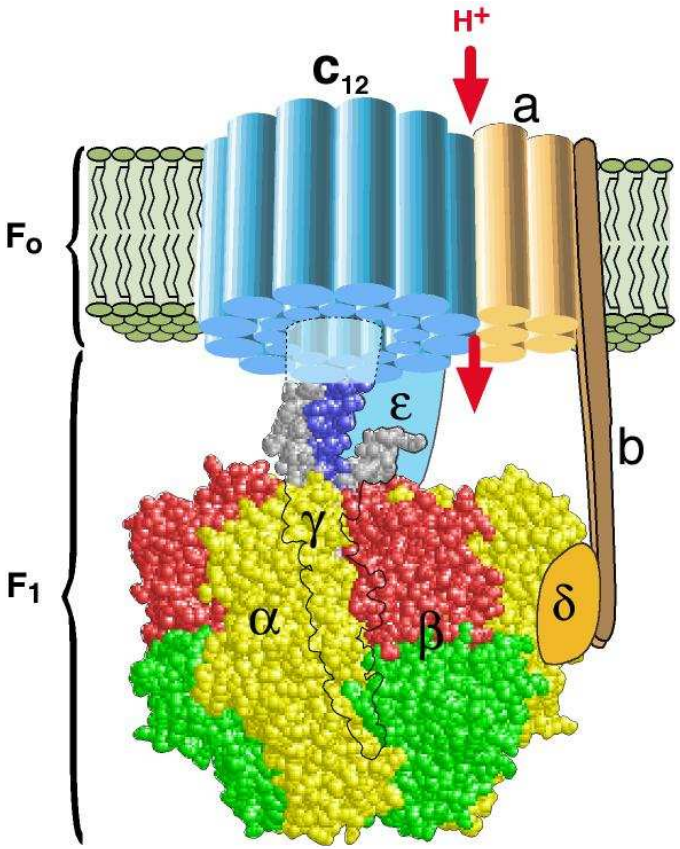


– linear loading: $\lambda(\tau) = x_0 + vt$

– periodic loading: $\lambda(\tau) = x_0 + a \sin \omega t$

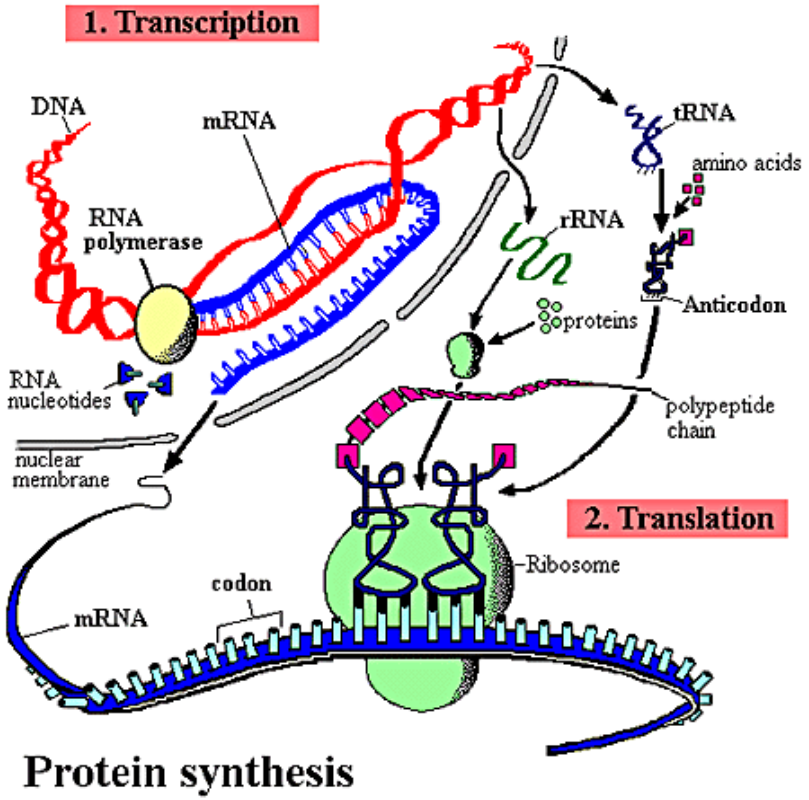
– Comparison: periodic forcing significantly better than linear

