Stochastic thermodynamics:

Energy conservation and entropy production along single trajectories

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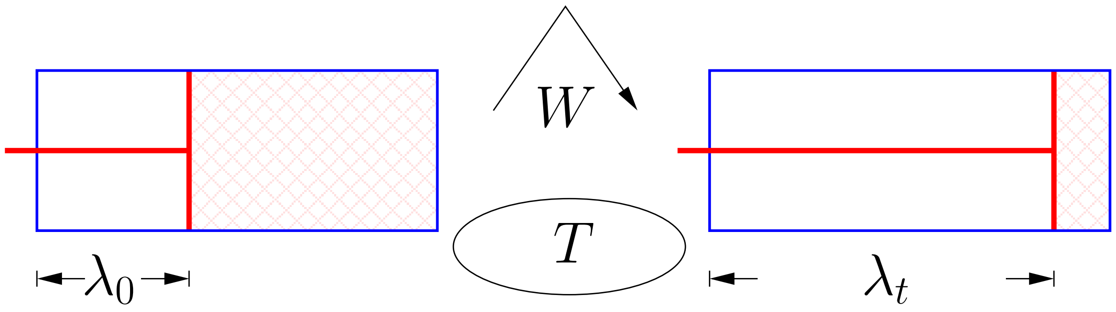
- Introduction

- Stochastic thermodynamics for Langevin systems
  - First law with experiment
  - Entropy production and F'theorems
  - Jarzynski relation
  - NESS: FDT and transitions between NESSs

- Stochastic thermodynamics for biochemical reactions

- General master equation dynamics
  - Stochastic entropy and F'th's
  - Experiment on driven two-level system

- Thermodynamics of macroscopic systems [19th cent]



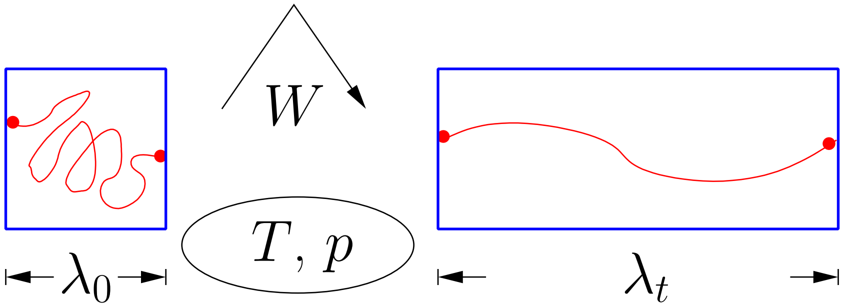
  - First law energy balance:

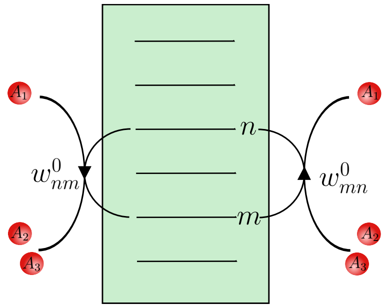
$$W = \Delta E + Q = \Delta E + T\Delta S_M$$

  - Second law:

$$\begin{aligned} S_{\text{tot}} &\equiv \Delta S + \Delta S_M > 0 \\ W &> \Delta E - T\Delta S \equiv \Delta F \\ W_{\text{diss}} &\equiv W - \Delta F > 0 \end{aligned}$$

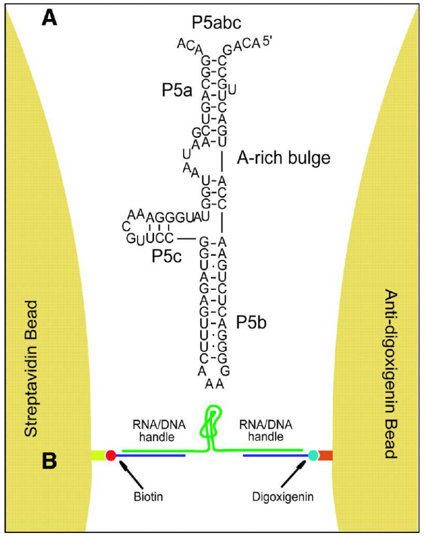
- Stochastic thermodynamics for small systems

