From stochastic thermodynamics

.... to thermodynamic inference

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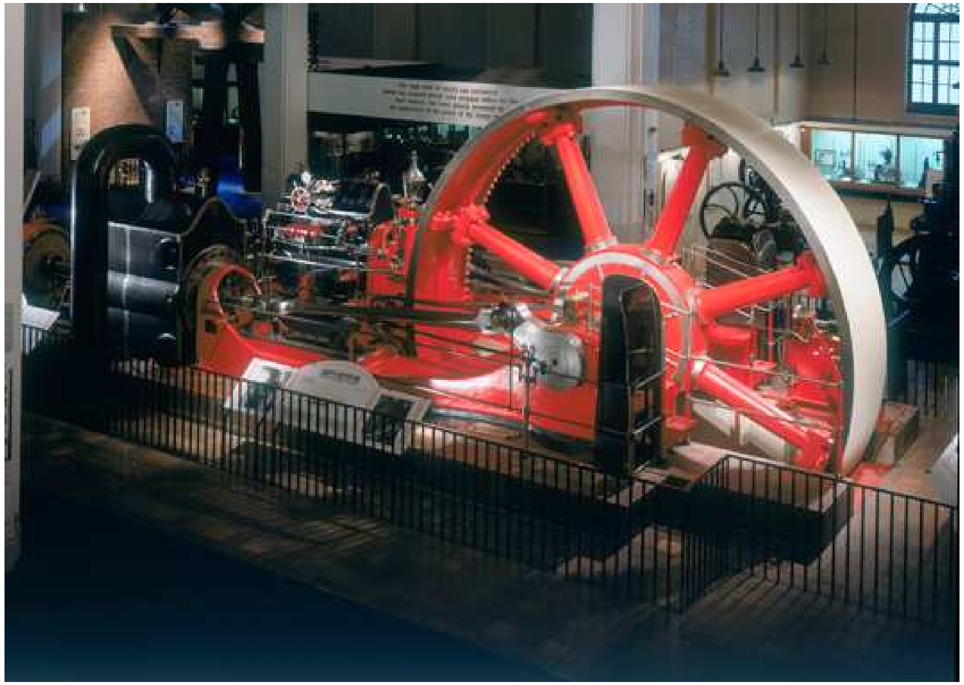
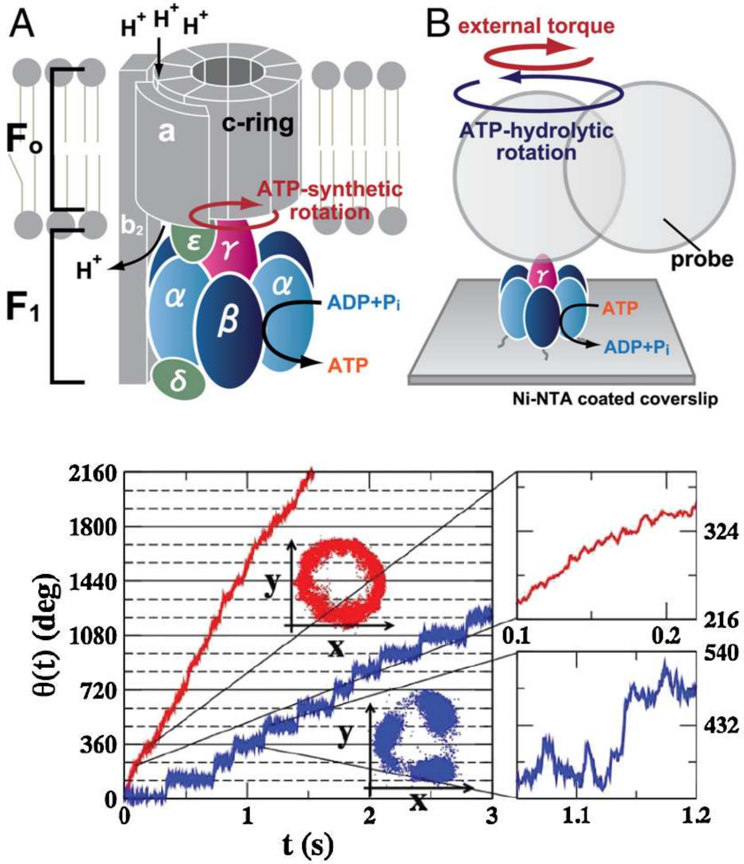
- Hamiltonian vs stochastic dynamics and the second law
- Principles of stochastic thermodynamics*
- Molecular motors as paradigm
- Thermodynamic uncertainty relation and generalizations**
- (Modelfree) inference from experimental data

*Review: U.S., Rep. Prog. Phys. **75** 126001, 2012.

**Review: U.S., Ann. Rev. Cond. Mat. Phys., in press

- From classical th'dynamics to stochastic th'dynamics



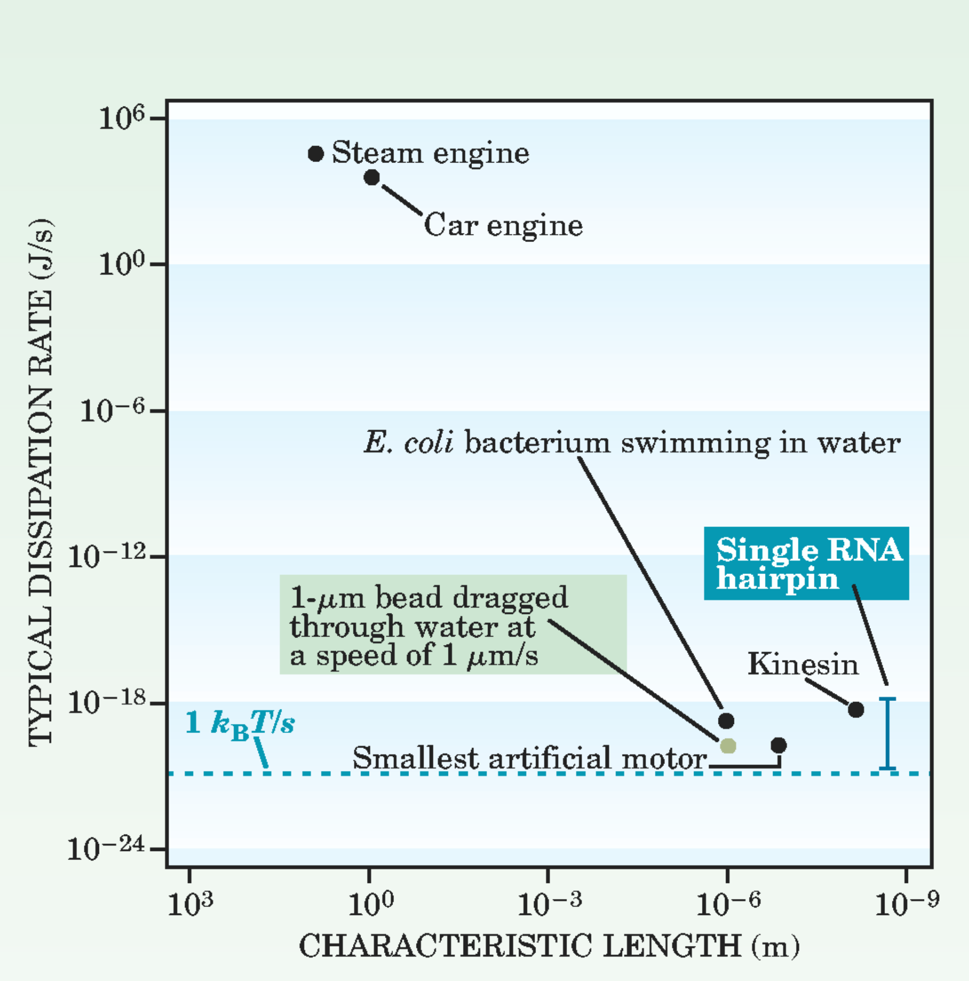


[K. Hayashi, ... H. Noji, PRL 104, 218103 (2010)]

