San Diego meeting, July 2009

Optimal Processes within Stochastic Thermodynamics

and beyond

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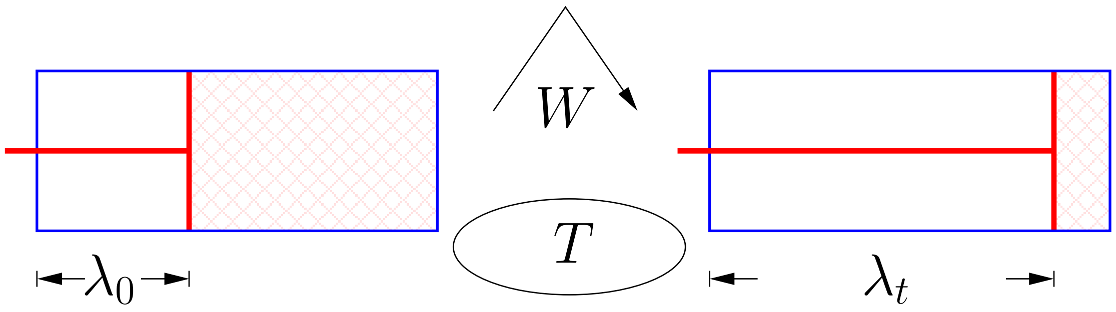
Thanks to Tim Schmiedl (PhD thesis work)

- Intro: Classical *vs* Stochastic thermodynamics
- Optimization
  - directed processes
  - cyclic processes
    - heat engines
    - temperature ratchets
    - biochemical machines: motor proteins
- beyond

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



- First law energy balance:

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

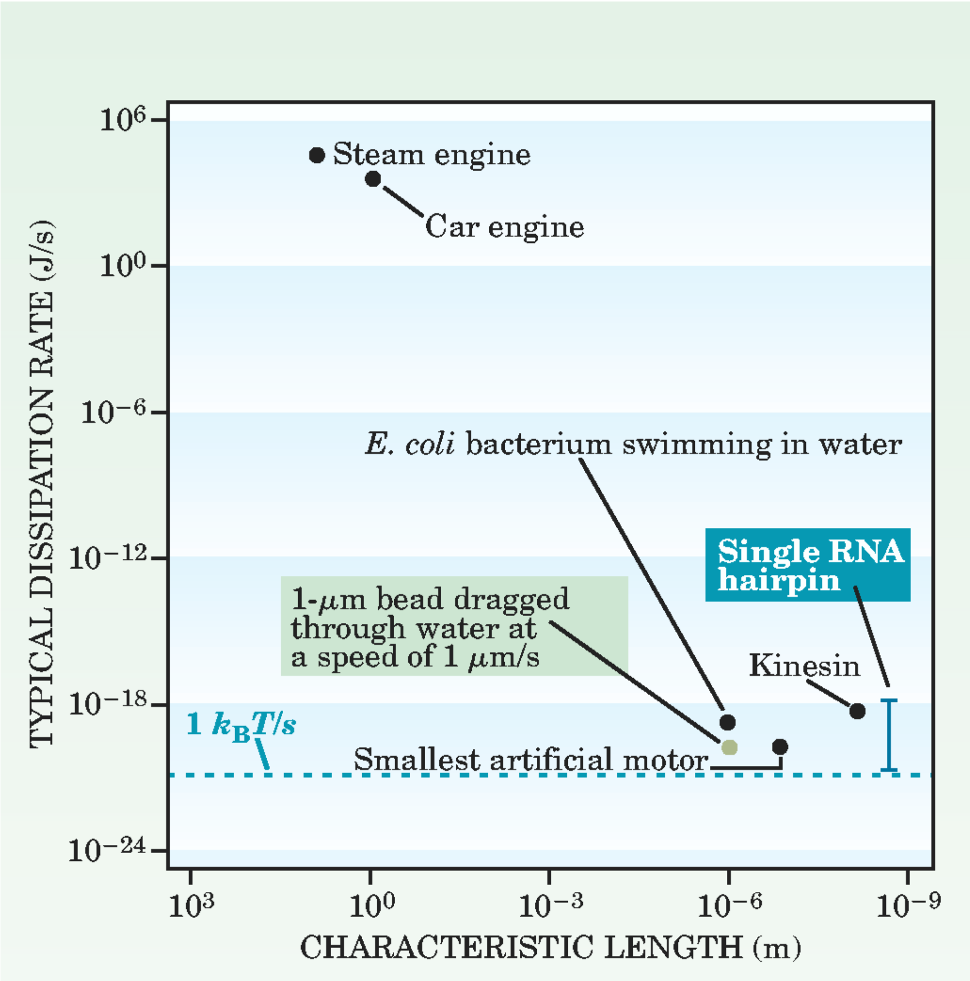
- Second law:

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

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

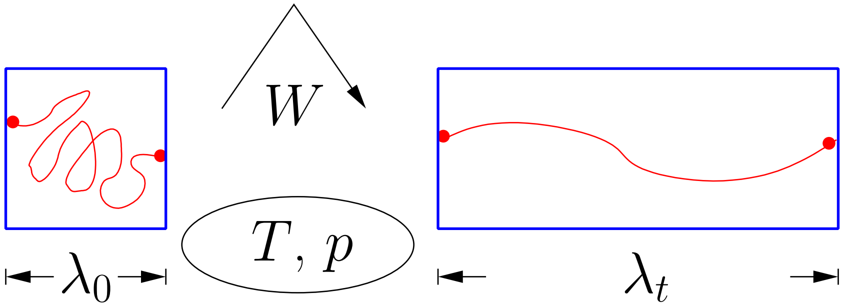
$$W_{\text{diss}} \equiv W - \Delta F > 0$$

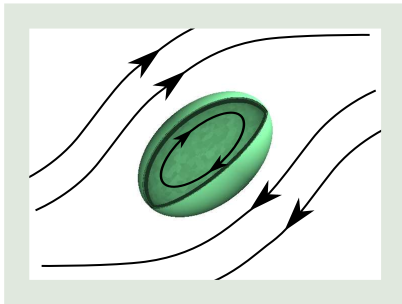
- Macroscopic *vs* mesoscopic *vs* molecular machines

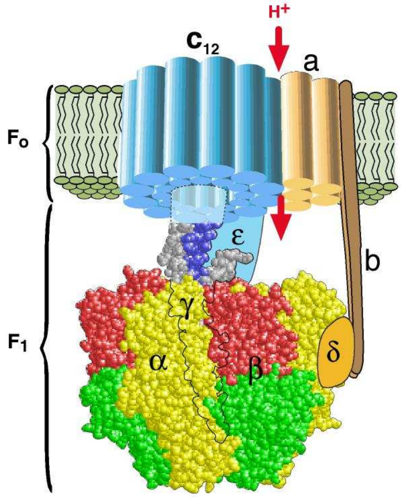


[Bustamante *et al*, Physics Today, July 2005]

