Workshop: rare events, Lyon, June 2012

Stochastic thermodynamics on NESS:

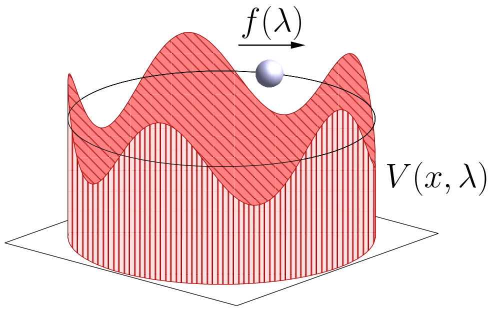
From the FDT to efficiency

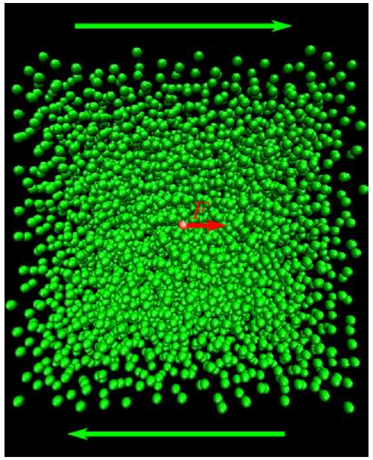
Udo Seifert

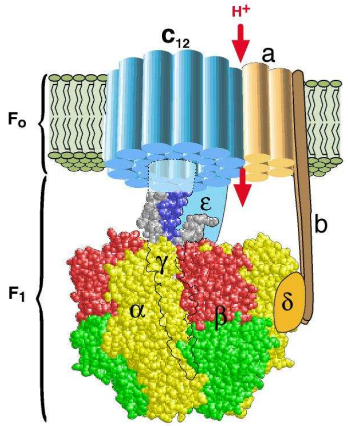
II. Institut für Theoretische Physik, Universität Stuttgart

recent review: U.S., arxiv 1205.4176

- NESSs: Examples and common characteristics







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

  – Time-independent driving beyond linear response regime
  – Broken detailed-balance
  – Persistent “currents” with permanent dissipation

- Fluctuation-dissipation (response) theorem in equilibrium
  - system with energy E and observable A
  - perturbation with a field f : $\quad E \to E - fB$

$$T \frac{\langle \delta A(t_2) \rangle}{\delta f(t_1)} = \partial_{t_1} \langle A(t_2) B(t_1) \rangle$$

  - any observable A, any time diff $t_2 - t_1$
  - formalizes Onsager's regression hypothesis

- FDT in a NESS ?

  – plethora of exact (rather formal) expressions

    Agarwal '72, ... Hänggi & Thomas, ... Vulpiani, ... Harada & Sasa '05, ...
    Baiesi, Maes & Wynants, Krüger & Fuchs, Prost, Joanny & Parrondo all '09

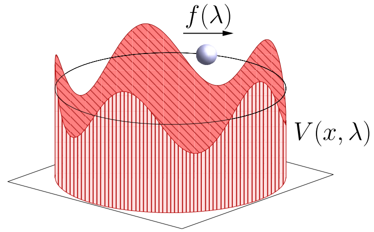
  – often (phenomenologically) modified by an effective temp:

    Culgiandolo, Kurchan & Peliti, '97 ...

$$T_{\text{eff}} \frac{\langle \delta A(t_2) \rangle}{\delta f(t_1)} = \partial_{t_1} \langle A(t_2) B(t_1) \rangle$$

- Paradigm for an FDT in a NESS

  [T. Speck and U.S., Europhys. Lett. **74**, 391, 2006]



– Langevin dynamics: $\dot{x} = \mu[-\partial_x V(x,\lambda) + f(\lambda)] + \zeta$ with white noise

– FDT in eq:

$$T \frac{\delta\langle \dot{x}(t_2)\rangle}{\delta f(t_1)}_{|f=0} = \langle \dot{x}(t_2)\dot{x}(t_1)\rangle_{\text{eq}}$$

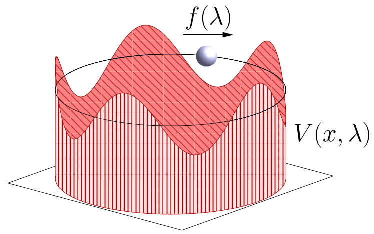
– extended FDT in non-eq:

$$T \frac{\delta\langle \dot{x}(t_2)\rangle}{\delta f(t_1)}_{|f\neq 0} = \langle \dot{x}(t_2)\dot{x}(t_1)\rangle_{\text{ness}} - \langle \dot{x}(t_2)\nu_s(x(t_1))\rangle_{\text{ness}}$$

with $\nu_s(x) \equiv \langle \dot{x}|x\rangle = j^s/p^s(x)$

– additive modification (rather than multiplicative)

- “Restoration” of equilibrium form



– extended FDT in a NESS:

$$T\frac{\delta\langle\dot{x}(t_2)\rangle}{\delta f(t_1)}_{|f\neq 0} = \langle\dot{x}(t_2)\dot{x}(t_1)\rangle_{\text{ness}} - \langle\dot{x}(t_2)\nu_s(x(t_1))\rangle_{\text{ness}}$$

– restoration of FDT in non-eq for renormalized velocity:

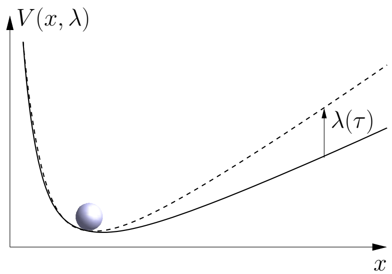
$v(t) \equiv \dot{x}(t) - \nu_s(x(t))$

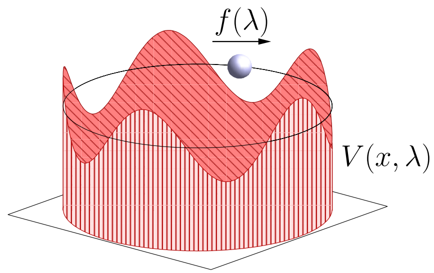
$$T\frac{\delta\langle v(t_2)\rangle}{\delta f(t_1)}_{|f\neq 0} = \langle v(t_2)v(t_1)\rangle_{\text{ness}}$$

– NESS version of Onsager’s regr hypothesis

– cf Chetrite and Gawedzki, J Stat Mech 2008, J Stat Phys 2009

- Stochastic th'dynamics of a colloidal particle





- Langevin dynamics $\dot{x} = \mu[-V'(x,\lambda) + f(\lambda)] + \zeta$
  with external driving $\lambda(\tau)$ and $\langle \zeta_1 \zeta_2 \rangle = 2\mu k_B T \delta_{12}$

- First law [(Sekimoto, 1997)]: $dw = du + dq$

  * applied work: $dw = \partial_\lambda V(x,\lambda) d\lambda + f\ dx$
  * internal energy: $du = dV$
  * dissipated heat: $dq = dw - du = [-\partial_x V(x,\lambda) + f]dx = T ds_\mathrm{m}$

- stochastic entropy: $ds \equiv -d\ [\ln p(x,t)] \quad \Rightarrow \langle \exp[-\Delta(s + s_\mathrm{m})] \rangle = 1$

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

- General FDT in a NESS

  [U.S and T. Speck, EPL 89: 10007, 2010]

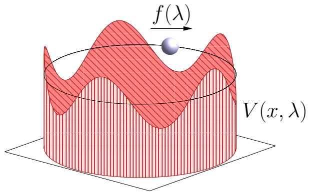
$$\text{NESS}: \quad \frac{\langle \delta A(t_2)\rangle}{\delta f(t_1)} = \langle A(t_2)\partial_f \dot{s}(t_1)\rangle$$

$$= -\underbrace{\langle A(t_2)\partial_f \dot{s}_{\mathrm{m}}(t_1)\rangle}_{}{}_{\mathrm{ness}} + \langle A(t_2)\partial_f \dot{s}_{\mathrm{tot}}(t_1)\rangle_{\mathrm{ness}}$$

$$\text{EQ}: \quad T\frac{\langle \delta A(t_2)\rangle}{\delta f(t_1)} = -\langle A(t_2)\partial_f \dot{E}(t_1)\rangle_{\mathrm{eq}}$$

  - stochastic entropy replaces energy
  - add to eq form the term conj to total entropy production
  - proof: (1) pert'theory of FPE + (2) use of det bal in equilibrium

- "Non-uniqueness" of the FDT in a NESS: Three canonical forms

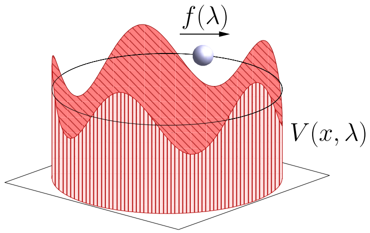


$$\boxed{\frac{\langle \delta A(t_2)\rangle}{\delta f(t_1)} = \langle A(t_2) B(t_1)\rangle}$$