- (Bio)chemically driven systems



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

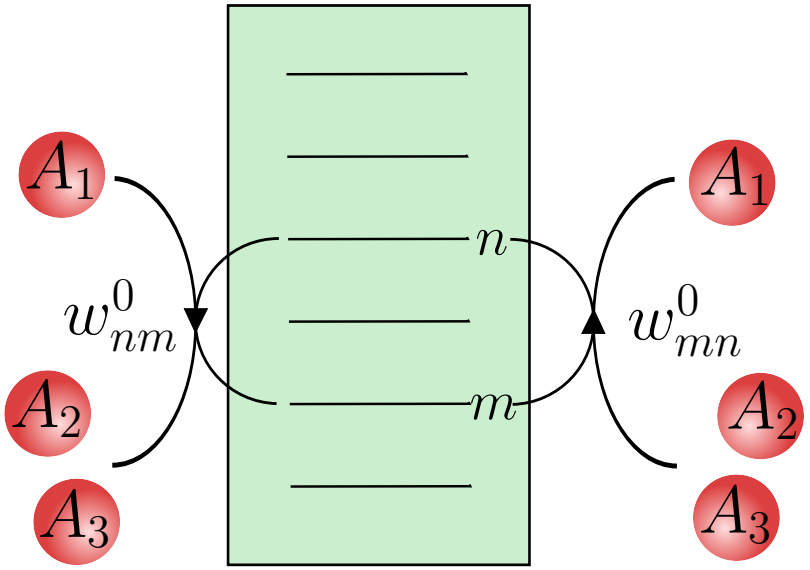
F1-ATPase



Protein synthesis

- Stochastic th'dynamics of a driven enzym with internal states

  [T.Schmiedl, T.Speck and U.S., J. Stat. Phys. **128**, 77 (2007)]

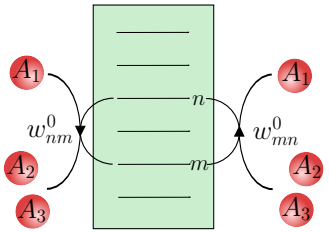


  - $A_1 + n \underset{w_{mn}}{\overset{w_{nm}}{\rightleftharpoons}} m + A_2 + A_3$
  - mass action law kinetics:
  - $\frac{w_{nm}}{w_{mn}} = \frac{w^0_{nm}}{w^0_{mn}} [A_1]/[A_2][A_3]$

  - Green enzym
    * internal states with (constrained) free energy $F_n = E_n - TS_n$
  - Red species
    * fixed (non-equilibrium) chemical potential

$$\mu_\alpha = \mu^*_\alpha + \ln\left\{[A_\alpha]\lambda^3_\alpha\right\}$$

- First law along stochastic trajectory



$w = \Delta E + q$ for a single step $A_1 + n \underset{w_{mn}}{\overset{w_{nm}}{\rightleftharpoons}} m + A_2 + A_3$

– chemical work: $w^{nm}_{\text{chem}} \equiv \mu_1 - \mu_2 - \mu_3$

– internal energy: $\Delta E^{nm} \equiv E_m - E_n$

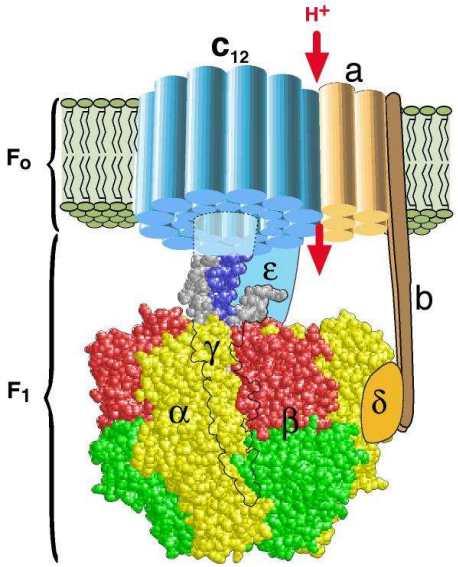
– dissipated heat:

$$\boxed{q^{nm} \equiv w^{nm}_{\text{chem}} - \Delta E^{nm} = \ln w_{nm}/w_{mn} - T\Delta S^{nm}}$$

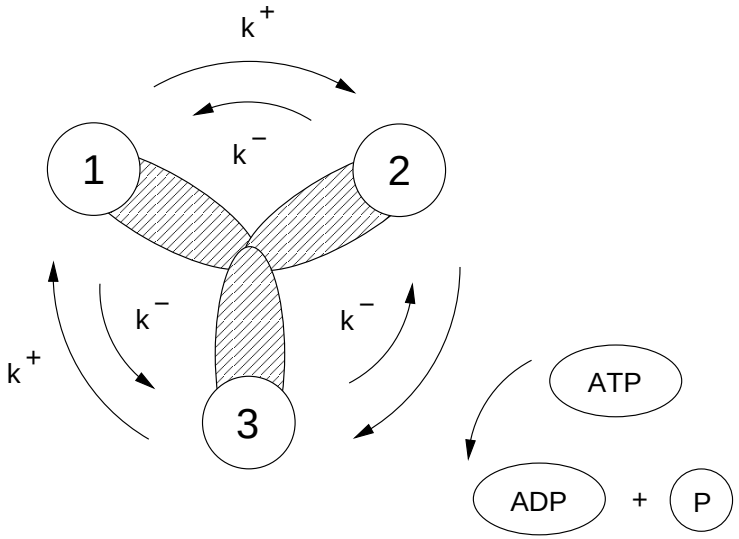
– can be summed over full reaction history