- Stochastic thermodynamics for small systems







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

driving: mechanical hydrodynamical (bio)chemical

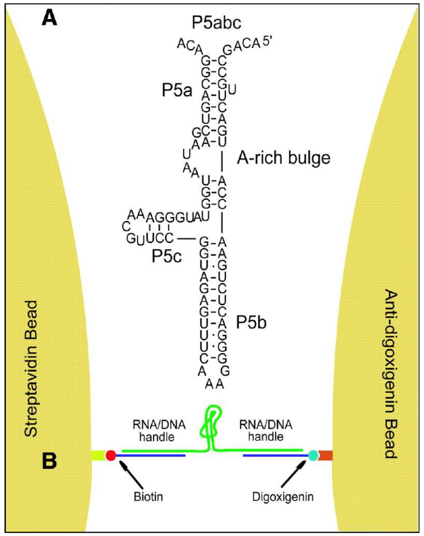
  - First law: how to define work, internal energy and exchanged heat?

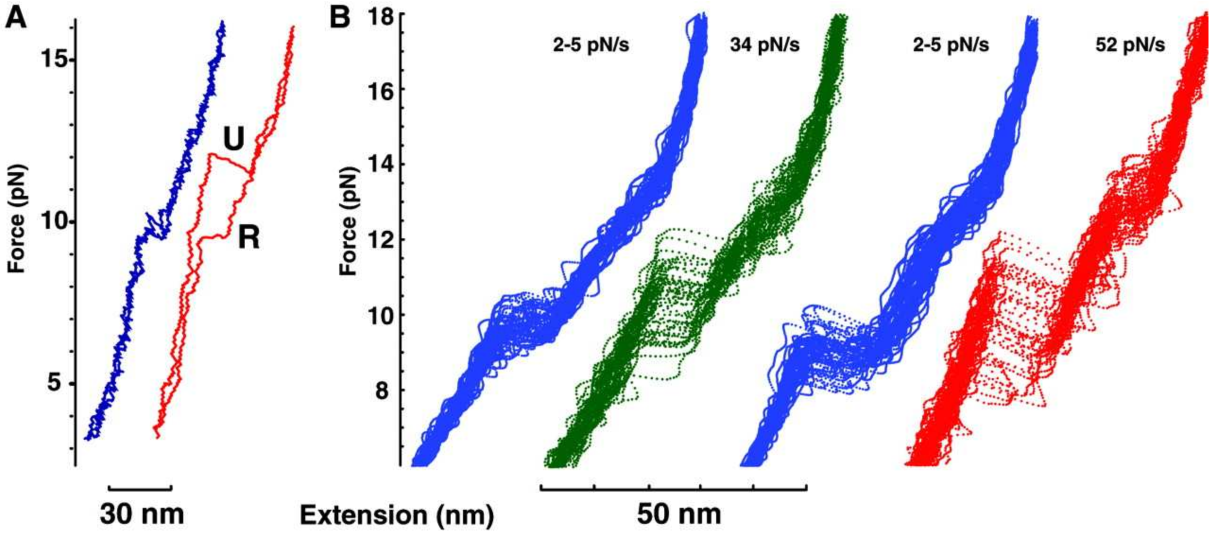
  - fluctuations imply distributions: $p(W; \lambda(\tau))$ ...

  - entropy: distribution as well?

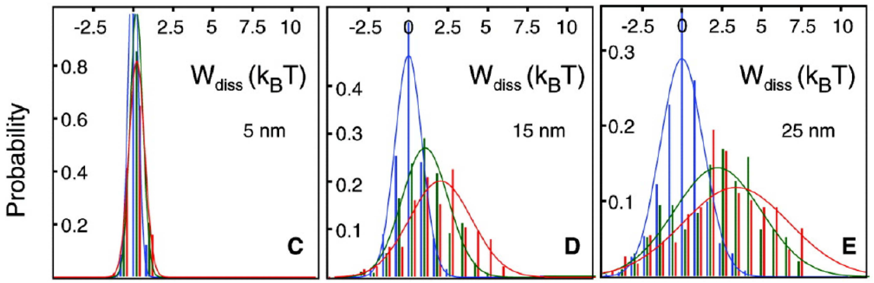
- Nano-world Experiment: Stretching RNA

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





– distributions of W_{diss}:



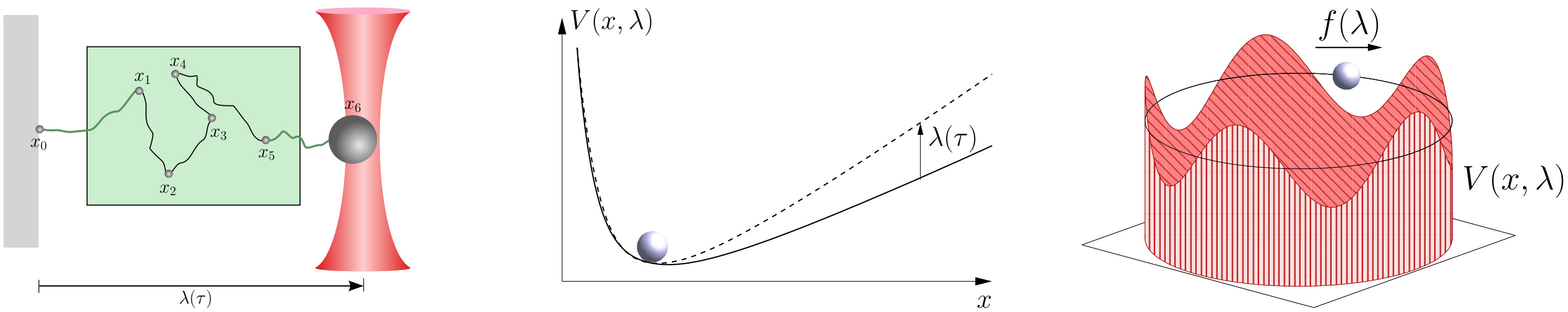
- **Stochastic thermodynamics** applies to such systems where
  - non-equilibrium is caused by mechanical or chemical forces
  - ambient solution provides a thermal bath of well-defined T
  - fluctuations are relevant due to small numbers of involved molecules

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

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

- Precursors:
  - notion "stoch th'dyn" by Nicolis, van den Broeck mid '80s (on ensemble level)
  - stochastic energetics (1^{st} law) by Sekimoto late '90s
  - ....