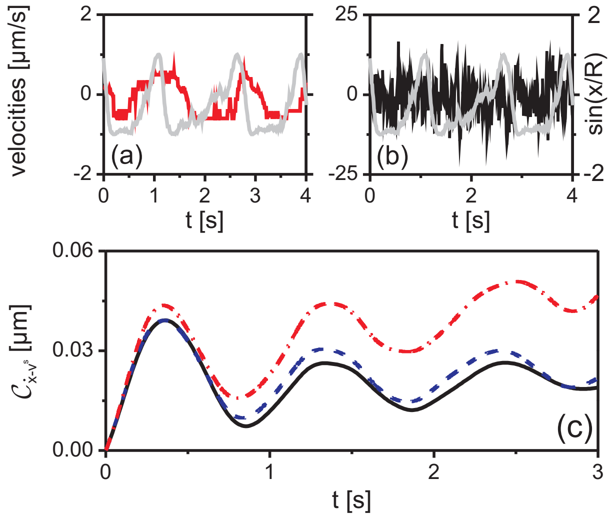
general: B		ring: B/T	unique property
$(p^s)^{-1} L_1 p^s$	Agarwal '72 ...	$\nu(x) - \mu F(x)$	state variable only
$-\partial_f \dot{s} = \partial_f \dot{s}_{\mathrm{m}} - \partial_f \dot{s}_{\mathrm{tot}}$	U.S & T. S. '10	$\ldots = \dot{x} - \nu(x)$	∂_t (state var)
$\frac{\delta \ln P[x(t),f(t)]}{\delta f}$	Baiesi et al PRL '09	$(\dot{x} - \mu F(x))/2$	no knowledge of p^s required

- Experimental accessibility

[J. Mehl, V. Blickle, U.S, and C. Bechinger. PRE 82, 032401, 2010.]



$$\frac{\langle \delta A(t_2)\rangle}{\delta f(t_1)} = \langle A(t_2) B(t_1)\rangle \quad (1)$$



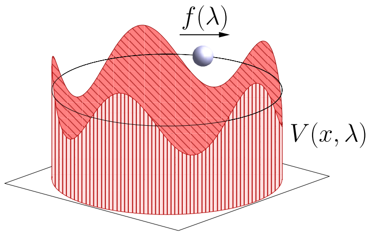
$A = \sin x/R$

$B_1 = \nu(x) - \mu F(x)$

$B_2 = \dot{x} - \nu(x)$

[cf experiment by Ciliberto et al, PRL 2009].

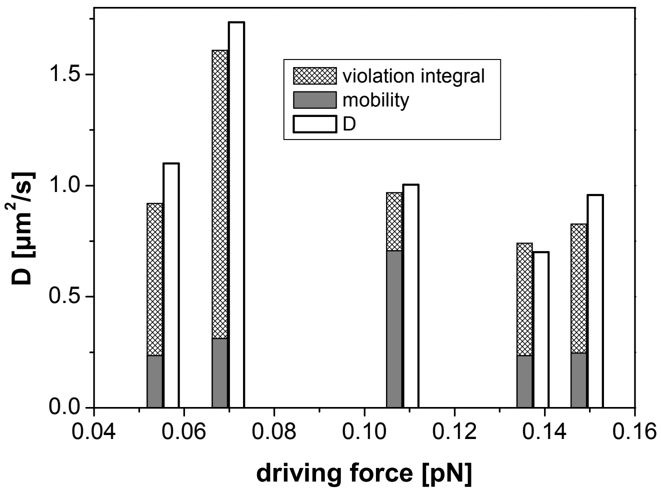
- Integrated version: Generalized Einstein relation



[Blickle, Speck, Lutz, U.S., Bechinger, PRL **98**, 210601 (2007)]

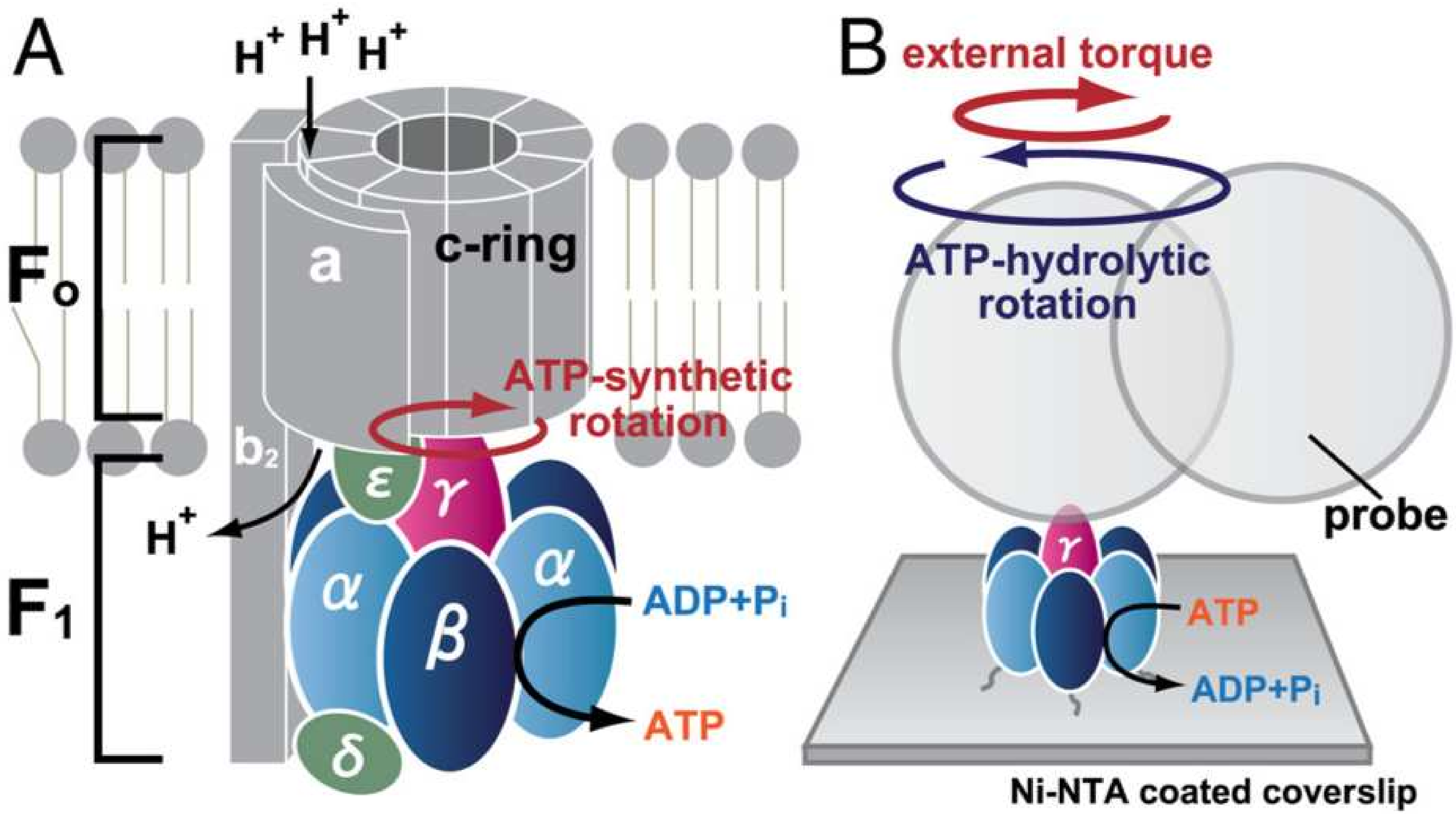
$$\frac{\delta\langle\dot{x}(t_2)\rangle}{\delta f(t_1)}_{|f\neq 0} = \langle\dot{x}(t_2)\dot{x}(t_1)\rangle_{\text{neq}} - \langle\dot{x}(t_2)\nu_s(x(t_1))\rangle_{\text{neq}}$$

$$\mu_{\text{eff}}(f) = D_{\text{eff}}(f) - \int_0^\infty dt\ I(t) \quad \text{with} \quad I(t) \equiv \langle\dot{x}(t)\nu_s(x(0))\rangle - \langle\nu_s(x)\rangle^2$$



— cf giant diffusion [Reimann et al 2001]