$\Rightarrow$ "chemical" Jarzynski relation, ...

- Illustration: F_1-ATPase [U.S., Europhys. Lett. 70, 36, 2005]



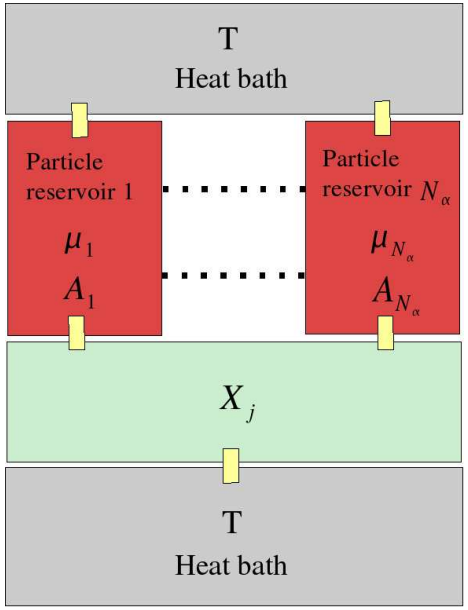
H. Wang and G. Oster (1998). Nature 396:279-282.



- $\partial_\tau p_1 = -(k^+ + k^-)p_1 + k^+ p_2 + k^- p_3$ & cyc
- $\Delta s_{\rm tot} = n \ln(k^+/k^-) = n[\mu_{ATP} - \mu_{ADP} - \mu_P]/T$
- Det. fluctuation theorem $\boxed{p(-\Delta s_{\rm tot})/p(\Delta s_{\rm tot}) = \exp[-\Delta s_{\rm tot}]}$
- equiv to asymmetric random walk $p(-n)/p(n) = \exp[-n \ln(k^+/k^-)]$

- Stochastic th'dynamics of general (bio)chemical reaction networks

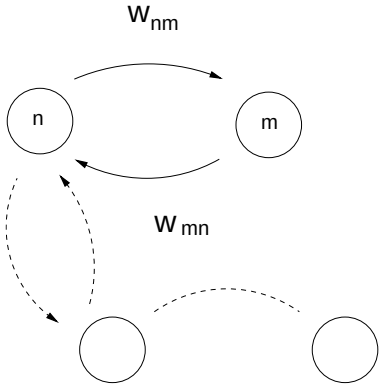
[T. Schmiedl and U.S., J. Chem. Phys. 126, 044101, 2007]

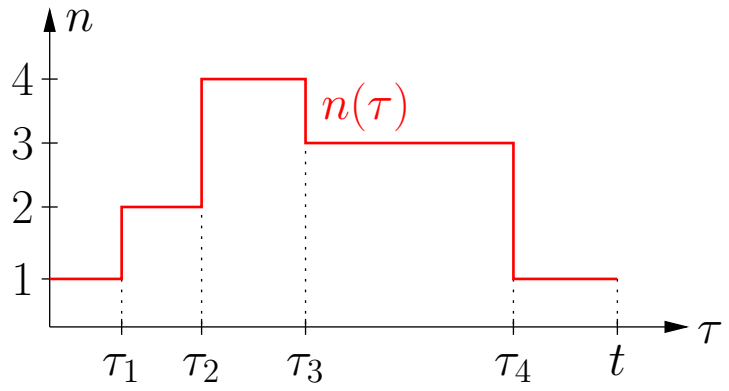


$$r_\alpha^\rho A_\alpha + p_j^\rho X_j \rightleftharpoons s_\alpha^\rho A_\alpha + q_j^\rho X_j$$

- two sorts of species:
  - chemiostated A_α (like ATP, ADP, ...)
  - number-tracked X_j with $n_j(\tau)$
- energy and entropy along a trajectory $\{n_j(\tau)\}$

- Stochastic entropy for arbitrary (athermal) networks [U.S., PRL '05]