- 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)]: $\boxed{dw = du + dq}$

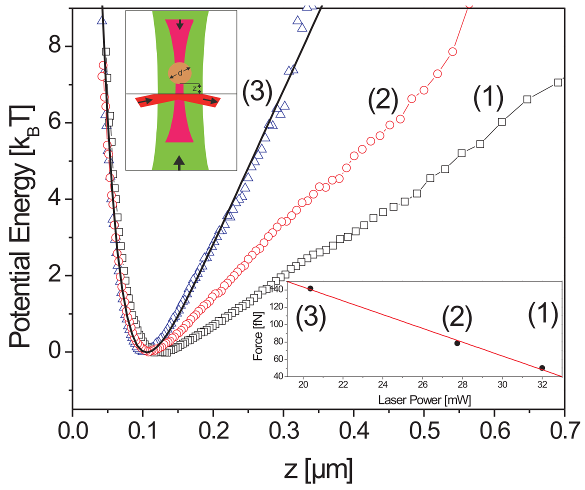
  – applied work: $dw = \partial_\lambda V(x,\lambda) d\lambda + f(\lambda) dx$

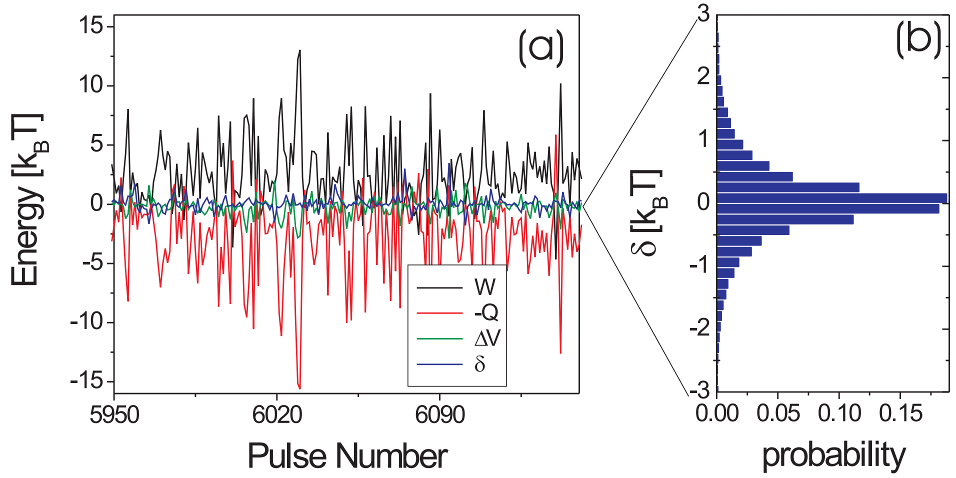
  – internal energy: $du = dV$

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

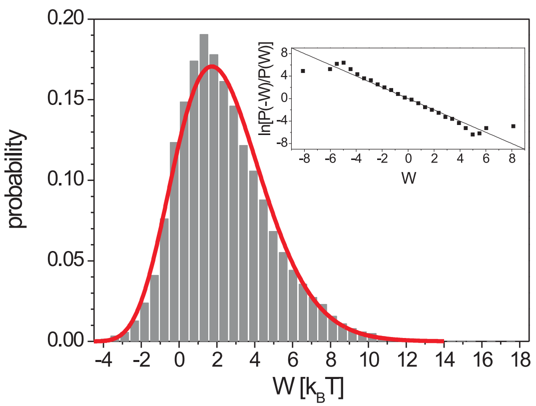
- Experimental illustration: Colloidal particle in $V(x, \lambda(\tau))$

  [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]

- 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 $[k_B \equiv 1]$

    $$S(\tau) \equiv -\int dx\; p(x,\tau) \ln p(x,\tau)$$

  - Stochastic entropy for a **single trajectory** $x(\tau)$

    $$s(\tau) \equiv -\ln p(x(\tau),\tau) \qquad \text{with } \langle s(\tau)\rangle = S(\tau)$$

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

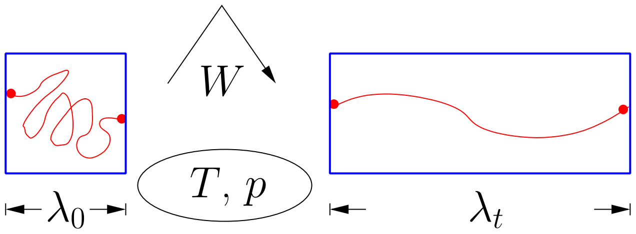
  - $\boxed{\langle \exp[-\Delta s_{\text{tot}}]\rangle = 1} \Rightarrow \boxed{\langle \Delta s_{\text{tot}}\rangle \geq 0}$

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

- 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)



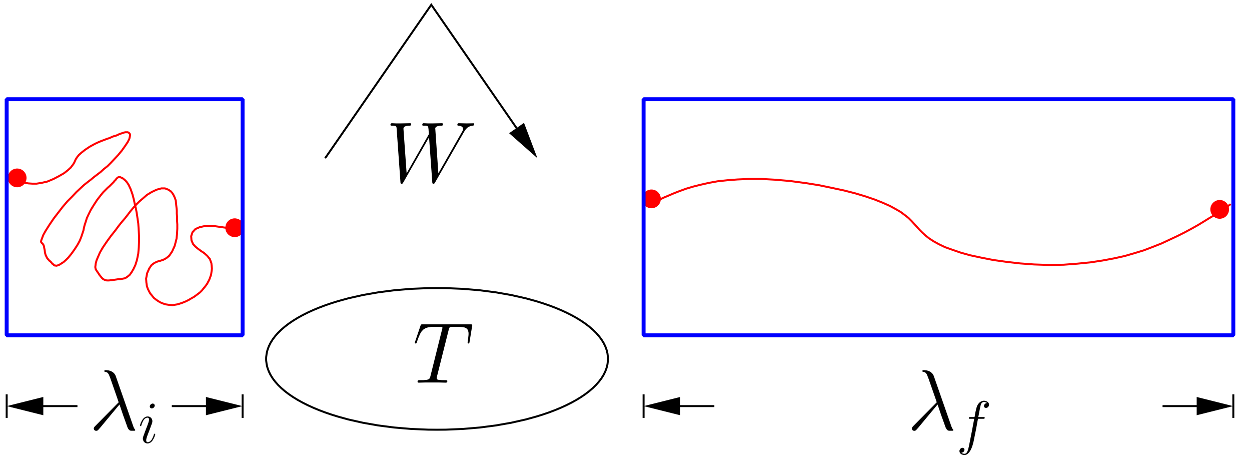
2^{nd} law:
$\langle W\rangle_{|\lambda(\tau)} \geq \Delta F \equiv F(\lambda_t)) - F(\lambda_0)$