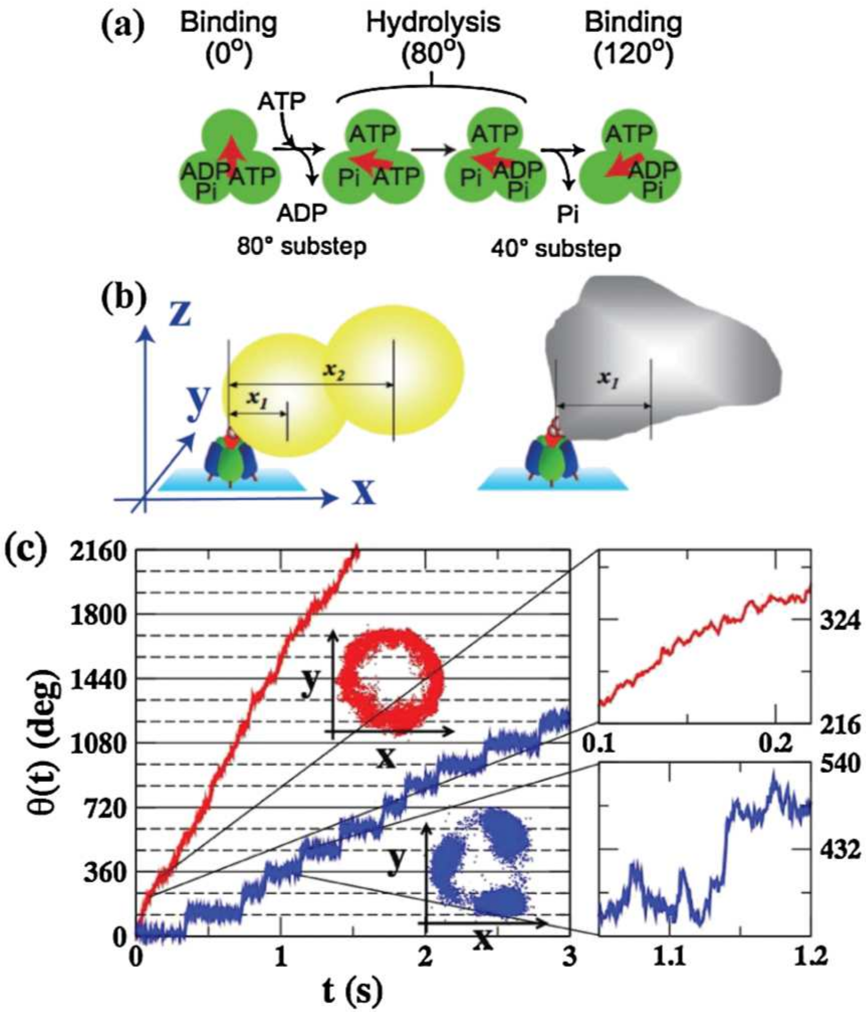
• An isothermal nano-rotor: F1-ATP-ase



from Toyabe et al, PNAS 2011

- Single molecule data for the F1-ATP-ase

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



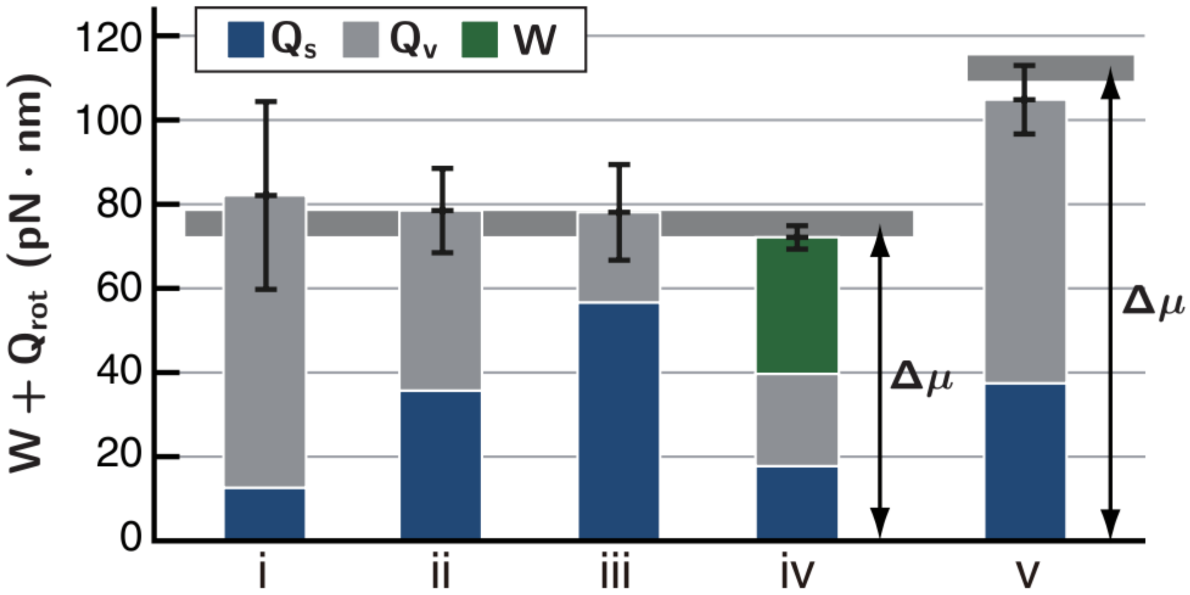
– kinetics vs thermodynamics

– first law?

– efficiency(ies)?

- Experiment: Efficiency of the F1-ATP-ase

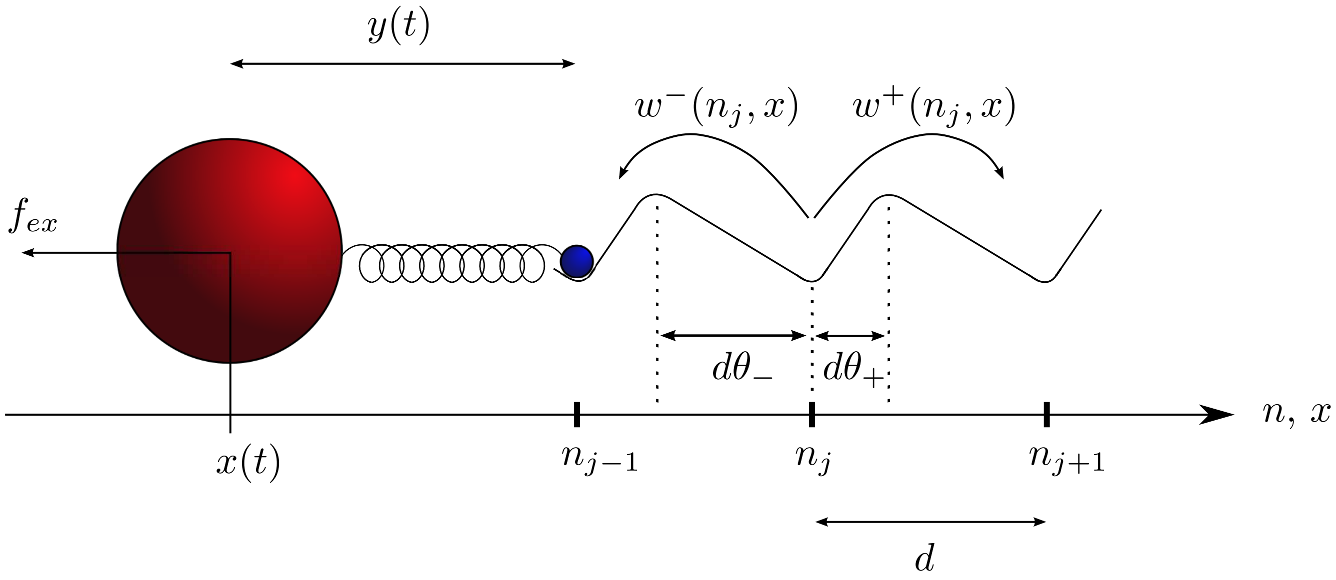
  [S. Toyabe et al, PRL 104, 198103 (2010)]



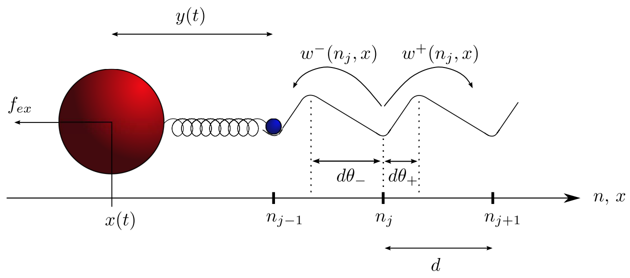
	i	ii	iii	iv	v
ATP (μM)	0.4	2	100	2	2
ADP (μM)	0.4	2	100	2	0.5
P$_i$ (μM)	1000	1000	1000	1000	0.5
v$_s$ (Hz)	2.47± 0.17	6.51± 0.35	11.2± 0.8	2.87± 0.27 **under load**	7.20± 0.44

main message: efficiency about 1

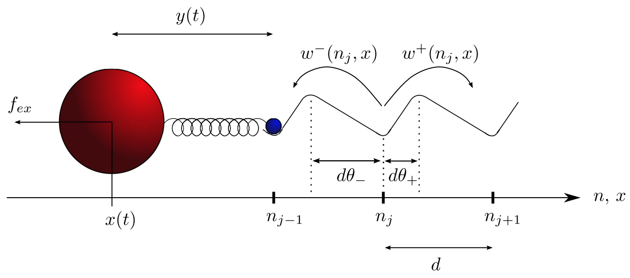
- Hybrid model [E. Zimmermann and U.S., NJP submitted]



  - angular $\rightarrow$ linear motion
  - observable: motion of the probe
  - hidden: steps of the motor
  - elastic linker between both: $V(n, x) = V(y) = ky^2/2$
  - each forward step: $ATP \rightarrow ADP + P$