Steam engine

F_1ATP-ase, fluctuations $\rightarrow$ probability distribution

- Macroscopic *vs* mesoscopic *vs* molecular machines



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

- Two types of dynamics
  - classical Hamiltonian (with two basic assumptions)
    - A1: An isolated driven system evolves according to Hamilton's equations $\xi^t = \xi^t(\xi^0)$.
    - A2: A system equilibrated in contact with a heat bath of (inverse) temperature β show the canonical probability distribution
$$p(\xi) = \exp[-\beta(H(\xi) - F(\beta))].$$
  - stochastic (assumptions follow later)

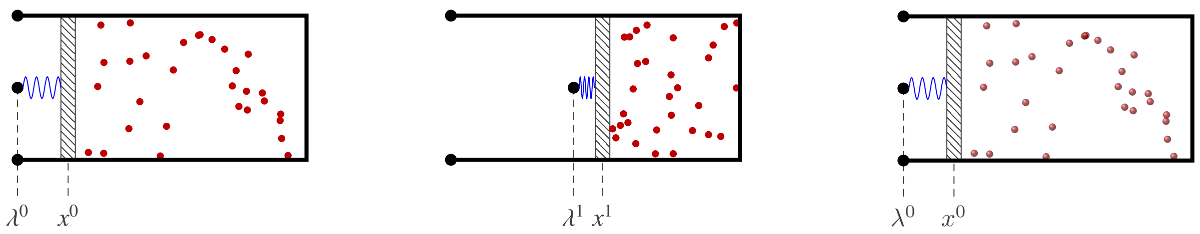
- Two versions of the second law
  - SL1 (Kelvin-Planck)

    It is impossible to devise a cyclically operating thermal engine, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.

  - SL2 (Clausius)

    Any process with a system in contact with a heat bath at temperature T obeys $\Delta S_{\text{sys}} + \Delta Q/T \geq 0$.

- Proof and sharpening of SL1 (Kelvin-Planck) for a driven isolated system (C. Jarzynski, PRL 1997).

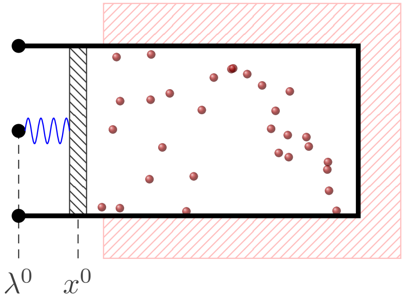


  - time-dependent Hamiltonian $H(\xi, \lambda^t)$ along a cyclic path $\lambda^{\mathcal{T}} = \lambda^0$
  - work $W(\xi^0) \equiv H(\xi^t, \lambda^{\mathcal{T}}) - H(\xi^0, \lambda^0)$ depends on the initial phase point ξ^0
  - initial phase point drawn from canonical distribution $\sim \exp[-\beta(H(\xi^0, \lambda^0)] \to p(W)$

$$
\begin{aligned}
1 &= \int d\xi^t \exp[-\beta[H(\xi^t, \lambda^0) - F(\beta, \lambda^0)]] \\
&= \int d\xi^0 \exp[-\beta[H(\xi^0, \lambda^0) + W(\xi^0) - F(\beta, \lambda^0)]] \\
&= \int dW p(W) \exp(-\beta W) = \langle \exp[-\beta W] \rangle
\end{aligned}
$$

  - implies via Jensen's inequality trivially $\langle W(\xi^0) \rangle \geq 0$
  - there must be events with $W(\xi^0) < 0$ ("violations of the second law")
  - holds even for a finite (small) system
  - doesn't work for microcanonical initial conditions (only in $N \to \infty$ limit)
  - no need to introduce entropy

- "Proof" and sharpening of SL2 (Clausius) for a closed driven system in contact with a heat bath



  - $H_{\text{tot}}(\xi_s, \xi_b, \lambda^t) = H_s(\xi_s, \lambda^t) + H_b(\xi_b)$ $(+H_{\text{int}}(\xi_s, \xi_b))$

  - initial distribution $p^0(\xi) = p_s^0(\xi_s)\,\text{exp}[-\beta(H_b(\xi) - F_b)]$ with arbitrary $p_s^0(\xi_s)$ and equilibrated bath

  - define a trajectory dependent entropy change

    * system: $\Delta S_{\text{sys}}(\xi^0) \equiv -\ln[p_s(\xi_s^t, t)/p_s^0(\xi_s^0)]$

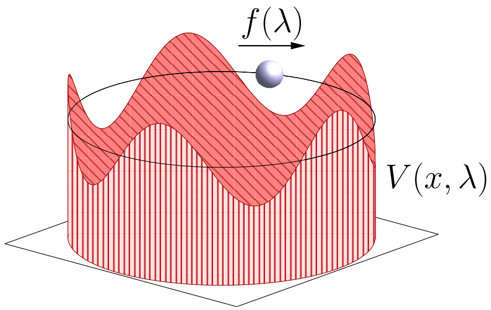
    * bath: $\Delta S_b(\xi^0) \equiv \beta Q(\xi^0) = \beta \Delta H_b(\xi^0)$

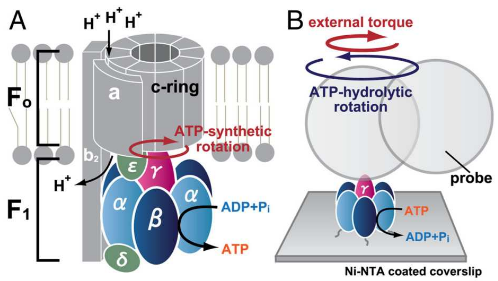
  - theorem [U.S., PRL **116** 020601, 2016] $\langle \text{exp}[-\Delta(S_{\text{sys}} + S_b)]\rangle = 1 \quad \Rightarrow \quad \langle \Delta S_{\text{tot}} \rangle \geq 0$

    * any initial distribution for the system, any driving, any time span $\mathcal{T}$.
    * entropy increases since correlations between system and bath are broken

  - holds suitably modified even in strong coupling

- Stochastic thermodynamics of non-equilibrium steady states





driven colloidal particle　　　　　molecular m/rotor

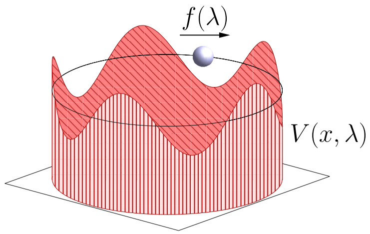
  - time-independent driving beyond the linear response regime around genuine equilibrium
  - stationary (non-Boltzmann) distribution

$$p^s(x) \neq \exp[-\beta V(x)] = p^e(x) \qquad\qquad p_i^s \neq \exp[-\beta F_i] = p_i^e$$

  - broken detailed-balance

$$w_{xy}/w_{yx} \neq p^s(y)/p^s(x) \qquad\qquad w_{ij}/w_{ji} \neq p_j^s/p_i^s$$

  - persistent "currents" with mean dissipation σ
  - time-scale separation: bath much faster than mesostates $x,\ i$



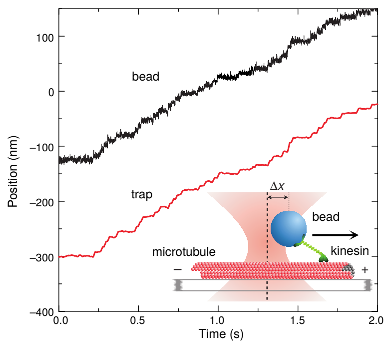
- Stochastic th'dynamics I: Driven colloidal particle
  - Langevin dynamics $\dot{x} = \mu[-V'(x,\lambda) + f(\lambda)] + \zeta$ with $\langle \zeta_1 \zeta_2 \rangle = 2\mu k_B T \delta(t_2 - t_1)$
  - first law [(Sekimoto, 1997)]: $\boxed{dw = du + dq}$
    - applied work: $dw = f \ dx + \partial_\lambda V(x,\lambda) d\lambda$
    - internal energy : $du = dV$
    - dissipated heat: $dq = dw - du = [-\partial_x V(x,\lambda) + f(\lambda)]dx = T ds_{\text{b}}$
  - probability for a whole trajectory $p[x(t)]$
  - total entropy as quantitive measure of broken time reversal symmetry $x(t) \to \tilde{x}(t) \equiv x(\mathcal{T} - t)$