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

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

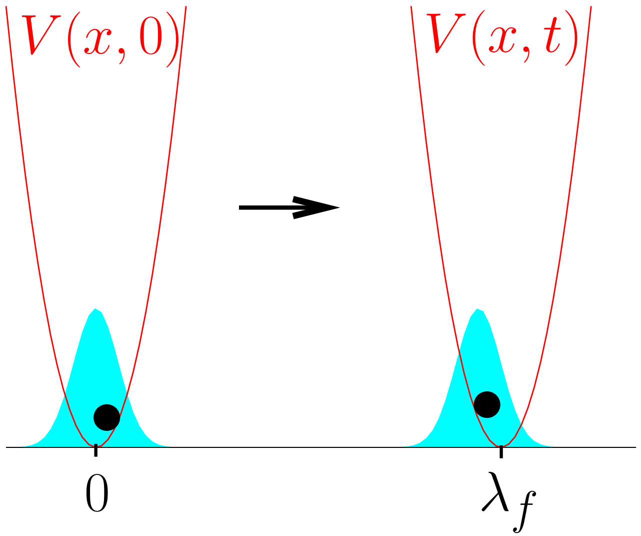
- Optimal finite-time processes in stochastic thermodynamics

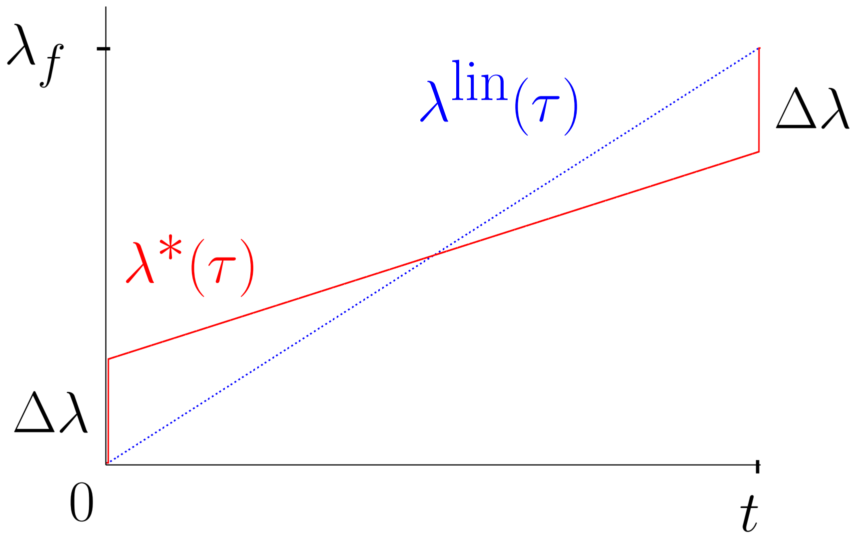
  [T. Schmiedl and U.S., PRL 98, 108301, 2007]



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

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

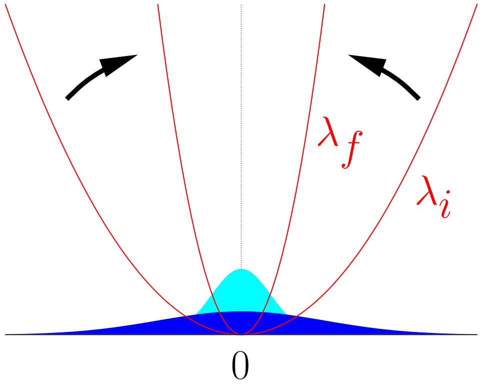


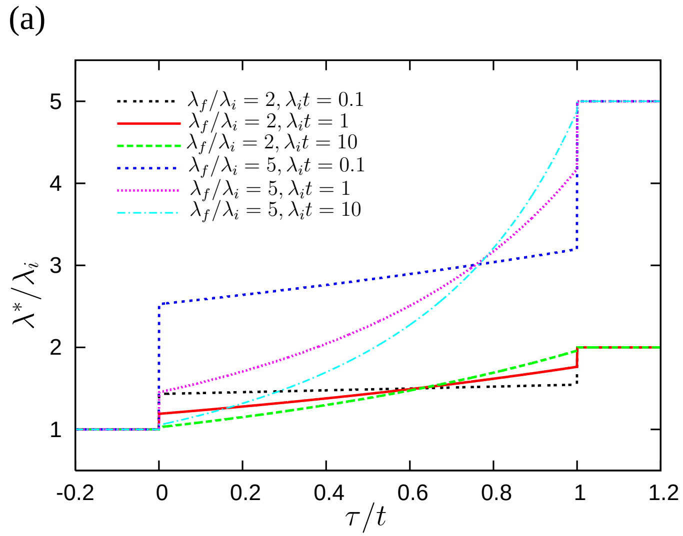


  - $\lambda^*(\tau)$ requires jumps at beginning and end $\qquad \Delta\lambda = \lambda_f/(t+2)$

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

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

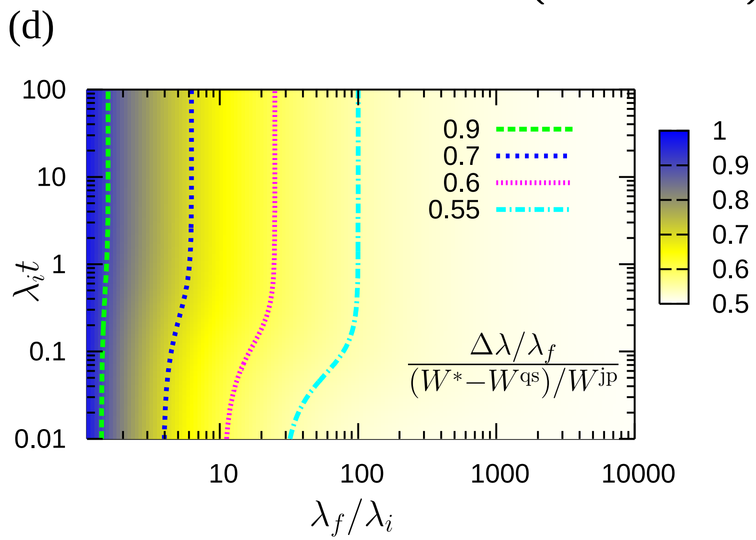




– jumps are generic

– typical size of the jump

$$\frac{\Delta\lambda/\lambda_f}{(W^* - W^{qs})/W^{jp}}$$



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

- Underdamped dynamics: role of inertia

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

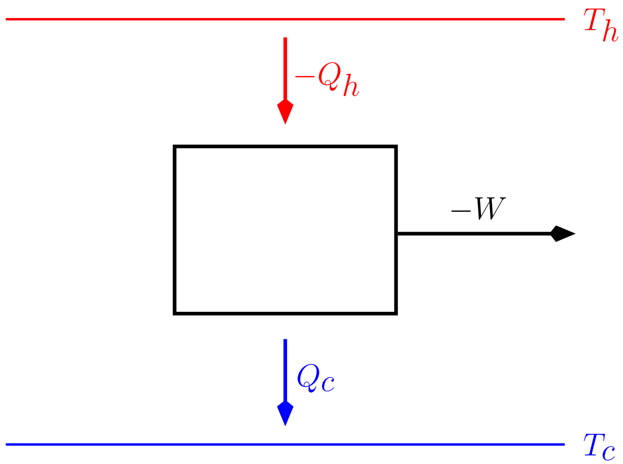
  $$m\ddot{x} + \gamma x + V'(x, \lambda) = \xi$$