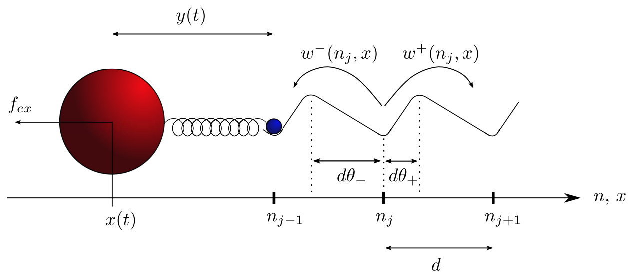


- Dynamics $[k_B T = 1]$
  - probe
    - $\dot{x} = \mu(-\partial_y V(y) + f^{\text{ex}}) + \zeta$ with $y(\tau) \equiv n(\tau) - x(\tau)$
  - motor
    - $w^+/w^- = \exp[\Delta\mu - V(n+d,x) - V(n,x)]$
    - $w^+ = w^{\text{eq}}\ \exp(\Delta\mu_T)\ \exp[-kd^2\theta_+{}^2/2 - ky\ d\theta_+]$
    - $w^- = w^{\text{eq}}\ \exp(\Delta\mu_D + \Delta\mu_P)\ \exp[-kd^2(1-\theta_+)^2/2 + ky\ d(1-\theta_+)]$



- First law

(i) probe	$-f^{\text{ex}}\Delta x$	$=$	$\Delta q_p + \Delta V_{\vert p}$	Sekimoto '97
(ii) motor	0	$=$	$\Delta q_m + \Delta V_{\vert m} + \Delta E_{sol}$	U.S., EPJE, 34, 26, 2011
mean (i)	$-f^{\text{ex}}v$	$=$	$\dot{Q}_p + \dot{Q}_m + \Delta\dot{E}_{sol}$	$\Delta E_{sol} = -\Delta\mu + T\Delta S_{sol}$
mean (ii)	$\dot{\Delta\mu} - f^{\text{ex}}v$	$=$	$\dot{Q}_p + \underbrace{\dot{Q}_m + T\dot{S}_{sol}}_{\text{not distinguishable}}$	



- Efficiencies

  - Thermodynamic efficiency [Parmeggiani et al, PRE 1999]

  $$\eta \equiv f^{\mathrm{ex}} v / \dot{\Delta} \mu$$

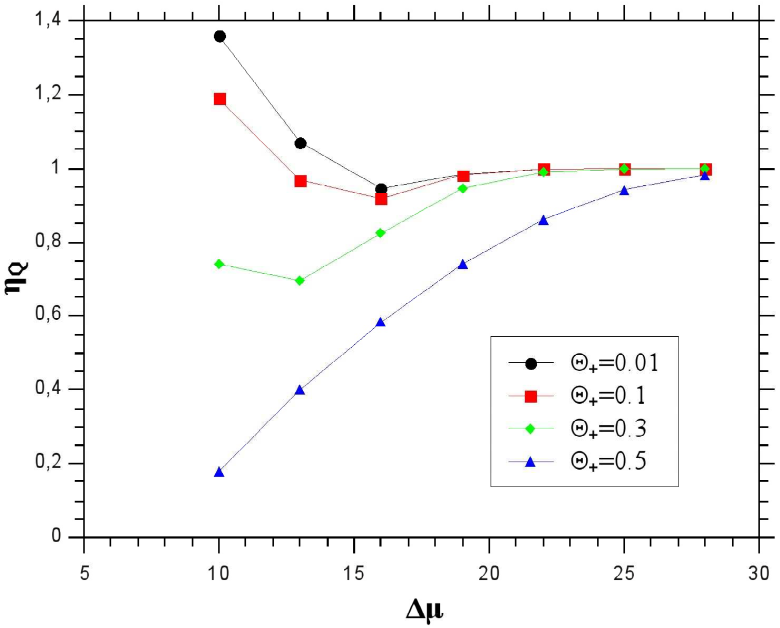
  - Pseudo efficiency [Toyabe et al, PRL 2010]

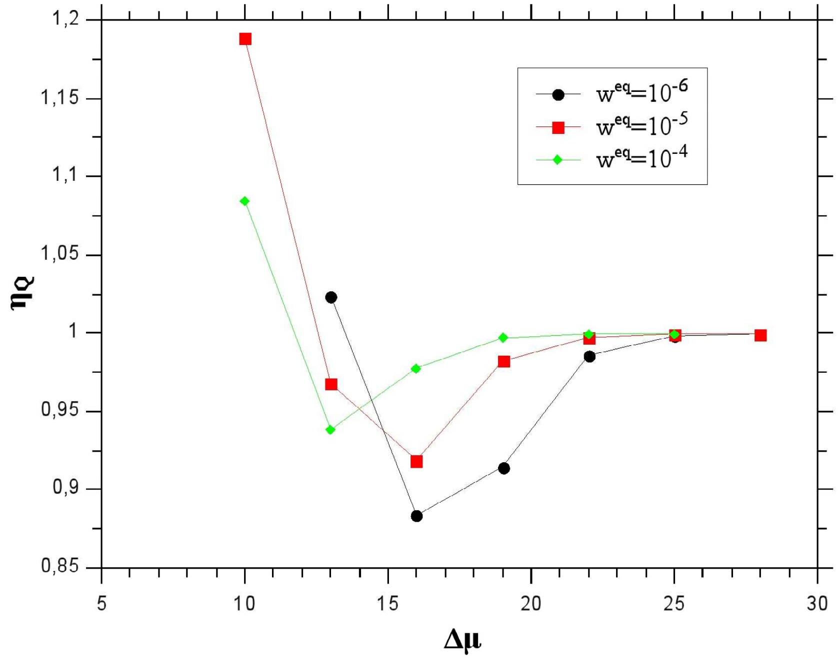
  $$\eta_Q \equiv \dot{Q}_p / \dot{\Delta} \mu$$

  - Stokes efficiency [Wang and Oster, EPL 2002]

  $$\eta_S \equiv v^2 / \mu (\dot{\Delta} \mu)$$

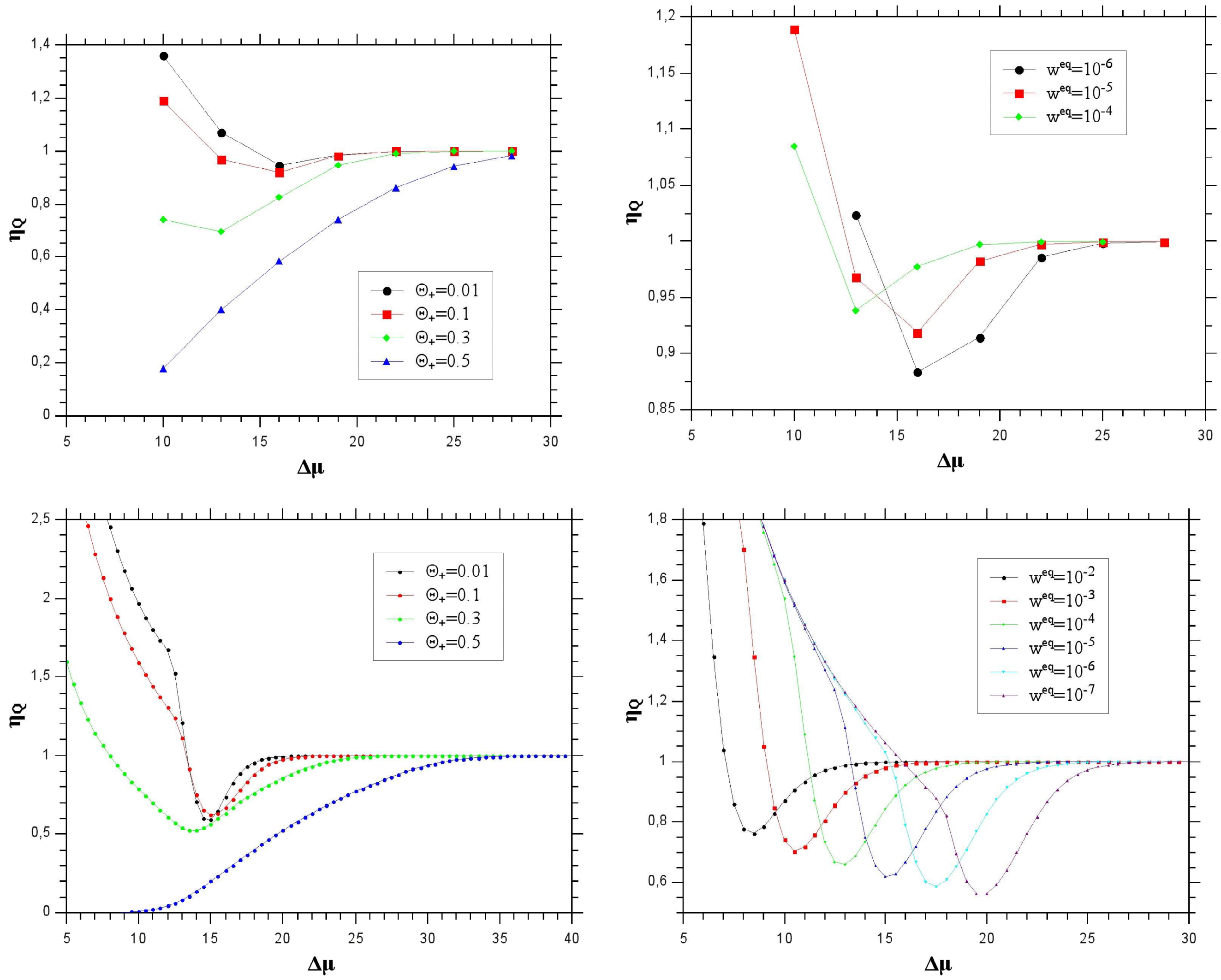
- Pseudo-efficiency $\eta_Q \equiv \dot{Q}_p / \dot{\Delta\mu}$