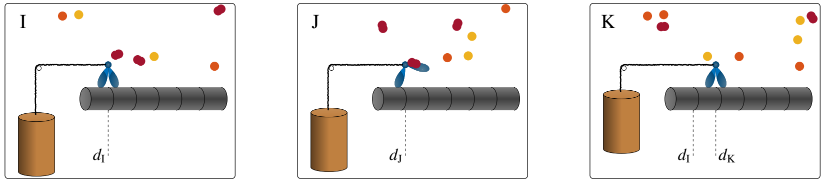
$$\boxed{\Delta s_{\text{tot}}[x(t)] \equiv \ln[p[x(t)]/\tilde{p}[\tilde{x}(t)] = \Delta[-\ln p(x,t)] + q/T}$$

  - integral fluctuation theorem for total entropy production $\boxed{\langle \exp[-\Delta s_{\text{tot}}] \rangle = 1 \Rightarrow \langle \Delta s_{\text{tot}} \rangle \geq 0}$

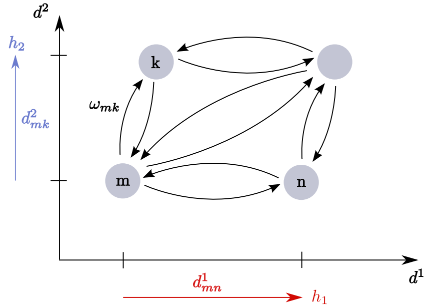
[U.S., PRL 95, 040602, 2005]

- Stochastic th'dynamics II: Master equation, paradigm: molecular motor





  - meso-states $k, m, n, \ldots$
  - master equation $\partial_t p_m(t) = \sum_j [-w_{mn} p_m(t) + w_{nm} p_n(t)]$



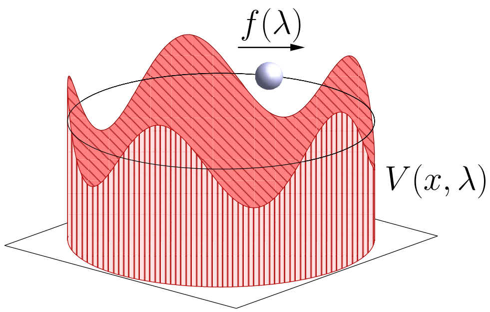
  - local detailed balance $\frac{w_{mn}(h)}{w_{nm}(h)} = \frac{w_{mn}}{w_{nm}}\Big|_{h=0} \exp\ (h_\alpha d^\alpha_{mn}/k_B T)$
  - with "fields" $h_\alpha \sim$ force or $\Delta\mu$ of a reaction
  - mean currents $j^s_{mn} \equiv p_m w_{mn} - p_n w_{nm}$
  - empirical/fluctuating currents $j_{mn}(\mathcal{T}) \equiv [n_{mn}(\mathcal{T}) - n_{nm}(\mathcal{T})]/\mathcal{T}$
  - entropy production

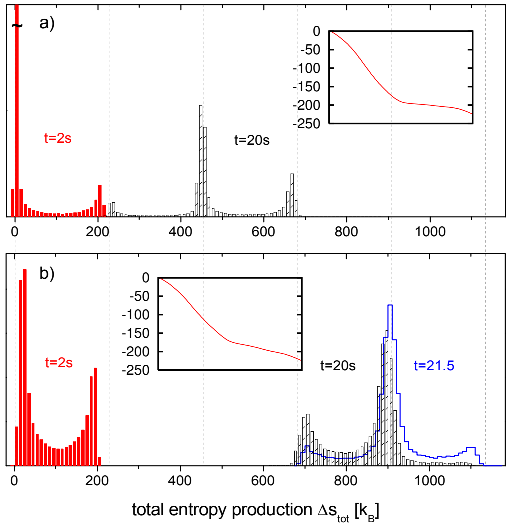
$$\dot{s}_{\text{tot}}(t) = \underbrace{-\sum_j \delta(t-t_j) \ln \frac{p^s_{n_j^+}}{p^s_{n_j^-}}}_{\equiv\ \dot{s}_{\text{sys}}(t)} + \underbrace{\sum_j \delta(t-t_j) \ln \frac{w_{n_j^+ n_j^-}}{w_{n_j^- n_j^+}}}_{\equiv\ \dot{s}_b(t)}$$

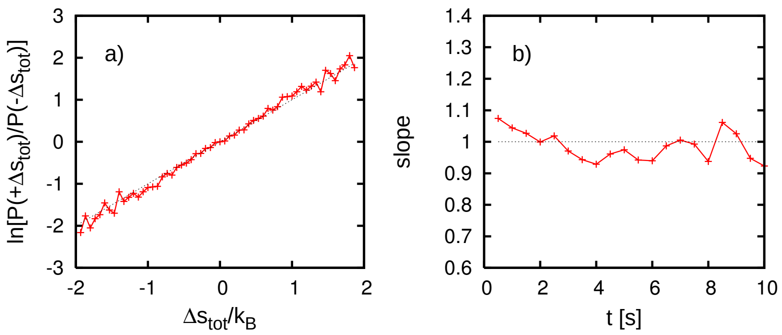
- Fluctuation theorem $\boxed{p(-\Delta s_{\mathrm{tot}})/p(\Delta s_{\mathrm{tot}}) = \exp(-\Delta s_{\mathrm{tot}})}$

  Evans et al (1993), Gallavotti & Cohen (1995), Kurchan (1998), Lebowitz & Spohn (1999), U.S. (2005)

  – experimental data [Speck, Blickle, Bechinger, U.S., EPL **79** 30002 (2007)]