  $*$ jumps and delta-functions at the boundaries

  $*$ $W^*/W^{lin} >> 1$ possible

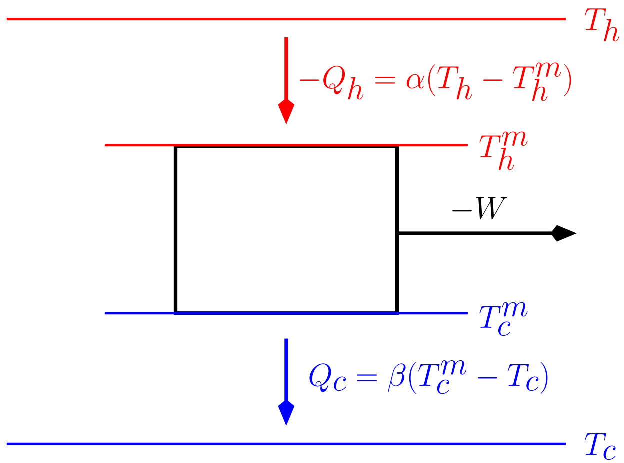
- Heat engines at maximal power

  - Carnot (1824)



  - $\eta_c \equiv 1 - T_c/T_h$
    but zero power

  - Curzon-Ahlborn (1975)

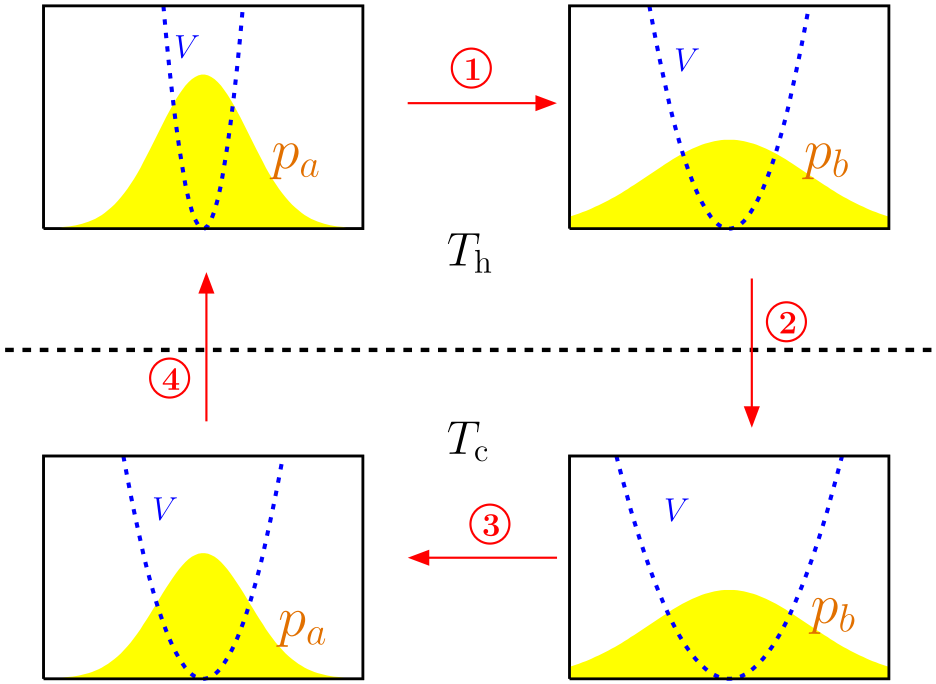


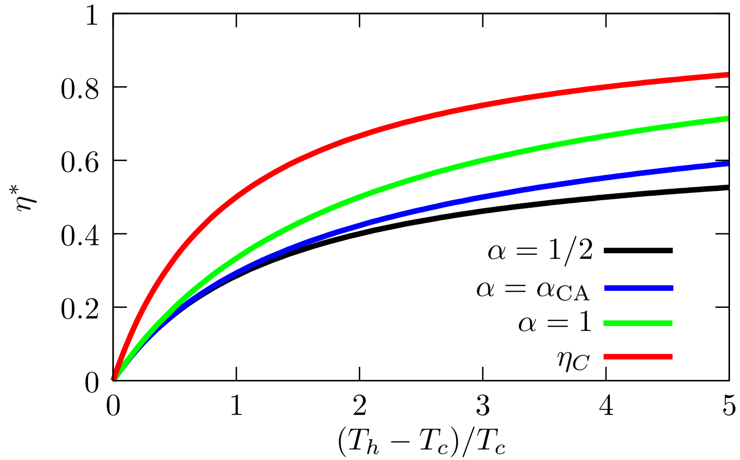
  - efficiency at maximum power
    $\eta_{ca} \equiv 1 - \sqrt{T_c/T_h}$
  - universality(?)
    [cf van den Broeck, PRL 2005]

  - what about fluctuations?

- Brownian heat engine at maximal power

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



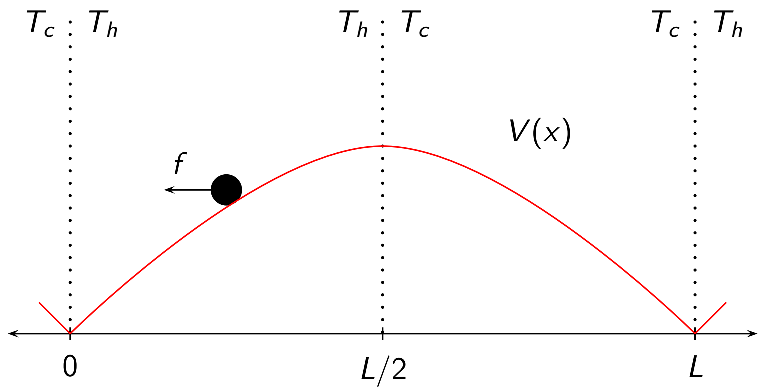


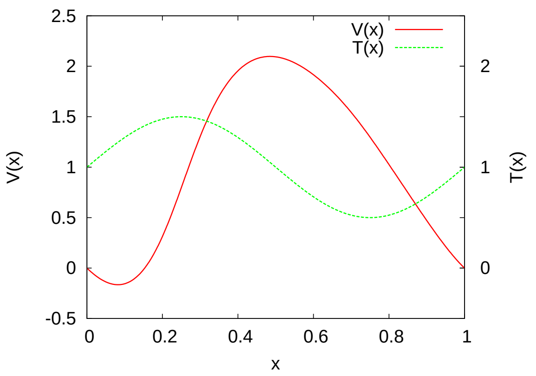
– $\boxed{\eta^* = \frac{\eta_c}{2 - \alpha\eta_c}}$ with $\alpha = 1/2$ for temp-independent mobility