  - small $\Delta\mu$: $\eta_Q > 1$
  - large $\Delta\mu$: $\eta_Q \approx 1$
  - small Θ_+: increases efficiency

- Pseudo-efficiency $\eta_Q \equiv \dot{Q}_p / \dot{\Delta\mu}$



– analytical results from best Gaussian approximation to $p^s(y)$

- Experimental determination of η_Q

  - Harada-Sasa relation [PRL 2006]

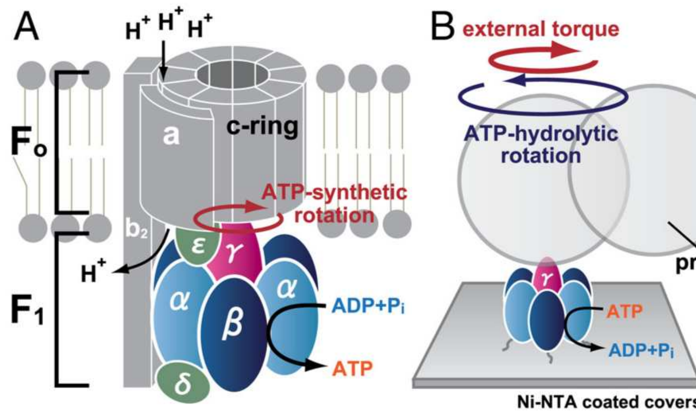
$$\mu \dot{Q}_{HS} = v^2 + \int d\omega [C_{\dot{x}}(\omega) - 2k_B T \ \mathrm{Re} R_{\dot{x}}(\omega)]$$

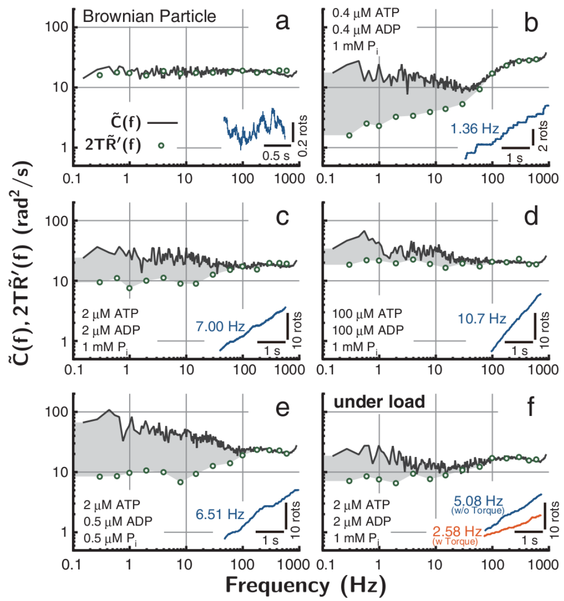
  - Stochastic energetics

    * $\dot{q}_P = (ky - f^{\mathrm{ex}})\dot{x}$

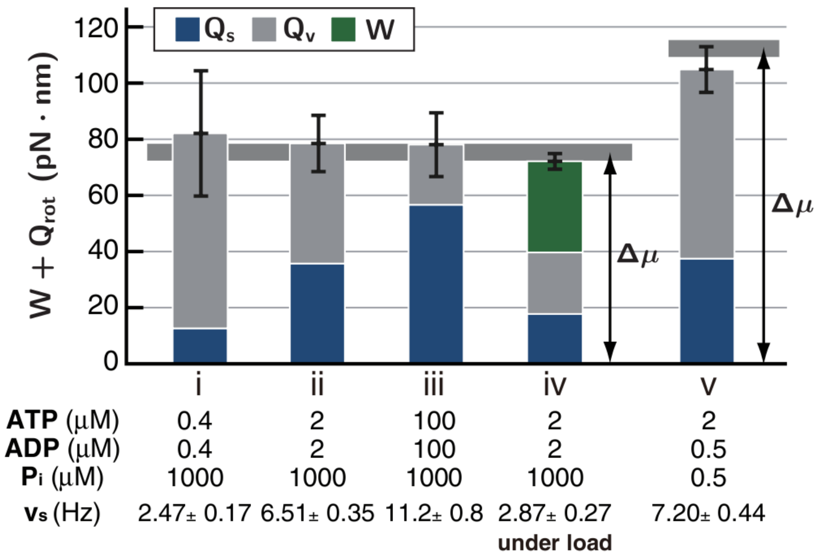
    * $\dot{Q}_P = \langle \dot{q}_p \rangle = \langle (ky - f^{\mathrm{ex}})\nu(y) \rangle = \dot{Q}_{HS}$

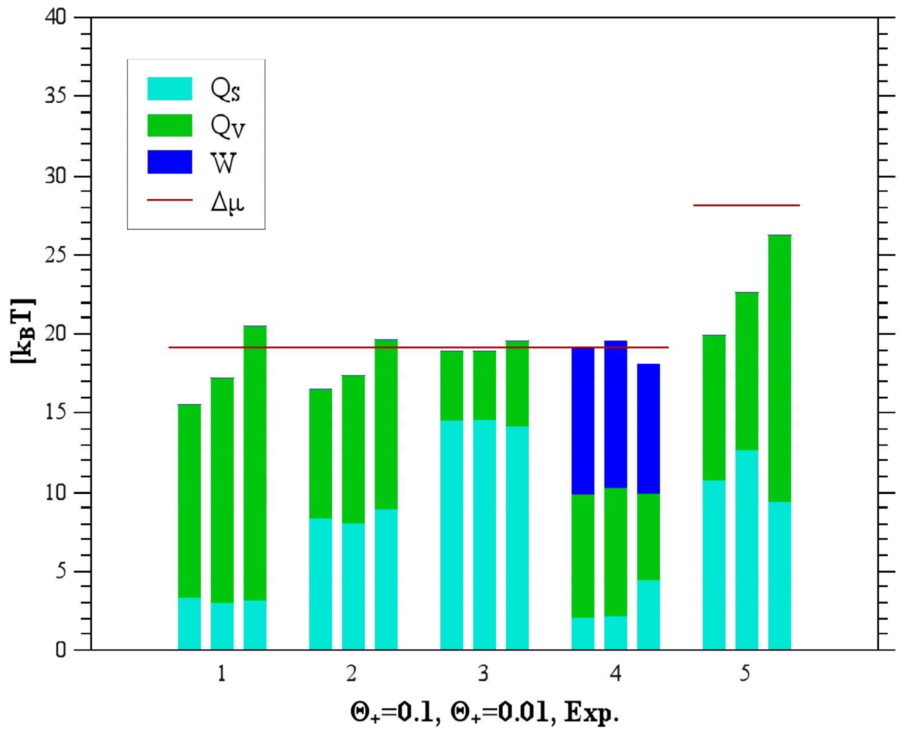
    with $\nu(y) \equiv \langle \dot{x} | y \rangle$





- Comparison to experiment





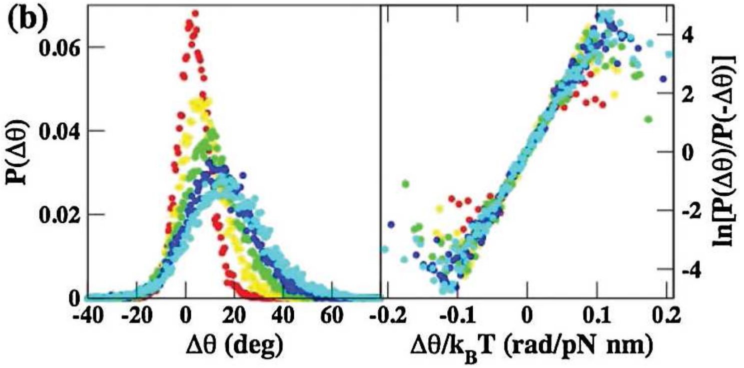
– $\mu\dot{Q}_{HS} = v^2 + \int d\omega [C_{\dot{x}}(\omega) - 2k_B T \; \mathrm{Re} R_{\dot{x}}(\omega)]$

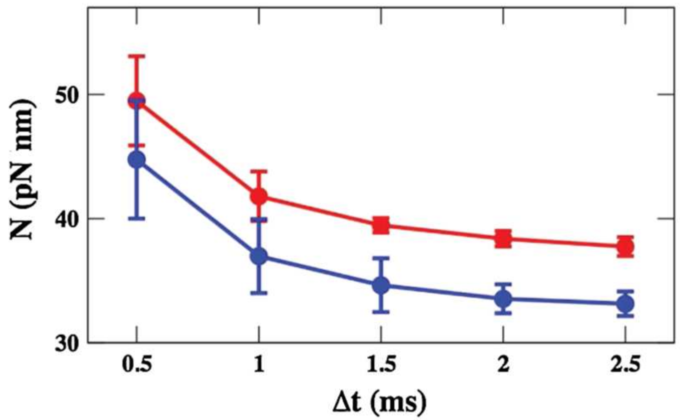
– quite reasonable agreement for small θ_+

– future: substeps of 90 + 30 degrees

- An aside: F1-ATPase and the fluctuation theorem

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





  – $\Gamma\dot{\theta} = N + \zeta \quad \langle\zeta_1\zeta_2\rangle = 2\Gamma k_B T \delta(\tau_1 - \tau_2)$

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

    independent of friction coefficient

time-dependence?