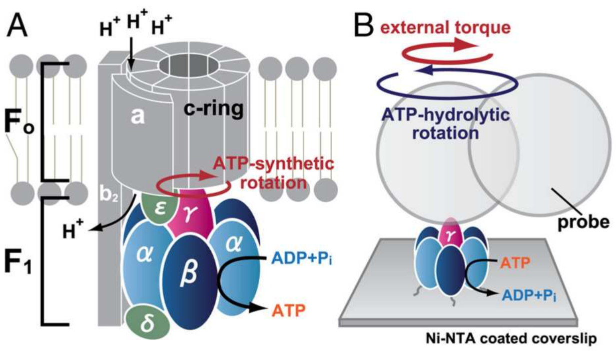


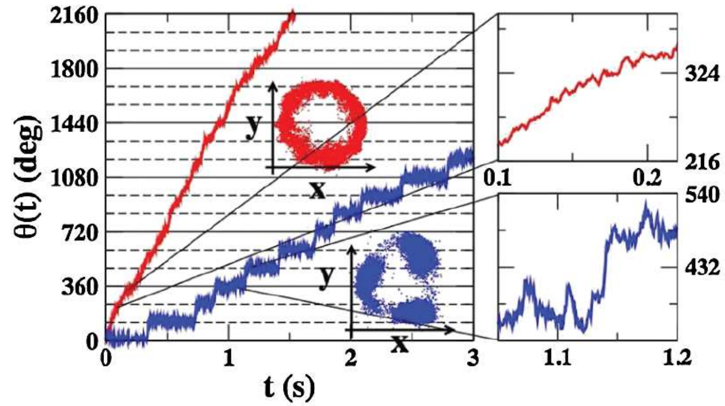


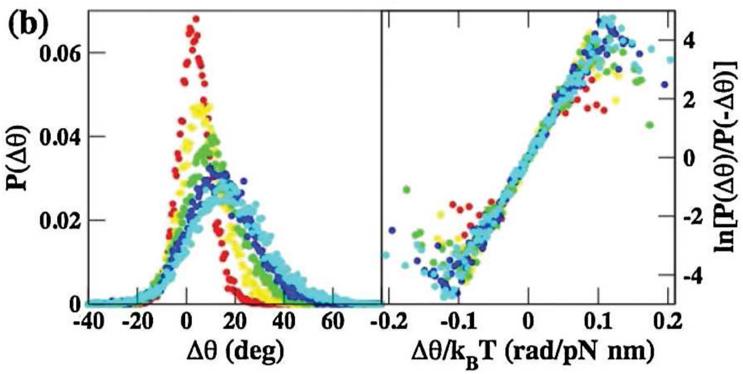


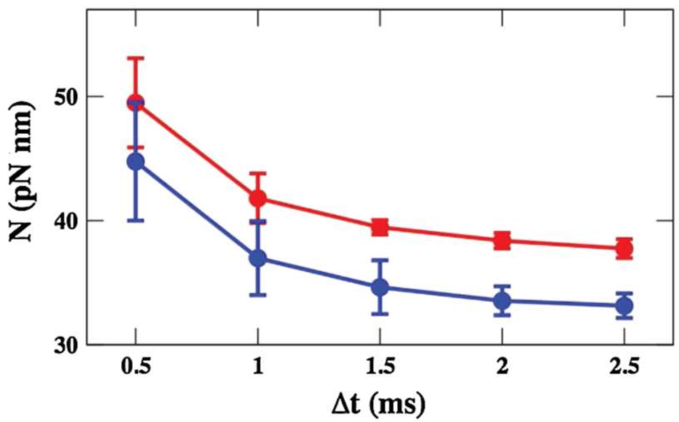
  – FT-representation:

- F1-ATPase and the fluctuation theorem [K. Hayashi et al, PRL 104, 218103 (2010)]









– $\Gamma\dot{\theta} = N + \zeta$

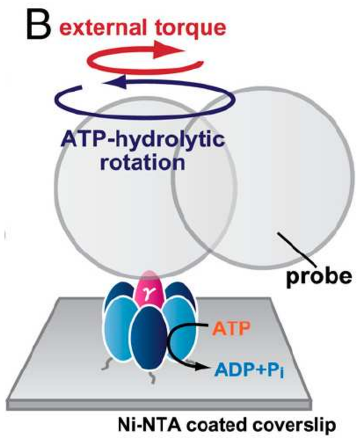
$\Rightarrow \ln[p(\Delta\theta)/p(-\Delta\theta)] = N\Delta\theta/k_BT$

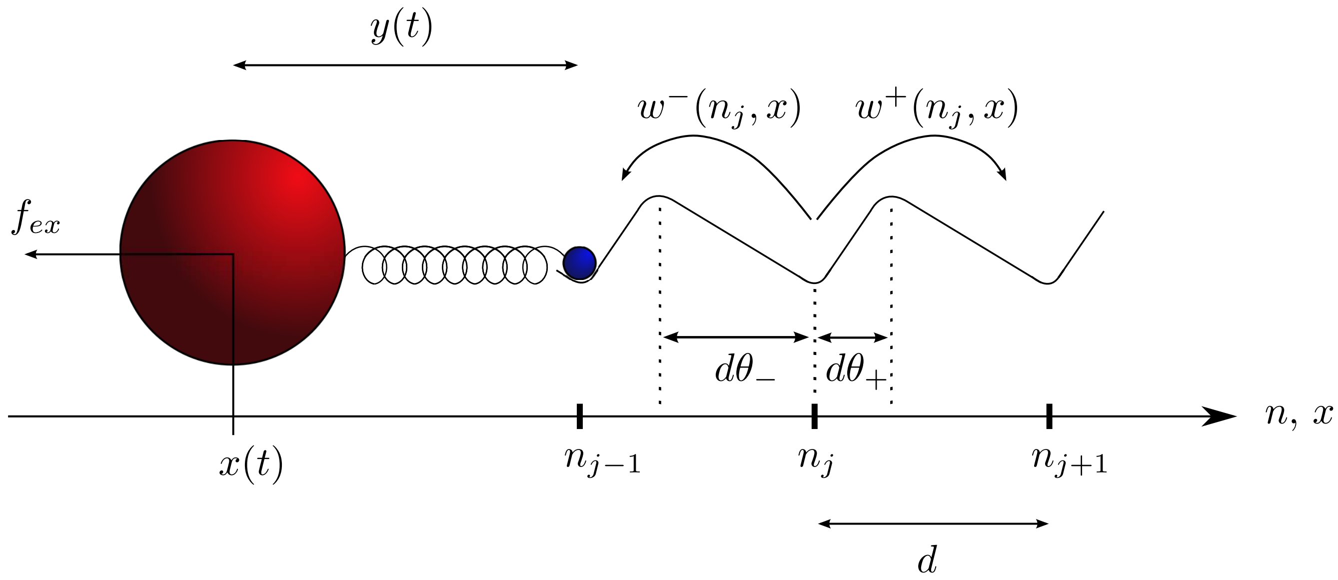
independent of friction coefficient Γ

time-dependence?

torque from $\Delta t \to \infty$?

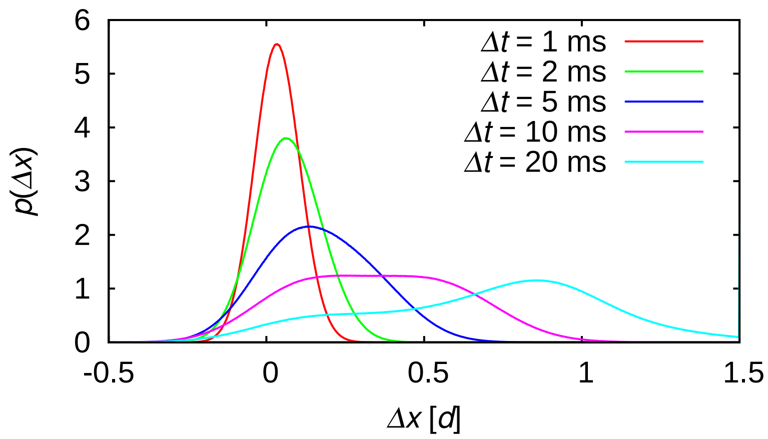
- Hybrid model [E. Zimmermann and U.S., New J. Phys. 14, 103023, 2012]