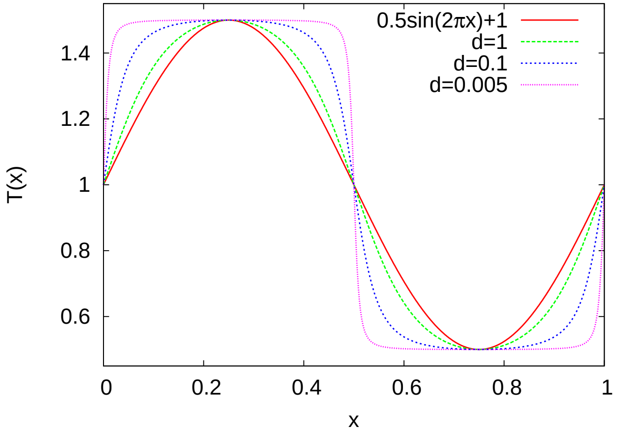
– Curzon-Ahlborn neither universal nor a bound

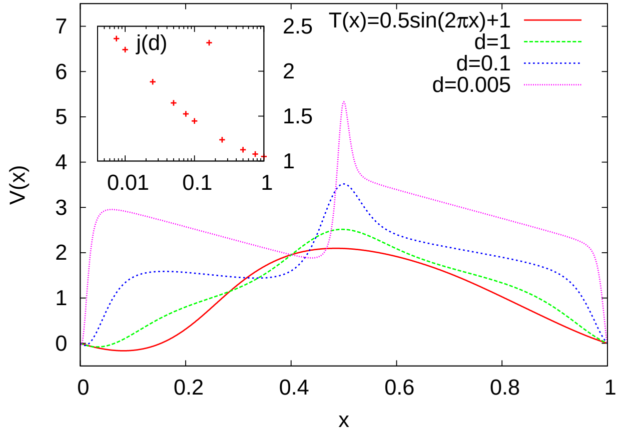
• Optimizing potentials for temperature ratchets

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



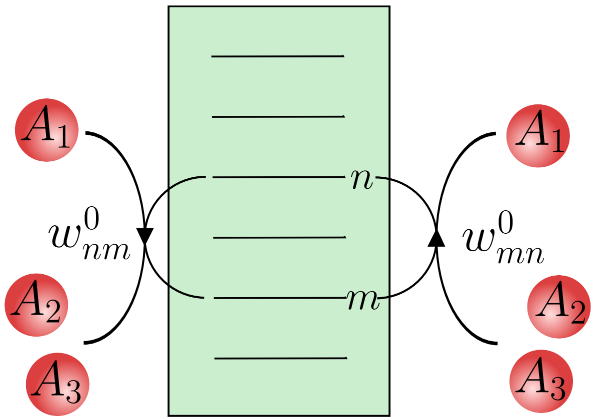






- Stochastic th'dynamics of a driven enzym with internal states

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



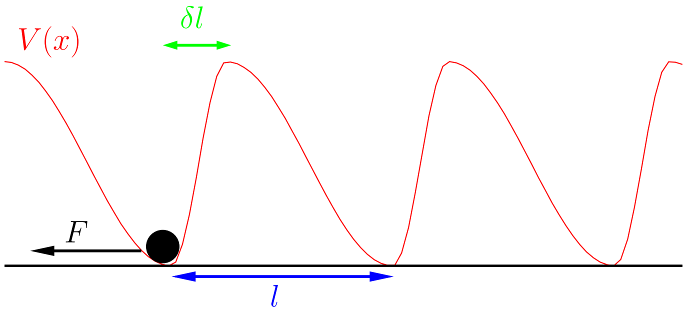
  - $A_1 + n \underset{w_{mn}}{\overset{w_{nm}}{\rightleftharpoons}} m + A_2 + A_3$
  - mass action law kinetics:
  - $\frac{w_{nm}}{w_{mn}} = \frac{w^0_{nm}}{w^0_{mn}}[A_1]/[A_2][A_3]$

- First law along a trajectory $w = \Delta E + q$ for a single reaction step ?

  - 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: $q^{nm} \equiv w^{nm}_{\text{chem}} - \Delta E^{nm} = \ln \frac{[A_1]}{[A_2][A_3]} \frac{w^0_{nm}}{w^0_{mn}} = \ln w_{nm}/w_{mn}$

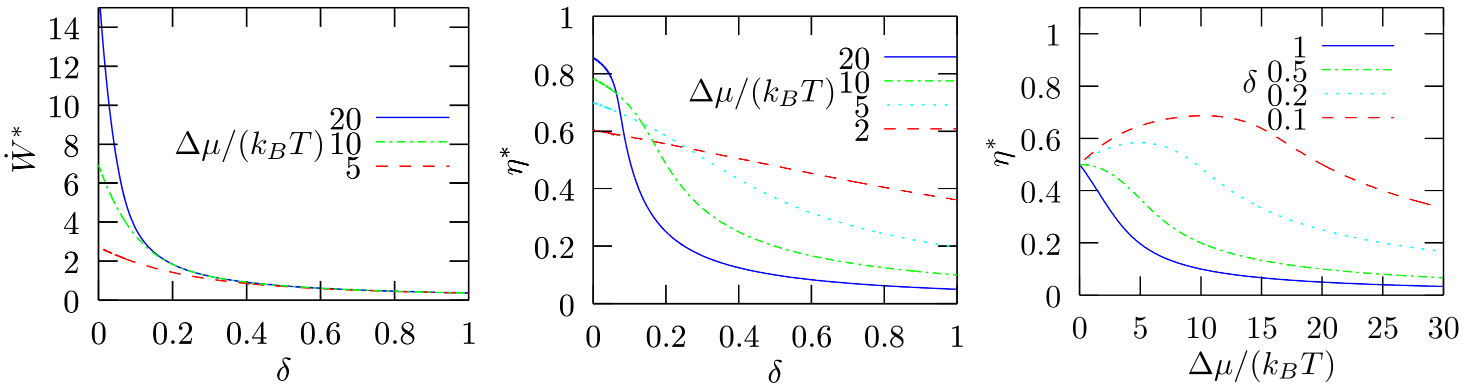
- Efficiency of molecular motors at maximum power