  – cf f'theorem

    $\ln[p(\Delta s_{\mathrm{tot}})/p(-\Delta s_{\mathrm{tot}})] = \Delta s_{\mathrm{tot}}/k_B$

- F'theorem and slow hidden degrees of freedom

  [J. Mehl, B. Lander, C. Bechinger, V. Blickle and U.S., PRL 108, 220601, 2012]

  – total entropy production in the NESS

  $$\Delta s_{\text{tot}} \equiv \int_0^t d\tau[\dot{x}_1\nu_1(x_1,x_2) + \dot{x}_2\nu_2(x_1,x_2)]$$

  with $\nu_1(x_1,x_2) \equiv \langle \dot{x}_1 | x_1, x_2 \rangle$

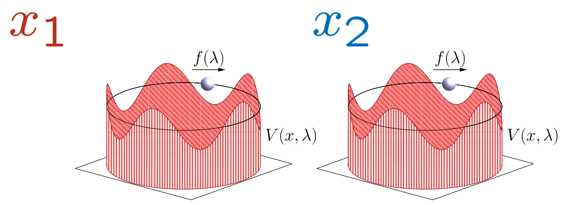
  obeys FT $\quad p(\Delta s_{\text{tot}})/p(-\Delta s_{\text{tot}}) = \exp \Delta s_{\text{tot}}$

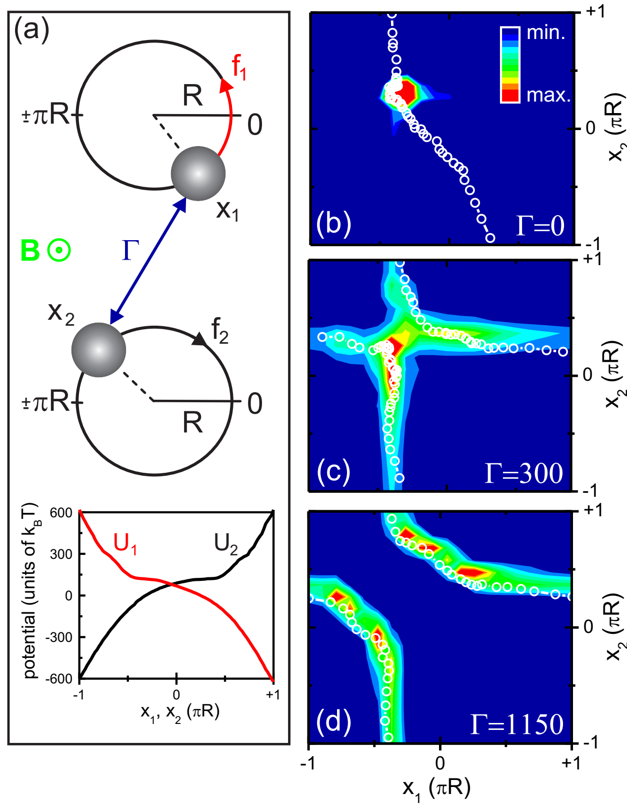
  – suppose x_2 is hidden:

  $$\tilde{\nu}_1(x_1) \equiv \int \nu(x_1,x_2)p(x_2|x_1)dx_2$$

  – apparent entropy production

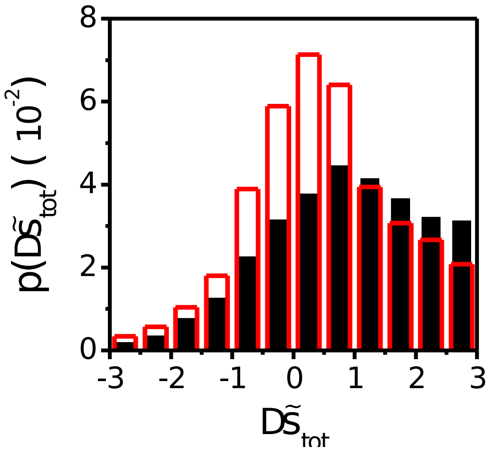
  $\Delta \tilde{s}_{\text{tot}} \equiv \int_0^t d\tau \dot{x}_1 \tilde{\nu}_1(x_1)$ obeys FT ??

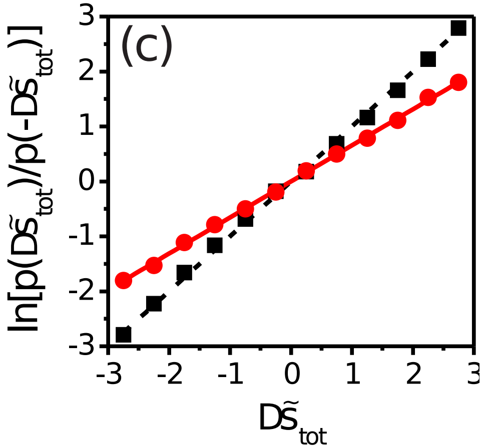


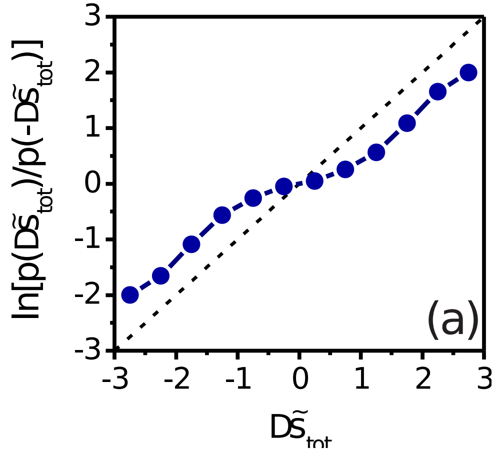


- Experimental data

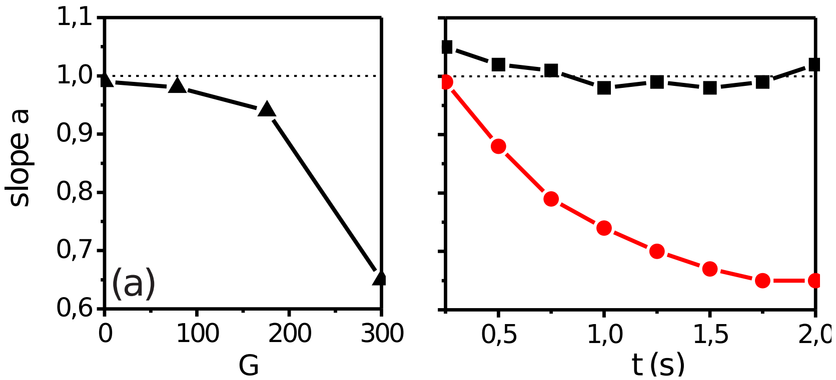
  – with and without coupling [rarely:]







  – slope α

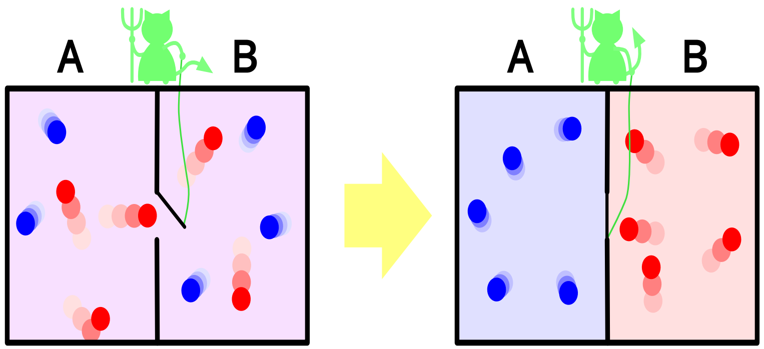


- Theory for $f(\sigma) \equiv \ln[p(\sigma)/p(-\sigma)]$ with $\sigma \equiv \Delta \tilde{s}_{\text{tot}}$
  - for small t : $f(\sigma) \approx \sigma + t^{1/2} g(\sigma) + O(t)$: FT universal
  - for any t is $f(\sigma)$ asymmetric by construction
    - $\sigma[\lambda(\tau)]1$: $f(\sigma) \approx \alpha(t)\sigma + \gamma(t)\sigma^3 + ...$
    - $\sigma \gg 1$: (i) $1 \overset{!}{=} \int d\sigma \; p(\sigma) \exp[-f(\sigma)]$
      (ii) if $p(\sigma) \geq$ Gaussian for $|\sigma| >> 1$

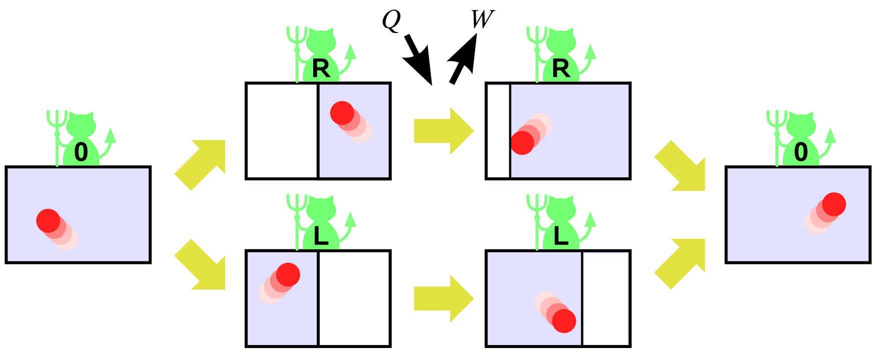
    $\overset{(i)+(ii)}{\Longrightarrow}$ linear slope expected, but typically $\alpha(\sigma \to 0) \neq \alpha(\sigma \to \infty)$

- Isothermal machines with feedback: Work from a single heat bath?