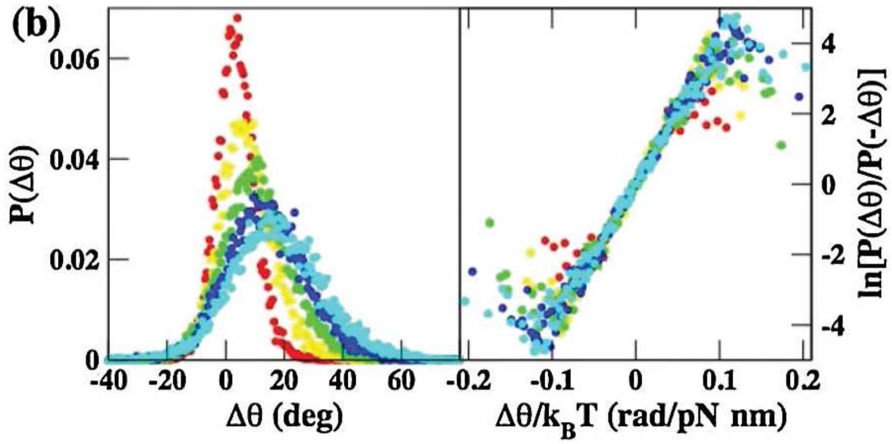


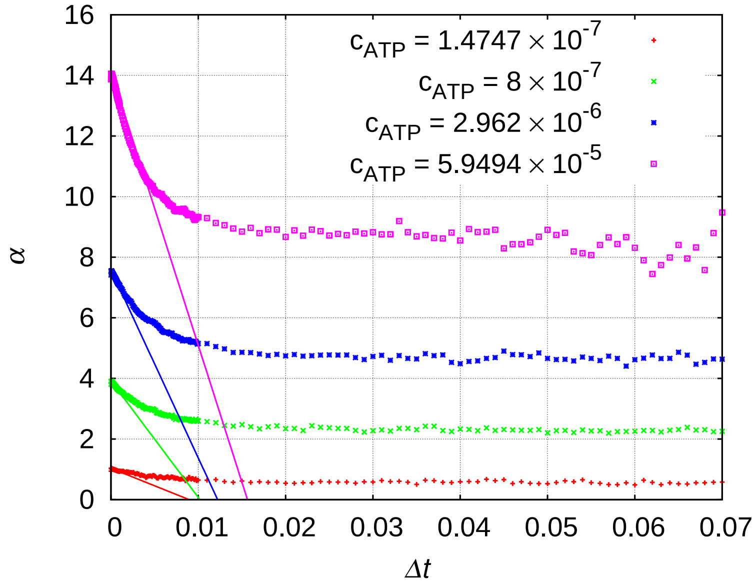


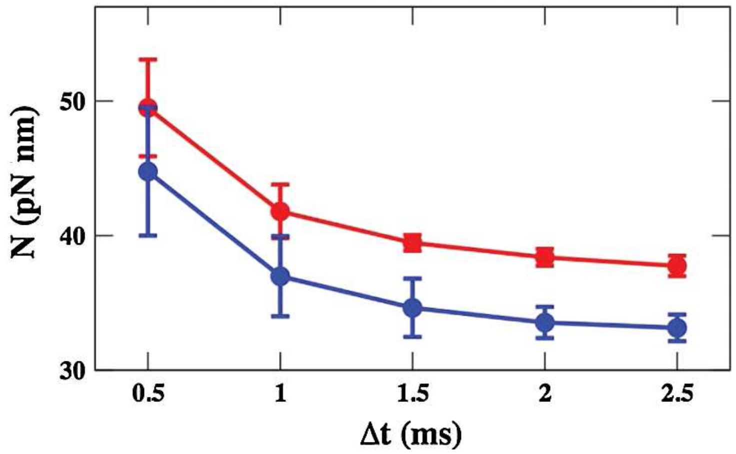
- probe particle
  - $\dot{x} = \mu(-\partial_y V(y) + f^{\text{ex}}) + \zeta$ with $y(\tau) \equiv n(\tau) - x(\tau)$
- motor
  - $w^+/w^- = \exp[\Delta\mu - V(n+d, x) - V(n, x)]$
  - local detailed balance condition

- FT-slope from simulations vs experiment



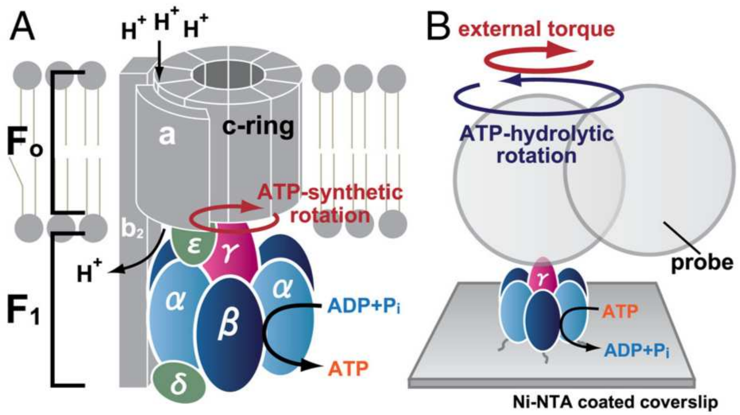


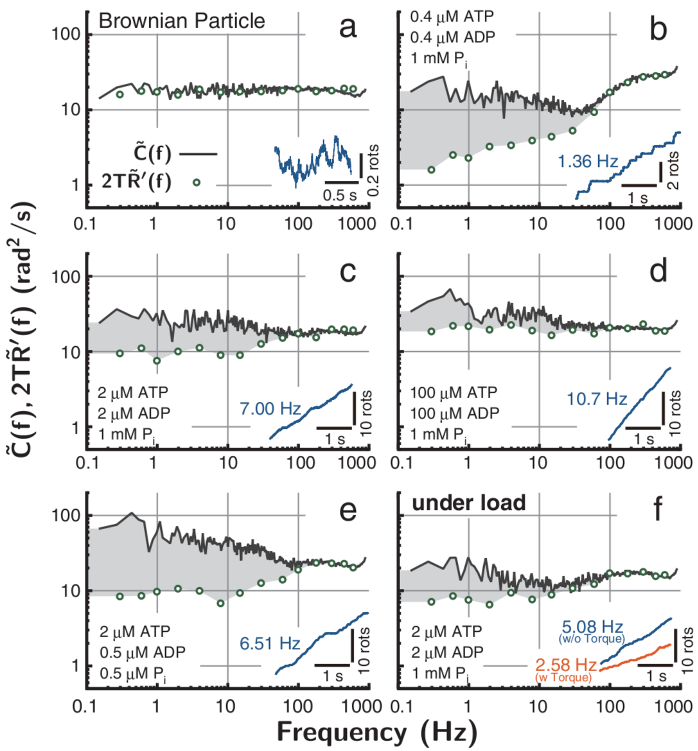




$\Delta t \to 0$ limit yields average force/torque

- Inferring the efficiency of a molecular motor [S. Toyabe et al, PRL 104, 198103 (2010)]



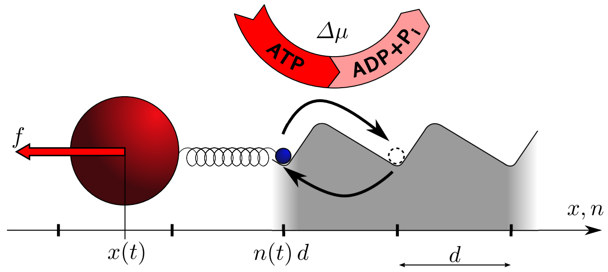


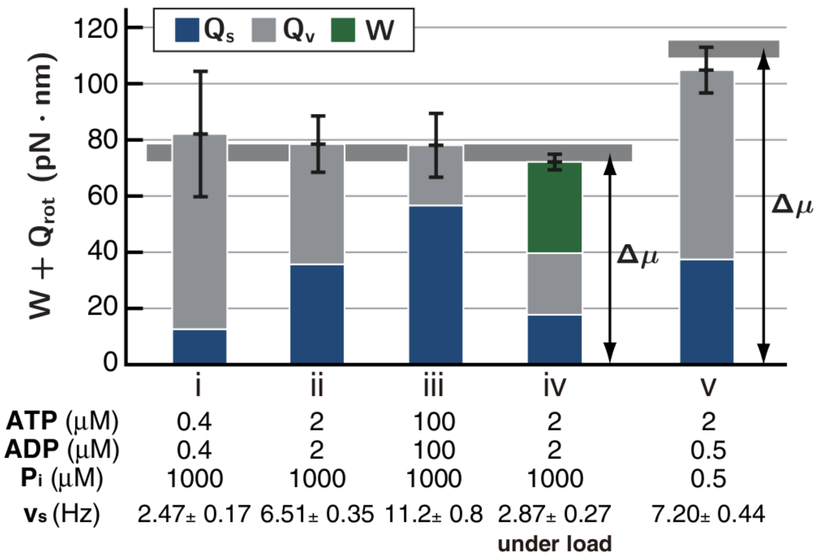
– Harada-Sasa relation [PRL 2006]