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



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

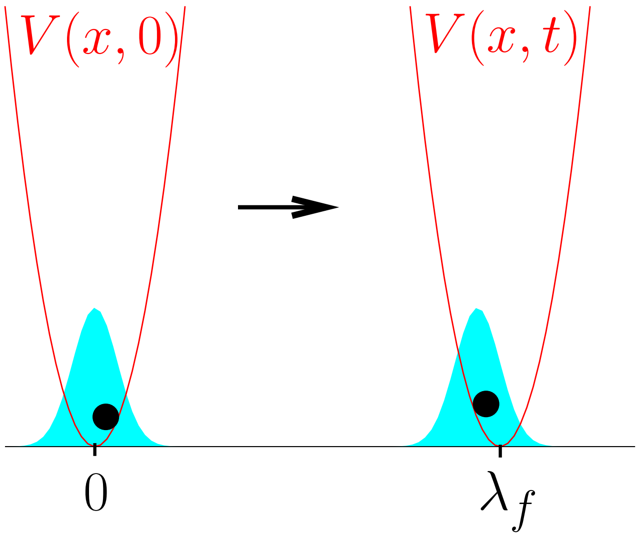
$$w^{-} = [ADP][P]k^{-} \exp[(1-\delta)l \ F]$$



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

- beyond stochastic dynamics

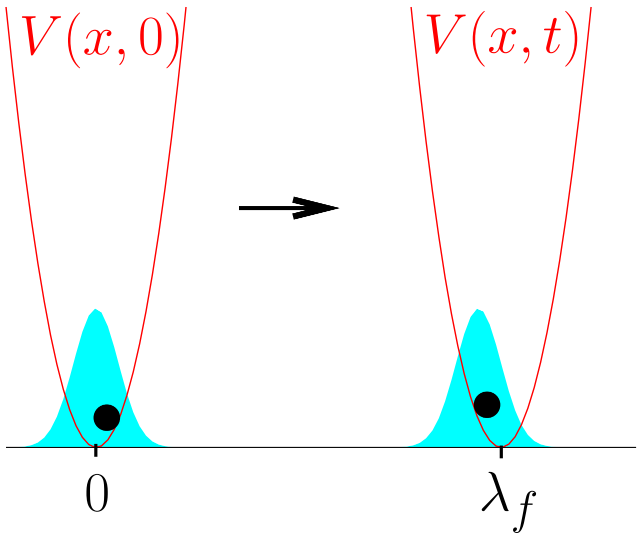
[T. Schmiedl, E. Dieterich, P.S. Dieterich, U.S., J Stat Mech, P07013 (2009)]



  - Hamiltonian dynamics

  - Quantum dynamics

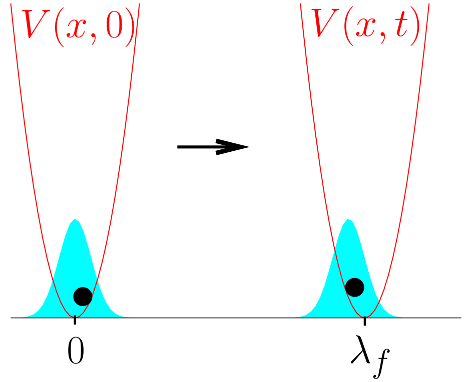
- Hamiltonian dynamics



  - $\partial_\tau \rho(x,p,\tau) = \left\{\rho, p^2/2m + V(x,\lambda(\tau))\right\}_{PB}$
  - $\rho(x,p,\tau=0) = \exp[-\beta(H-\mathcal{F})]$
  - $\lambda_i \rightarrow \lambda_f$ in finite t
  - adiabatic=quasistatic work $W^{ad} \neq \Delta F$

- $W = [\ \frac{\langle p \rangle^2}{2m} + \frac{k}{2}\ (\langle x \rangle - \lambda)^2\ ]_0^t$

  $\Rightarrow \quad W = 0$ if $\langle p(t) \rangle = 0$ and $\langle x(t) \rangle = \lambda$

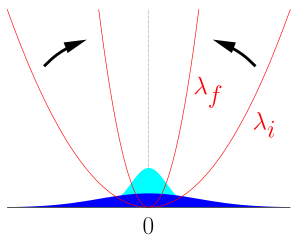


- only two conditions on $\lambda(\tau)$
  $\Rightarrow$ optimal protocol highly degenerate

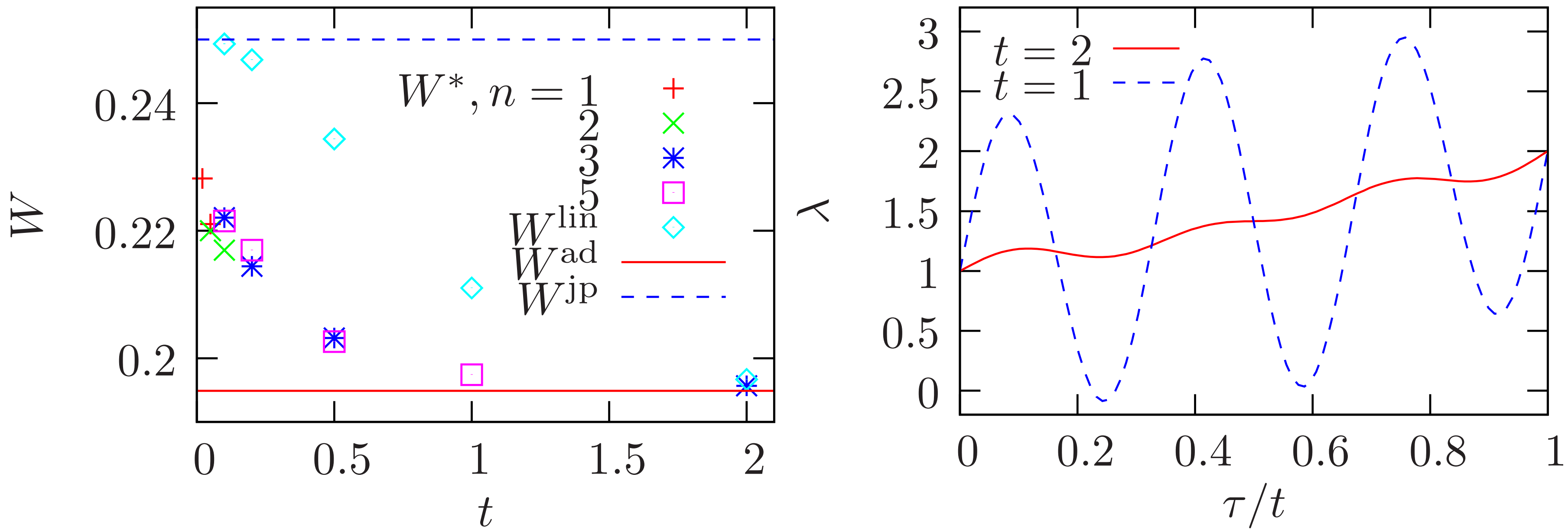
- adiabatic work can be reached in $0 + \epsilon$ time
  (price: extreme λ-values)