– $\partial_t p_n = \sum_m [w_{mn}(\lambda) p_m - w_{nm}(\lambda) p_n]$

– $s(\tau) \equiv -\ln p_{n(\tau)}(\tau)$ where $p_n(\tau)$ solves master eq

– entropy change along t: $\Delta s = \Delta s_{\rm tot} - \Delta s_{\rm m}$ $(\equiv \ln w_{nm}/w_{mn})$

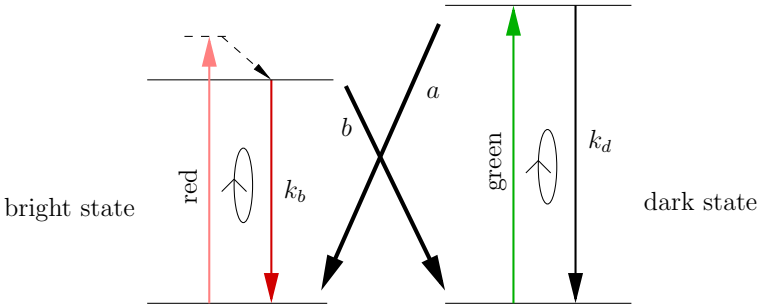
– two fluctuation theorems for finite times

* Integral FT for arbitrary driving: $\boxed{\langle \exp(-\Delta s_{\rm tot}) \rangle = 1}$

* Detailed FT in a NESS: $\boxed{p(-\Delta s_{\rm tot})/p(\Delta s_{\rm tot}) = \exp(-\Delta s_{\rm tot})}$

- Entropy production in an optically driven defect center

[C.Tietz, S. Schuler, T. Speck, U.S. and J. Wrachtrup, PRL 97, 050602, 2006]



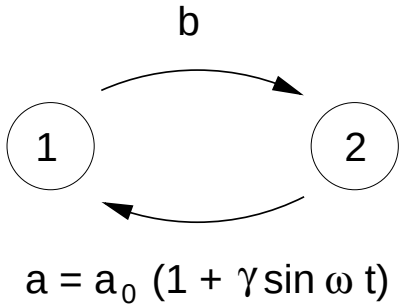
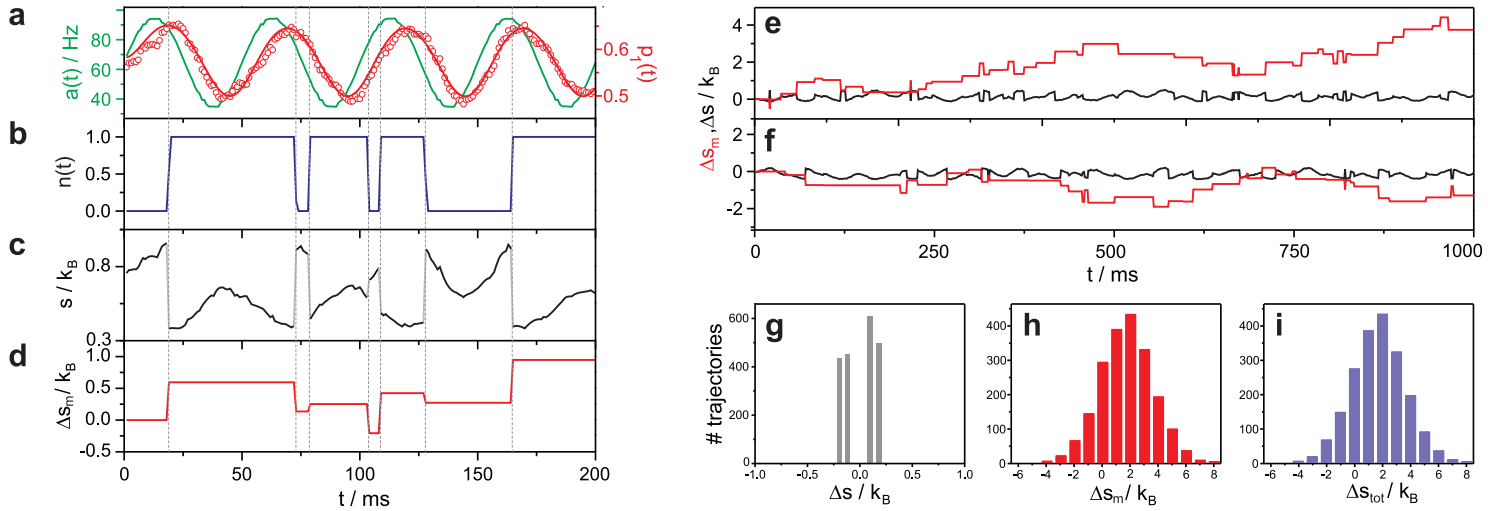
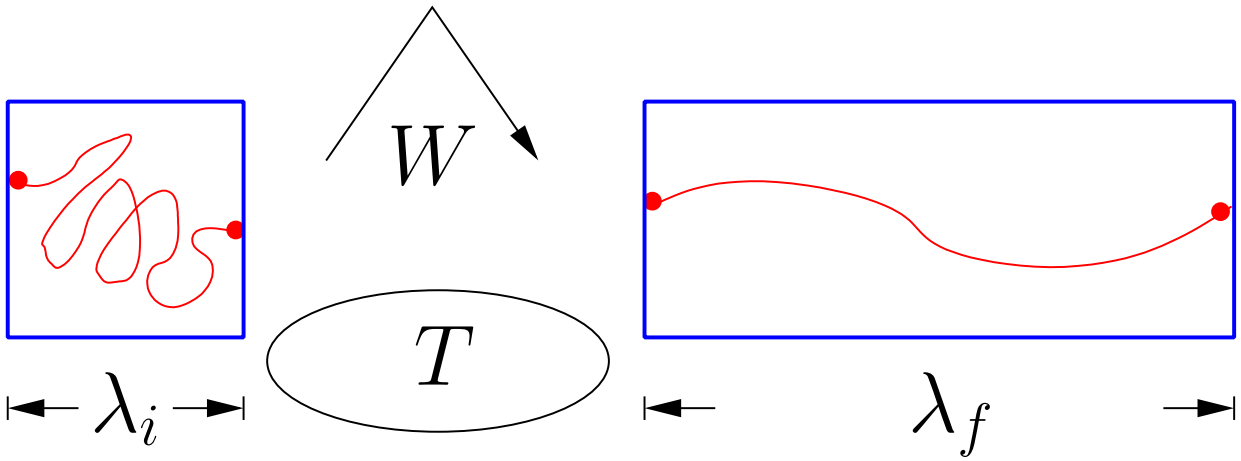