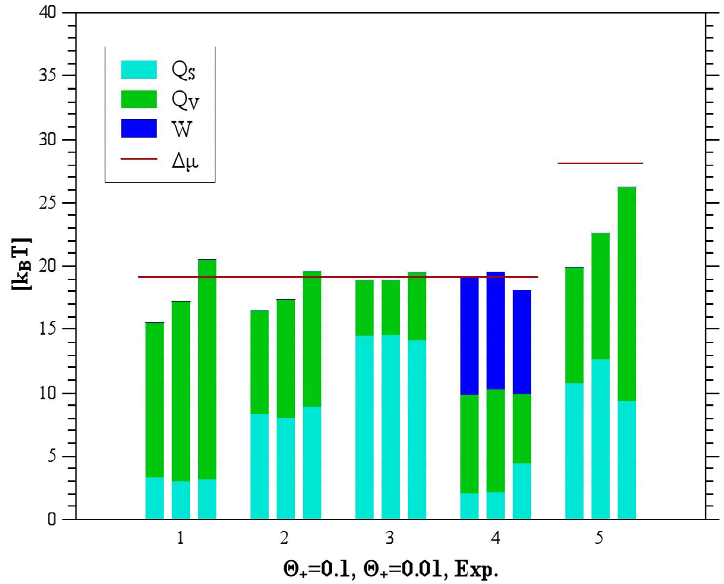
$$\mu \dot{Q}_P = v^2 + \int d\omega [C_{\dot{x}}(\omega) - 2k_B T \ \mathrm{Re} R_{\dot{x}}(\omega)]$$

from violation of fluc-diss-theorem

• Comparison experiment theory





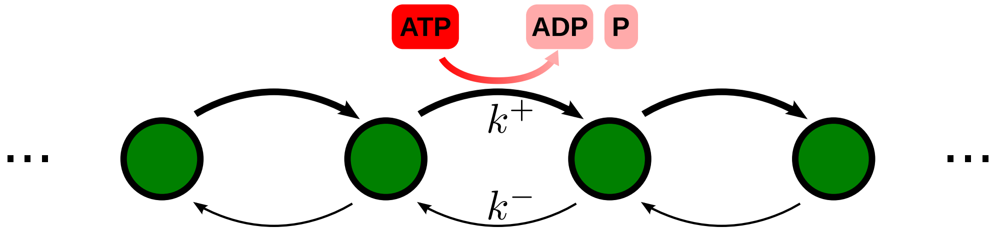


[S. Toyabe et al, PRL 104, 198103 (2010)]

[E. Zimmermann and US, NJP 2012]

- Thermodynamic uncertainty relation: Cost of precision

  [AC Barato and US, Phys. Rev. Lett. 114, 158101, 2015; full proof by Gingrich et al, PRL 2016]



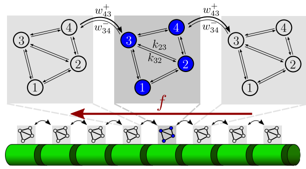
  – output $n(t)$ with $\langle n\rangle = Jt = (k^+ - k^-)t$

  – variance $\langle (n(t) - \langle n\rangle)^2\rangle = 2Dt = (k^+ + k^-)t$

  – uncertainty $\epsilon^2 \equiv \text{var}/\text{output}^2 = 2D/J^2t$

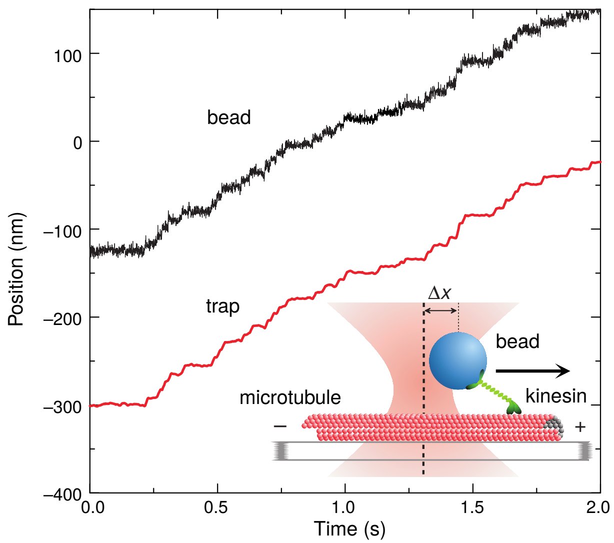
  – th'dyn cost $\mathcal{C} = \sigma t = (k^+ - k^-)\ln(k^+/k^-)t$ with $\sigma \equiv$ rate of entropy production

  – $\boxed{\mathcal{C}\epsilon^2 = 2\sigma D/J^2 \geq 2k_BT}$ independent of run time t



  – inevitable, universal cost of precision (within any model based on a stationary Markov process)

- Thermodynamic inference: Efficiency of a molecular motor



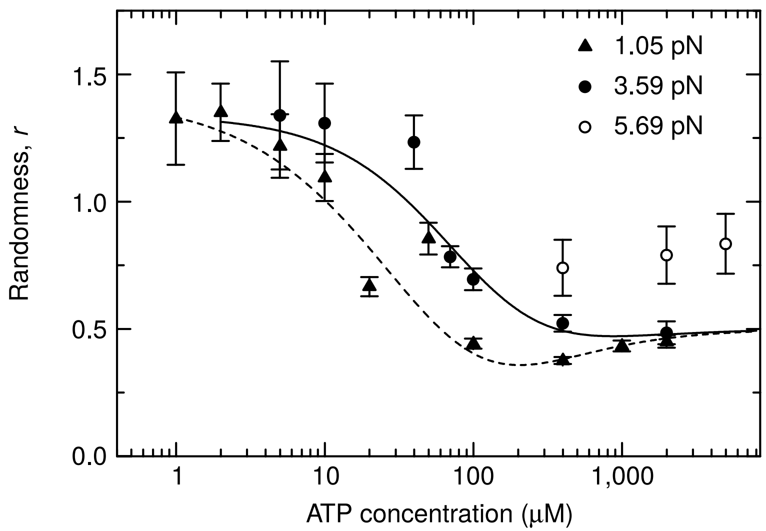
[Visscher et al, Nature, 1999]

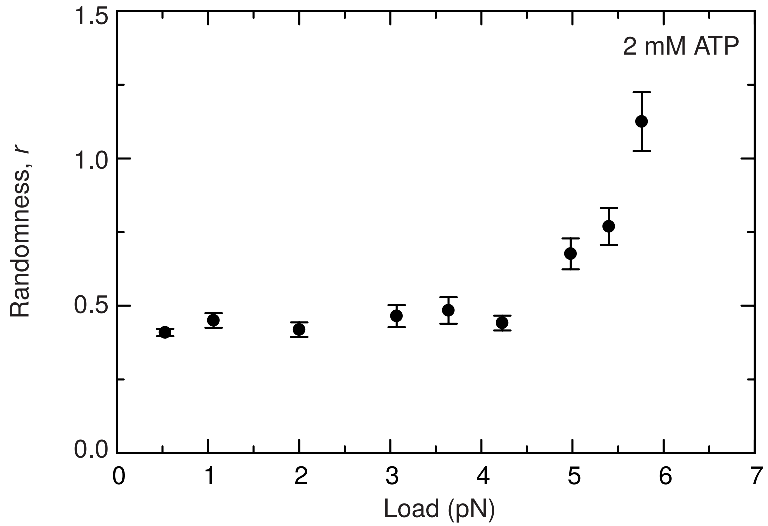
– experimental data on

  * velocity v

  * diffusion constant D

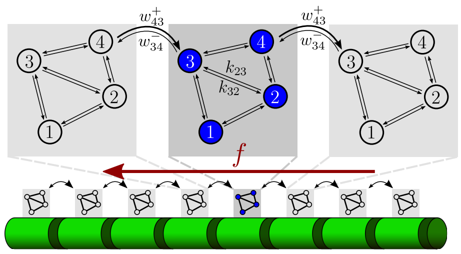
  * randomness parameter $r \equiv 2D/v\ell$





- Thermodynamic inference: Universal bound on the efficiency of molecular machines

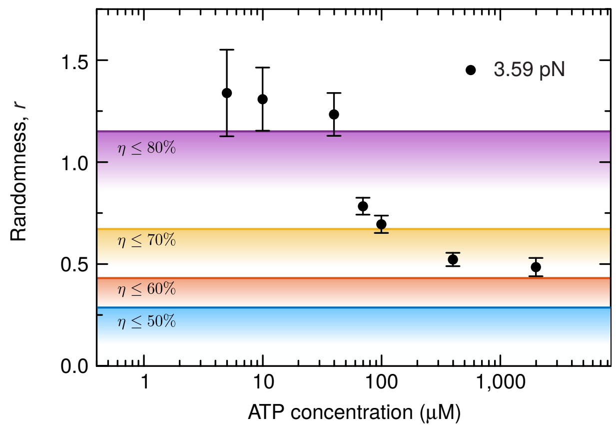
  [P. Pietzonka, AC Barato, U.S., J Stat Mech, 124004, 2016; U.S., Physica A 504, 176, 2018]