  – Maxwell's demon (1867)



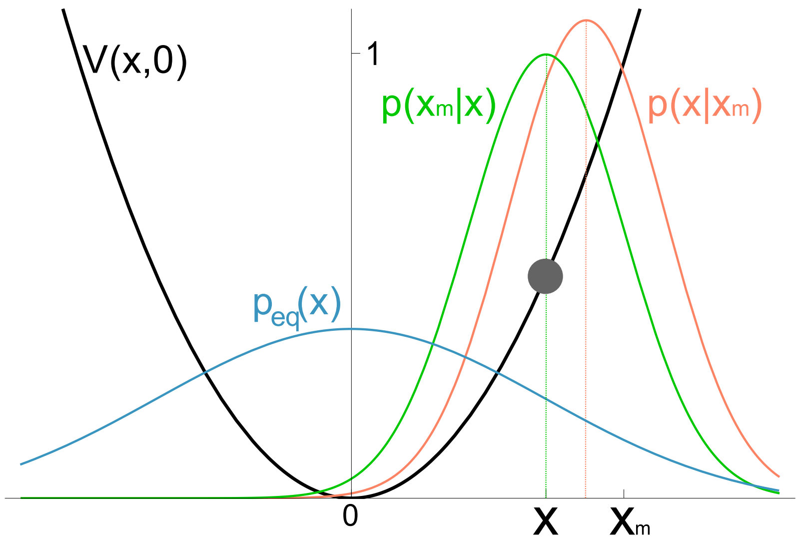
  – Szilard engine (1929)



but: Landauer's principle (erasure of 1 bit of information costs $k_{\mathrm{B}}T \ln 2$)

- Measurement and feedback: Brownian particle in a harmonic trap

  [D. Abreu and U.S., EPL **94**, 10001, 2011]



  – initially thermal equilibrium $p^{eq}(x)$

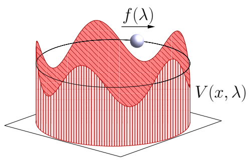
  – measurement yields $x_{\rm m}$ ($\pm y_{\rm m}$, precision)

  – acquired (traj' dependent) information: $\mathcal{I} \equiv \ln \frac{p(x|x_m)}{p^{eq}(x)}$

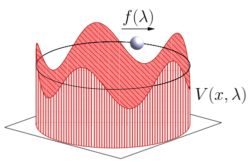
    similar to stochastic entropy

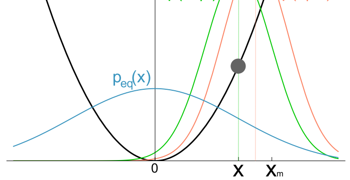
  – subsequent control $\lambda(\tau)|x_m$ in order to extract work

- Fluctuation theorems with measurement and feedback

fixed λ	without	with
equilibrium	$\langle \exp[-(w - \Delta F)] \rangle = 1$ Jarzynski, PRL'97	$\langle \exp[-(w - \Delta F - \mathcal{I})] \rangle = 1$ Sagawa and Ueda, PRL'08
NESS	$\langle \exp[-\Delta s^{tot}] \rangle = 1$ U.S., PRL'05	$\langle \exp[-(\Delta s^{tot} + \mathcal{I})] \rangle = 1$
	$\langle \exp[-(\Delta(s^{tot} - s^{hk})] \rangle = 1$ Hatano and Sasa, PRL'01	$\langle \exp[-(\Delta(s^{tot} - s^{hk} + \mathcal{I})] \rangle = 1$ D. Abreu & U.S., PRL **108** 030601, 2012 with concise "universal" proof

- Fluctuation theorem implies bounds on power

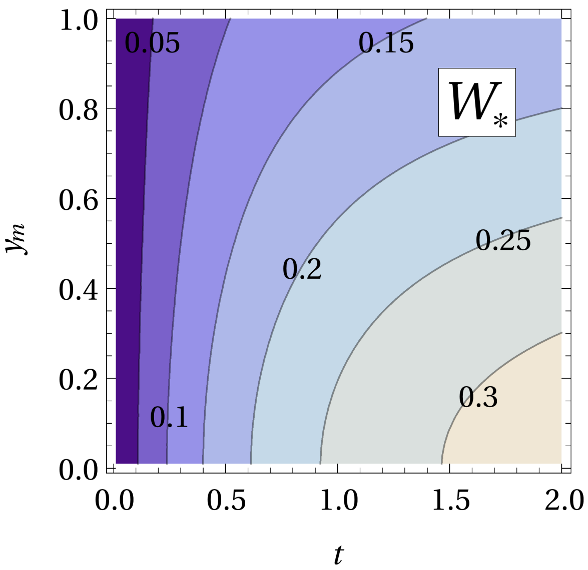
	IFT	"2^{nd} law"
equilibrium	$\langle \exp[-(w - \Delta F + \mathcal{I})] \rangle = 1$	$W^{\text{out}} \leq -\Delta F + \mathcal{I}$
NESS	$\langle \exp[-(\Delta s^{tot} + \mathcal{I})] \rangle = 1$	$\Delta S^{tot} \geq -\mathcal{I}$
	$\langle \exp[-(\Delta(s^{tot} - s^{hk} + \mathcal{I})] \rangle = 1$	$\Delta S^{tot} \geq \Delta S^{hk} - \mathcal{I}$
		$\Rightarrow$ $\boxed{\dot{W}^{\text{out}} \leq \dot{W}^{in} - \dot{Q}^{hk} + \dot{\mathcal{I}}}$



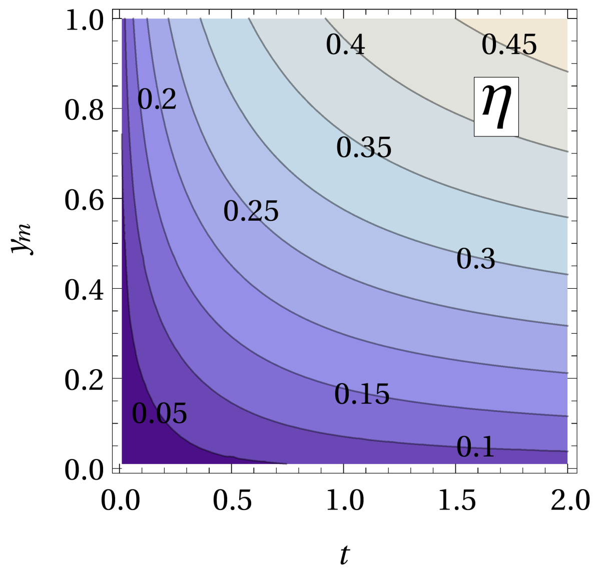
- Cyclic operation: Efficency of an information machine

[M. Bauer, D. Abreu and U.S., J. Phys. A: Math. Theor. 45, 162001, 2012]

case I: Control only center of trap



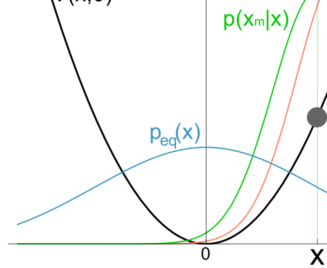
ext work/cycle



efficiency $\eta \equiv \dot{W}/\dot{\mathcal{I}}$

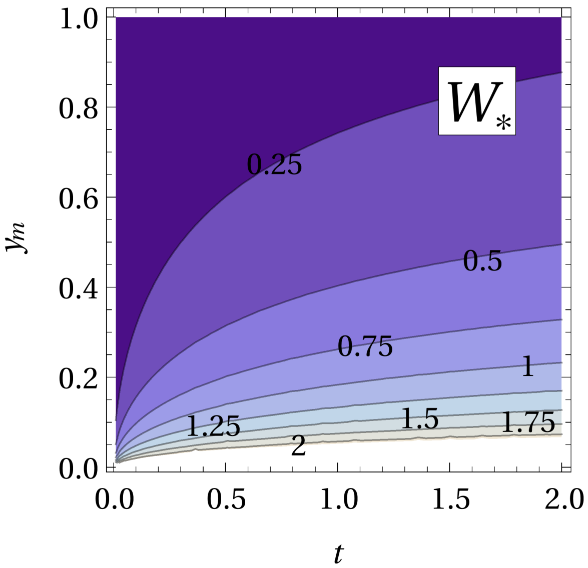
* $\eta = 0$ at max power ($t \to 0$)