Figure 1



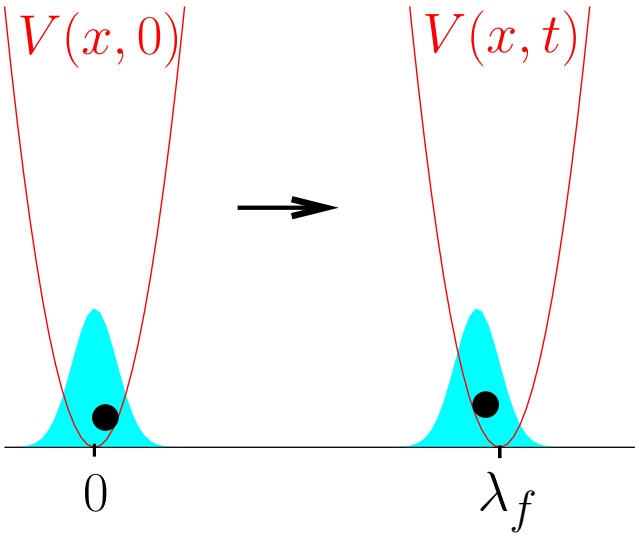
- Optimal finite-time processes in stochastic thermodynamics

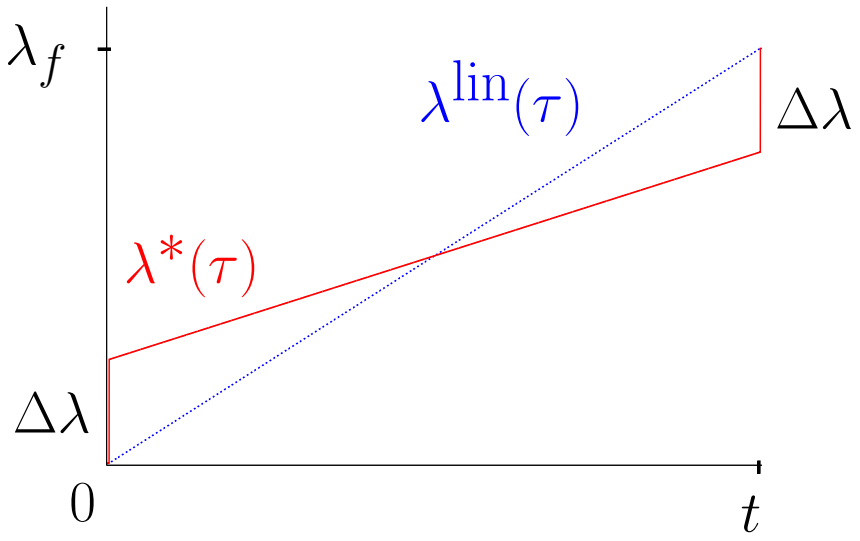
  [T. Schmiedl and U.S., PRL 98, 108301, 2007]