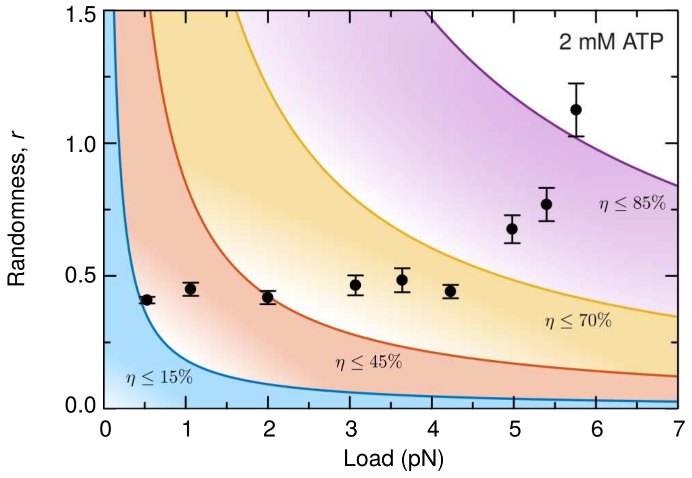


  – entropy production rate $\sigma = P^{\text{in}} - P^{\text{out}} = \text{"chem energy"} - fv \geq v^2/D$

  – efficiency

$$\eta \equiv \frac{P^{\text{out}}}{P^{\text{in}}} = \frac{fv}{\text{unknown}} = \frac{fv}{fv + \sigma} = \leq \frac{1}{1 + vk_BT/(Df)}$$



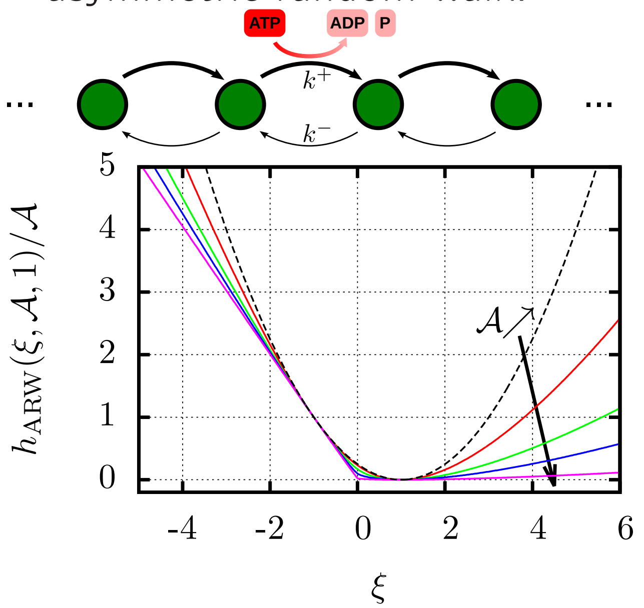


  – completely independent of the specific chemo-mechanical cycles and of $\Delta\mu$

- Generalization I: bound on ldf for an arbitrary current J in any (multicyclic) network

  [P Pietzonka, AC Barato and US, PRE 93, 052145, 2016, TR Gingrich et al, PRL 2016]

– asymmetric random walk:

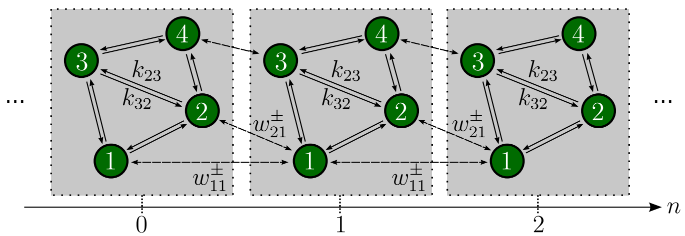


– scaled current:

$$\xi \equiv X(t)/\langle X \rangle = j(t)/j^s$$

– rate function: $p(\xi, t) \sim \exp[-th(\xi)]$

– arbitrary, multicyclic network



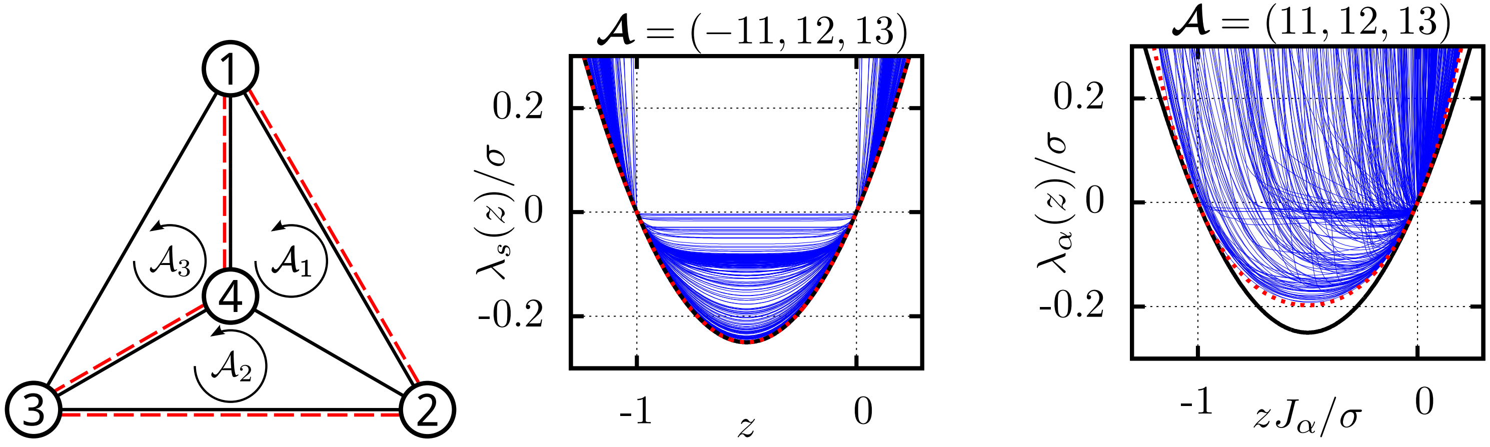
– global, universal bound:

$$\boxed{h(\xi) \leq \frac{1}{4}\sigma(\xi - 1)^2}$$

– fluct's of any current globally constrained by mean entropy production σ

- Generalzation II: Affinity and topology-dependent bound

  [P Pietzonka, AC Barato and US, J. Phys. A **49** (2016) 34LT01]



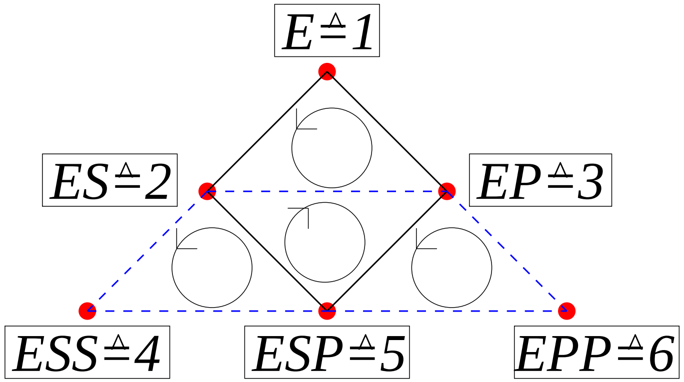
for the Legendre trafo of rate function $h(\xi)$