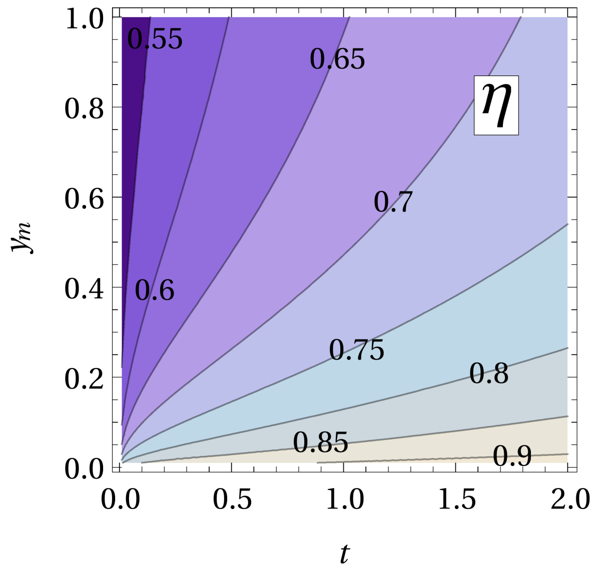
* $\eta = 1$ for $t \to \infty$ (but zero power)



- Cyclic operation: Efficency of an information machine cont'd

case II: Control center and stiffness of trap





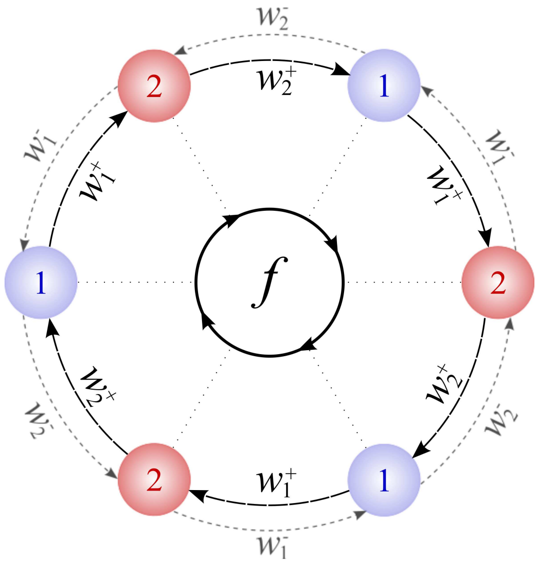
* $\eta = 1$ for $y_m \to 0$ at any cycle time t

* $\eta = 1/2$ for $t \to 0$ [cf lin response]

* $\eta \geq 1/2$ throughout

- Feedback with genuine non-equilibrium states

[D. Abreu and U.S., PRL **108**, 030601 (2012)]

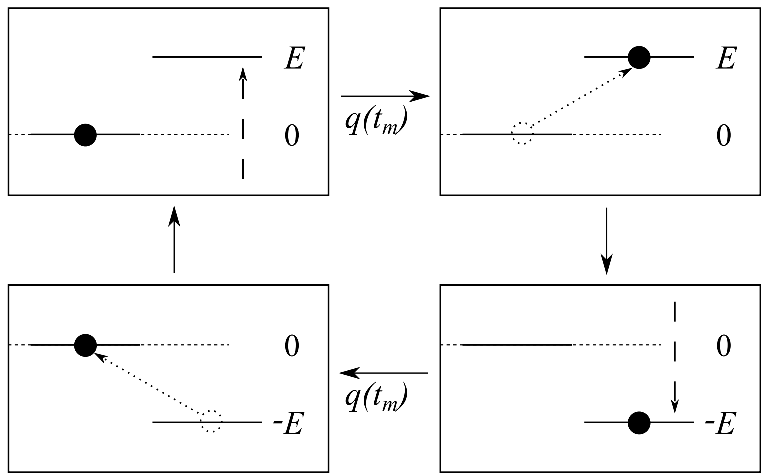


$$w_1^+ = e^{(f-E)/2} = 1/w_1^-$$

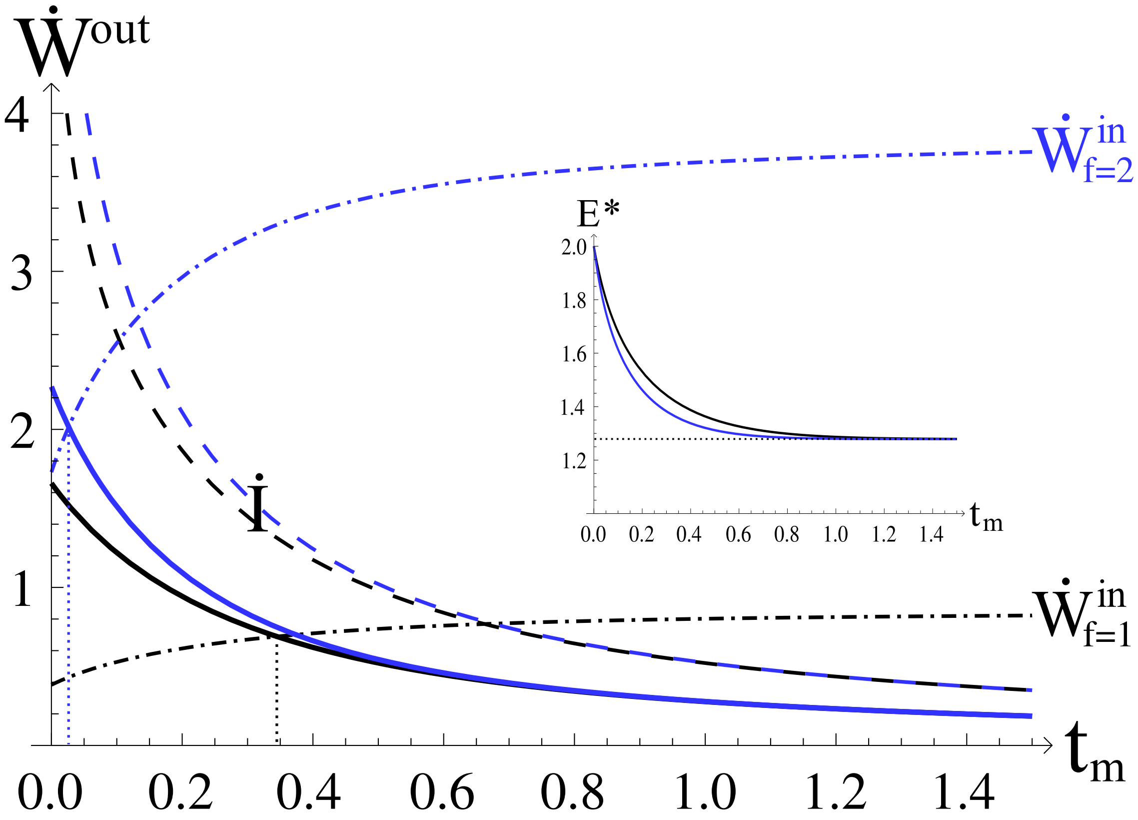
$$w_2^+ = e^{(f+E)/2} = 1/w_2^-$$

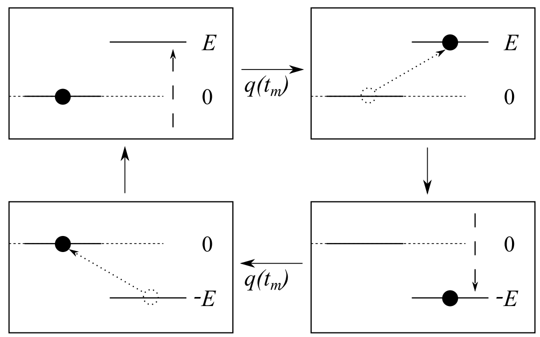
- measure position every t_m

- adjust energy of state 2 as $\pm|E|$



- Results for cyclic operation





- optimal $E(f, t_m)$
- for $t_m \to \infty$: $\dot{W}^{in} \approx \dot{Q}^{hk}$
- for $t_m \to 0$: $\dot{\mathcal{I}} \to \infty$
- net gain for $t_m < t_m^*$

$$\langle \exp[-(\Delta(s^{tot} - s^{hk} + \mathcal{I})] \rangle = 1 \Rightarrow \boxed{\dot{W}^{out} \le \dot{W}^{in} - \dot{Q}^{hk} + \dot{\mathcal{I}}}$$

- Summary
  - FDT in a NESS
    * involves entropy production
    * equivalence relation for conjugate observable
    * (emergence of T_{eff} for sheared suspensions)
  - effiency(ies) of a NESS machine: F1-ATPase
  - fluc'theorem under coarse-graining
  - efficiency of Brownian information machines