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

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

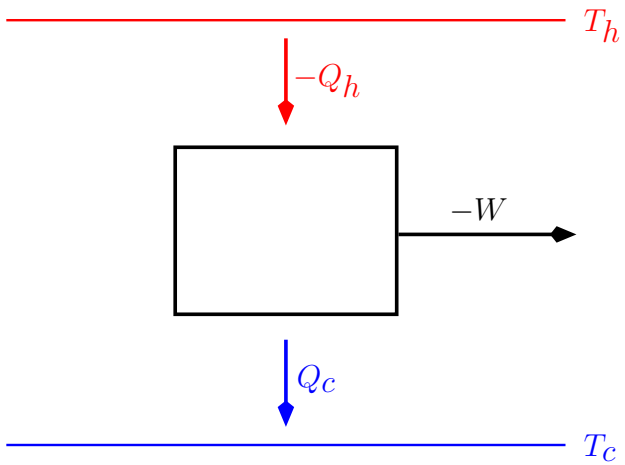




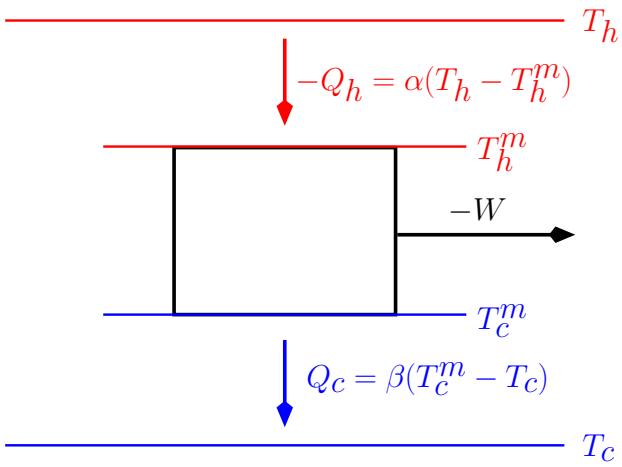
  - $\lambda^*(\tau)$ requires jumps at beginning and end $\Delta\lambda = \lambda_f/(t+2)$
  - gain $1 \geq W^*(t)/W^{lin}(t) \geq 0.88$
  - jumps are generic!
  - generalization: underdamped dynamics $\Rightarrow$ delta-peaks

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

- Heat engines at maximal power
  - Carnot (1824)



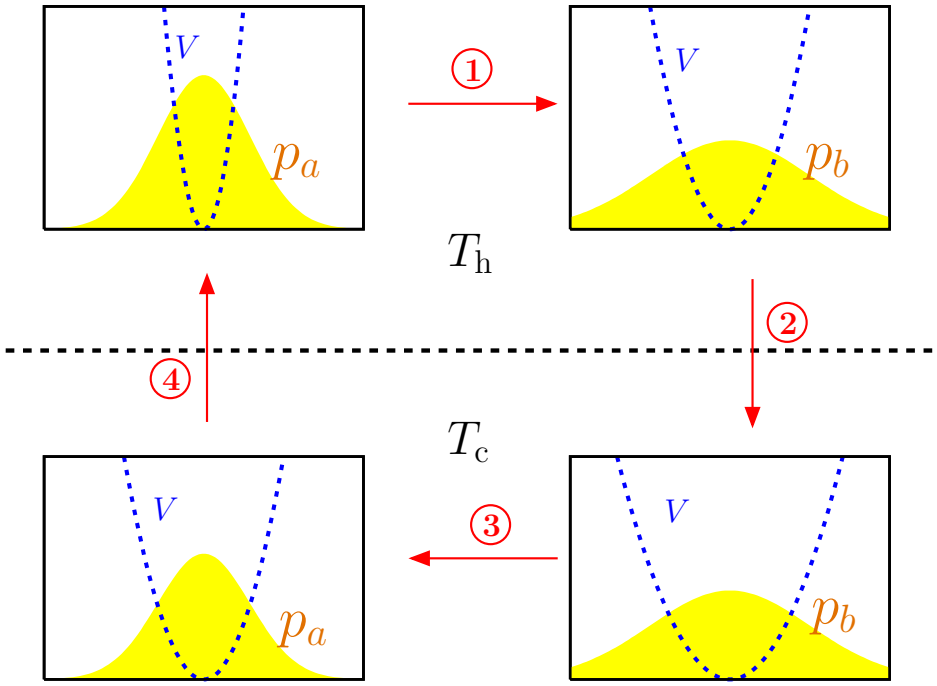
  - $\eta_c \equiv 1 - T_c/T_h$
    but zero power
  - Curzon-Ahlborn (1975)