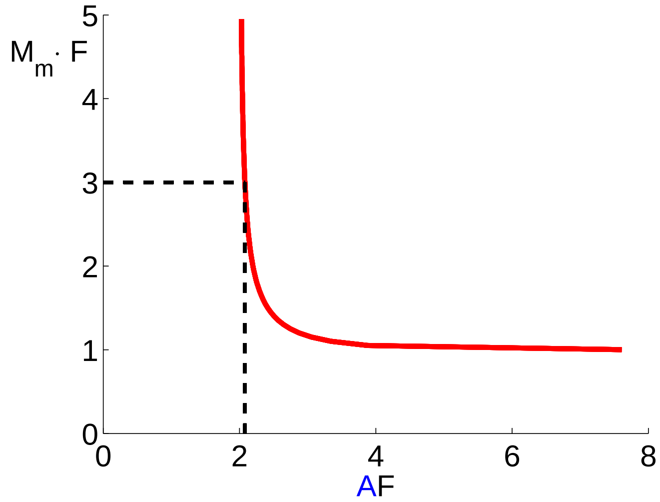
$$\lambda(z) \geq \sigma \frac{\cosh[(zJ/\sigma + 1/2)\mathcal{A}^*/n^*] - \cosh[\mathcal{A}^*/(2n^*)]}{(\mathcal{A}^*/n^*)\,\sinh\,[\mathcal{A}^*/(2n^*)]}$$

$\mathcal{A}^*/n^*$: cycle with minimal affinity per site

- Thermodynamic inference in single enzyme (statistical) kinetics

  [AC Barato and U.S., J. Phys. Chem. B, 2015, 119, 6555, 2015; PRL 115, 188103, 2015]





  - Fano factor

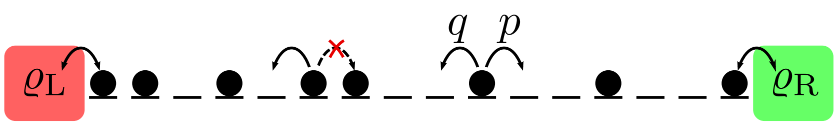
$$\mathcal{F} \equiv \frac{\langle (X - \langle X \rangle)^2 \rangle}{\langle X \rangle} \geq \frac{1}{M_{\text{max}}} \coth[\mathcal{A}/2M_{\text{max}}] \geq \frac{2}{\mathcal{A}}$$

    bounded by the cycle with the largest effective length $M = (N/n)$

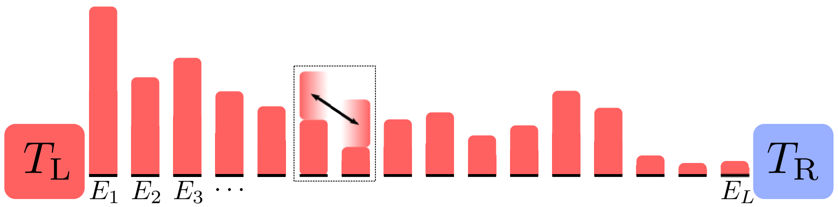
  - diagnostic tool for network topology:
    Ex: $F = 1/2$, $\mathcal{A} = 4.5 \ \rightarrow M_{\text{max}} > 3$, i.e. simple MM-scheme not possible

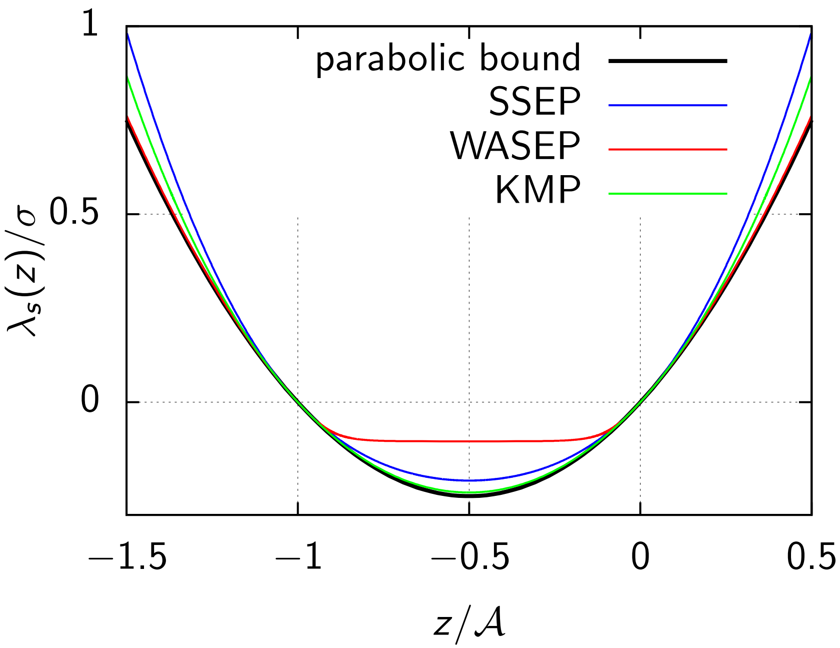
- Bound applied to lattice gas models

WASEP



KMP (Kipnis, Marchioro, Presutti, JSP 1982)

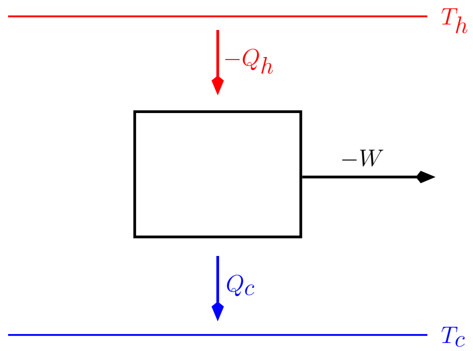




compared to $\lambda(z)$ from additivity principle [Bodineau and Derrida, PRL 2004]

[Gorissen and Vanderzande, PRE 2012, Hurtado and Garrido, PRE 2010]

- Carnot efficiency with finite power?



  - common wisdom: $\eta_c \equiv 1 - T_c/T_h$ requires quasistatic conditions and hence implies zero power

  - cyclic engines:
    2013 PRL: Allahverdyan and co-workers: possible with special couplings
    2016 NatComm: Campisi and Fazio: critical fluid as working substance

  - steady state engines:
    2011 PRL: Benenti et al: in principle allowed in lin irr th'dynamics in a magnetic field
    2013 PRL+NJP: K. Brandner and U.S.: not in a $N < \infty$-terminal machine

    case studies:

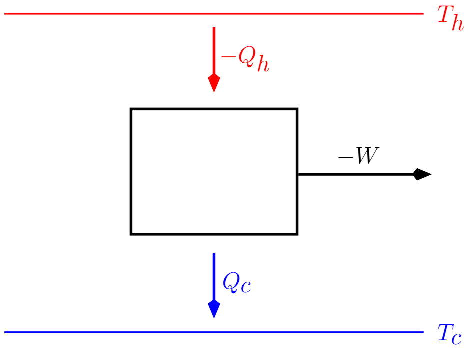
    * two-cycle engines with diverging affinities (M. Polettini and M. Esposito, EPL 2017)
    * a specially designed Feynman-Smoluchowski ratchet (Lee and Park, Sci Rep 2017)
    * with a singular transport law (Shiraishi PRE 2015, Koning and Indekeu EPJB 2016)

  - analytical results: $P < A(\eta_c - \eta)$

    2015 PRE: K. Brandner and U.S. in lin response; 2016 PRL: N. Shiraishi, K. Saito and H. Tasaki beyond

- Universal bound on power of steady state heat engines from unc'relation

  [P. Pietzonka and U.S, PRL 120, 190602, 2018]



  - uncertainty relation for work current (=power)

$$\sigma > j_w^2/D_w$$

  - universal bound on power

$$j_w = P \leq \frac{(\eta_C - \eta)D_w}{\eta \; T_c}$$

  - singular limit towards η_c with "finite" power requires diverging power fluctuations

  - trade-off between power, efficiency and constancy

    [cf Holubec JStatMech 2014, & Ryabov PRE 2017]

- Summary
  - stochastic thermodynamics along individual trajectories
    - first law
    - flucuation theorems as refinements of the second law
    - complications with hidden slow degrees of freedom
  - universal bounds through the thermodynamic uncertainty relation for NESSs
    - thermodynamic inference can reveal hidden properties of molecular motors and biochemical networks

- Acknowledgments
  - molecular motor   P Pietzonka ($\rightarrow$ U of Cambridge), E Zimmermann
  - thermodynamic uncertainty relation and bounds   AC Barato ($\rightarrow$ U of Houston), P Pietzonka