- Hamiltonian dynamics beats Langevin evolution
  ($W^* \to W^{jp} = k\lambda_f^2/2$ for $t \to 0$)

- qualitatively similar for case II:

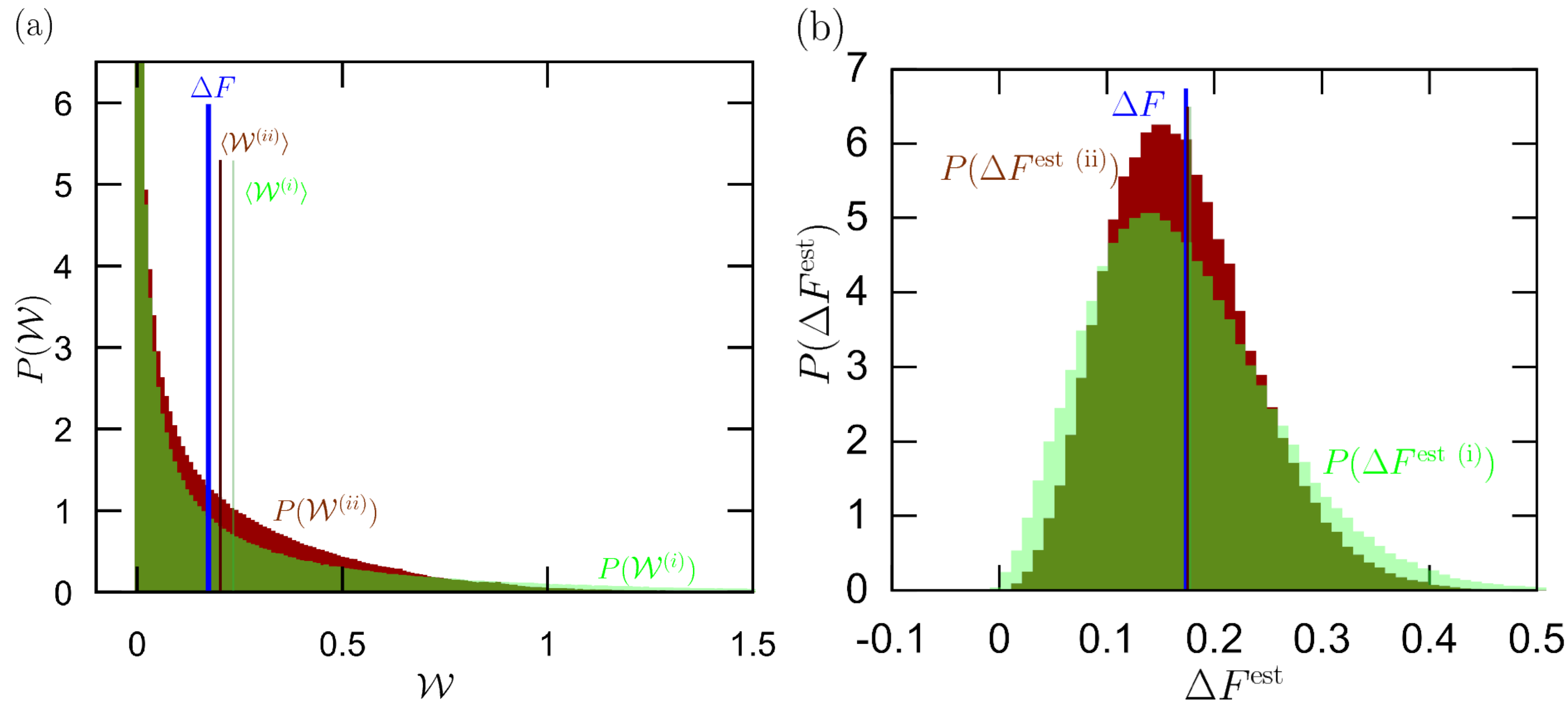


- Anharmonic potential $V(x, \lambda) = \lambda x^4/4 \quad \lambda(0) = 1 \to \lambda(t) = 2$

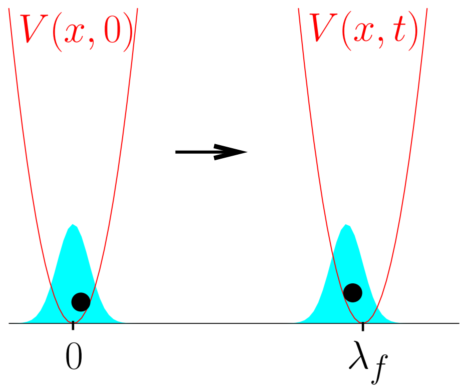


  - Fourier protocol better than linear
  - $W^*(0 + \epsilon) < W^{jp} = 0.25$
  - W^{ad} reached in finite time ??

• Improvement for Jarzynski estimate: $V(x, \lambda) = \lambda x^4/4 \quad \lambda = 1 \rightarrow 2$



- Schrödinger dynamics



$$-i\hbar\ \partial_t \rho = \left\{\rho, p^2/2m + V(x,\lambda(t))\right\}_-$$

$$\rho(t=0) = \exp[-\beta(H-\mathcal{F})]$$

$$\lambda_i = 0 \to \lambda_f \text{ in finite } t$$

  - Talkner et al PRE 2008: $p(W)$ depends only on $z \equiv \int_0^t \dot{\lambda}(t')e^{i\omega t'}dt'$

  - $z = 0$ for an adiabatic transition

    $\Rightarrow W^* = W^{ad}$ for any $t > 0$ possible !

  - case II similarly

  - general case: open

- Conclusions and perspectives

  - Optimal protocols in stoch th'dynamics:

    - directed processes: remarkable singularities
    - cyclic processes: efficiency at max power
    - optimization wrt other quantities like ΔS_{tot} ?
    - ...

  - Hamiltonian and quantum dynamics

    - systematics beyond case studies?
    - open quantum systems?

  - Efficient algorithms for finding optimal protocols?