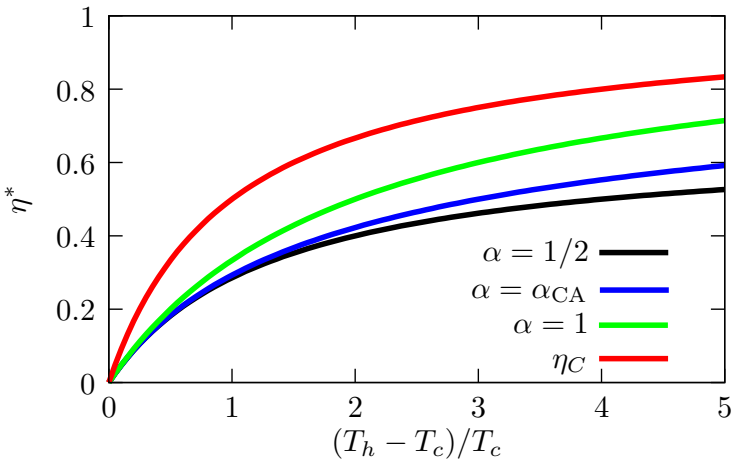


  - efficiency at maximum power
    $\eta_{ca} \equiv 1 - \sqrt{T_c/T_h}$
  - recent claims for universality(?)
  - what about fluctuations?

- Brownian heat engine at maximal power

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



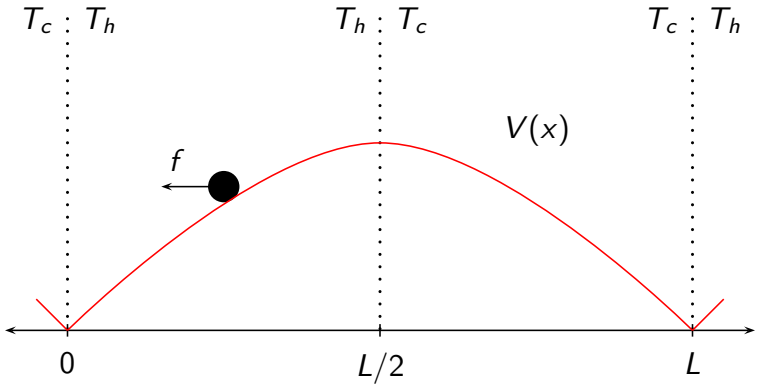


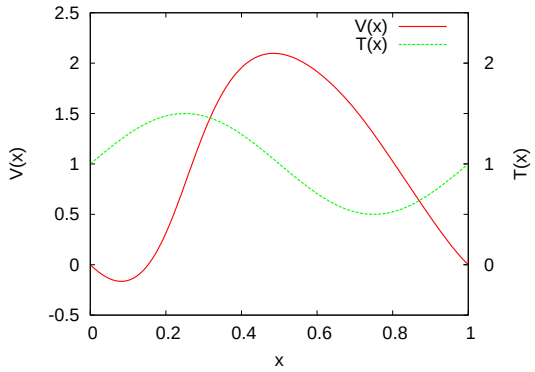
- $\eta^* = \frac{\eta_c}{2-\alpha\eta_c}$ with $\alpha = 1/2$ for temp-independent mobility

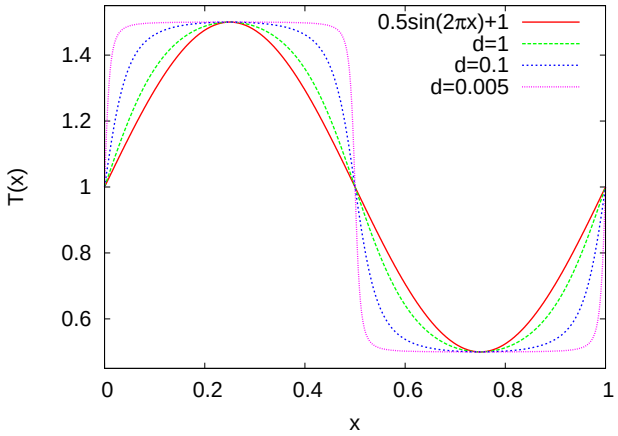
- Curzon-Ahlborn neither universal nor a bound

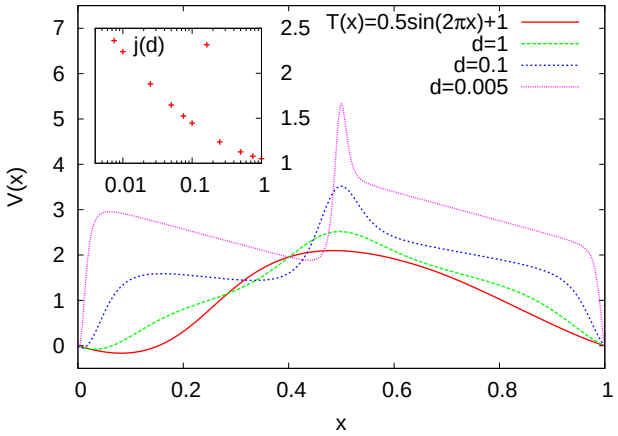
- Optimizing potentials for temperature ratchets

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



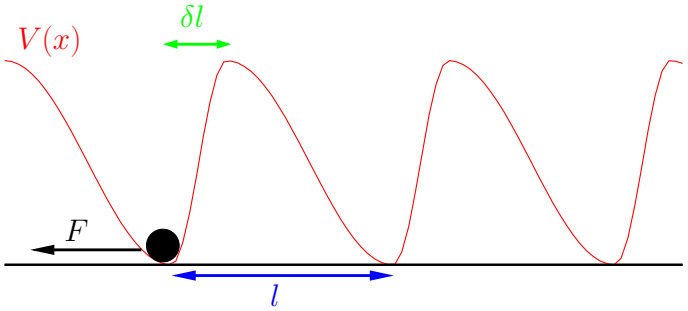






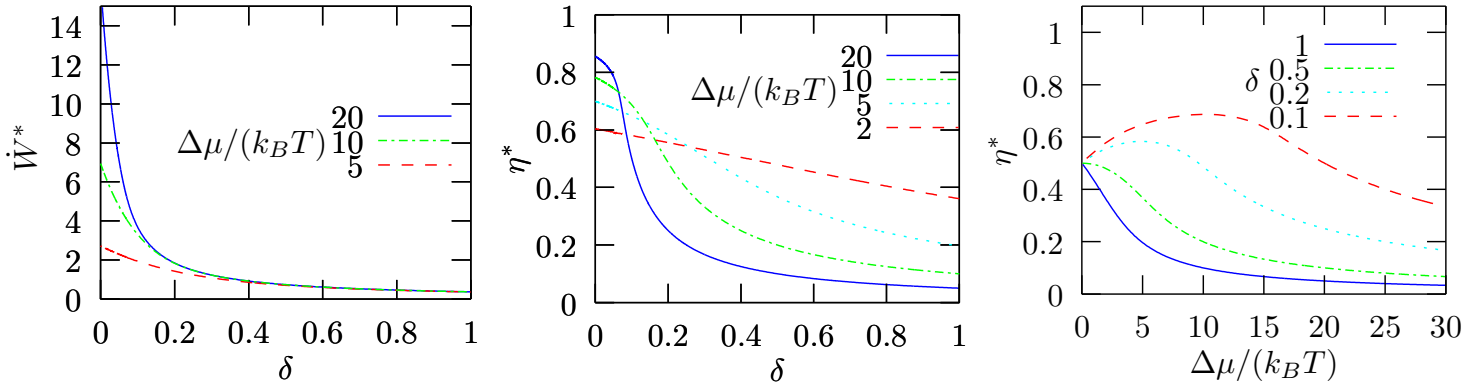
- Efficiency of molecular motors at maximum power

  [T. Schmiedl and U.S., EPL 83, 30005, 2008]



$$w^+ = [ATP]k^+ \exp[-\delta l \ F]$$

$$w^- = [ADP][P]k^- \exp[(1-\delta)l \ F]$$



- "Power stroke" ($\delta \simeq 0$) highest efficiency at max power
- η^* can increase beyond lin response regime ($\eta^* = 1/2$)

- **Stochastic thermodynamics** along single trajectories

  - formulation of the 1^{st} law
  - refinement of the 2^{nd} law

    * mechanically driven: colloids, polymers, proteins
    * biochemically driven: single enzyms, motors, reaction networks
    * optically driven: defect centers, other quantum systems ....

    * flow driven systems [T. Speck, J Mehl and U.S., PRL **100** 178302, 2008]
    * in a magnetic field [P. Pradhan and U.S., EPL 2010]

- Non-equilibrium steady states ($\rightarrow$ second lecture)

- ..... ultimate goal: **a systematic theory of non-eq phenomena**