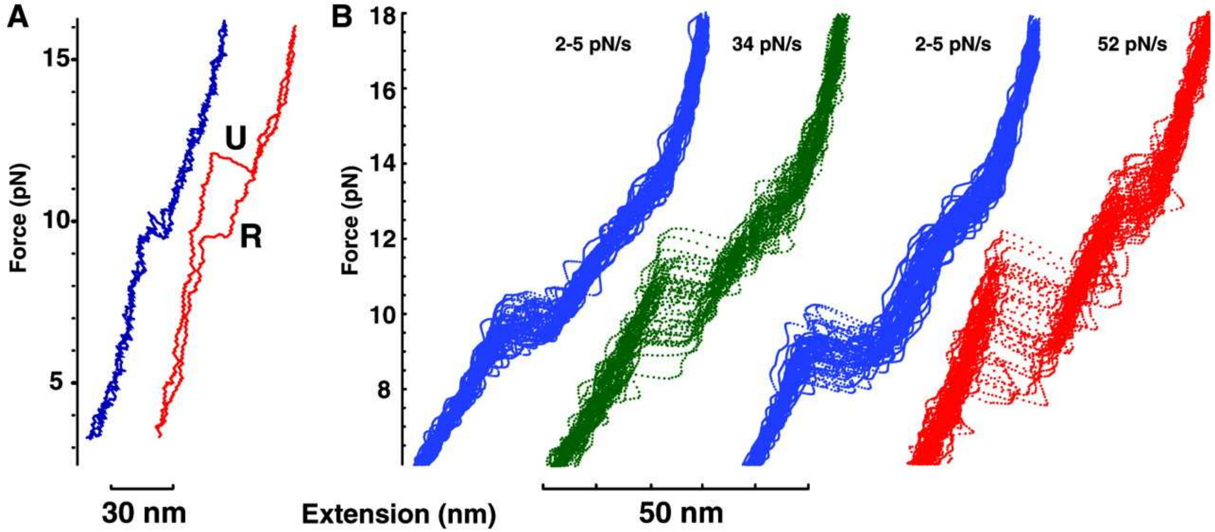




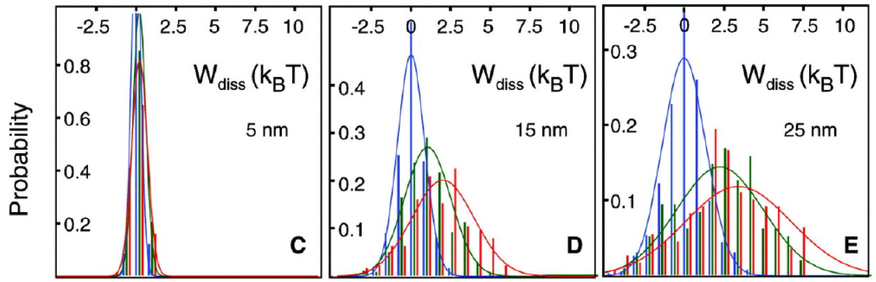
  - First law: how to define work, internal energy and exchanged heat?
  - whole distribution of work spent: $p(W; \lambda(\tau))$ ...
  - Entropy: distribution as well?

- Experiment: Stretching RNA [Liphardt et al, Science **296** 1832, 2002.]

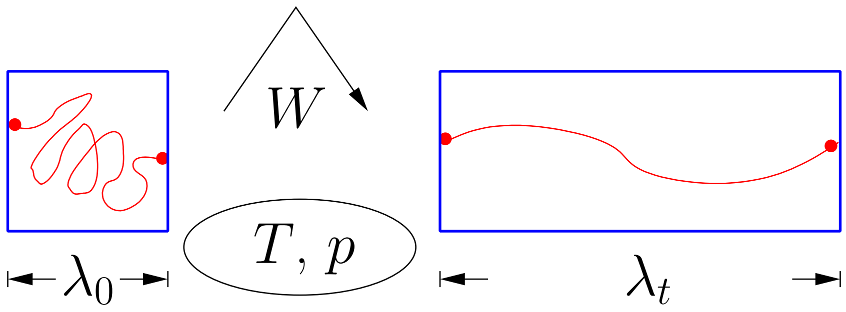




– distributions of W_{diss}:

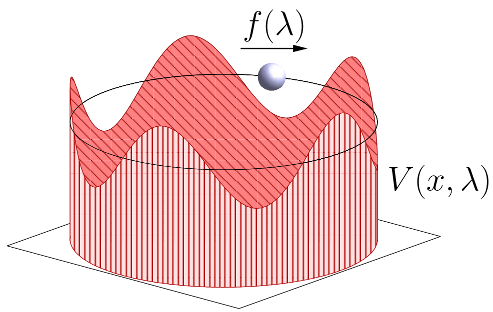


- Jarzynski relation (1997) $(k_B T = 1)$



  - Second law: $\langle W \rangle_{|\lambda(\tau)} \geq \Delta F \equiv F(\lambda_t)) - F(\lambda_0)$
  - Jarzynski: $\boxed{\langle e^{-W} \rangle_{|\lambda(\tau)} \stackrel{!}{=} e^{-\Delta F}}$
  - with $\langle ... \rangle_{|\lambda(\tau)}$ average over thermal initial distribution and many experiments with fixed protocol $[\lambda(\tau)]$
  - valid beyond linear response
  - allows to extract free energy differences from non-eq data

Paradigm: One degree of freedom: Colloidal particle



- Langevin equation

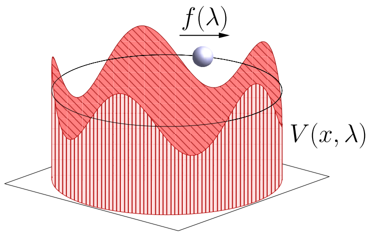
  $\dot{x} = \mu F(x,\lambda) + \zeta,$

  - Total force $F(x,\lambda) = -\partial_x V(x,\lambda) + f(\lambda)$
    depends on external driving or protocol $[\lambda(\tau)]$
  - Gaussian noise: $\langle \zeta(\tau)\zeta(\tau') \rangle = 2D\delta(\tau - \tau')$
    with Einstein relation $D = \mu \; k_B T$
  - weight of a trajectory:

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

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

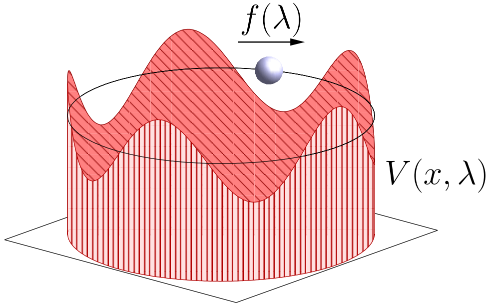
- Classification



$$\dot{x} = \mu[-\partial_x V(x,\lambda) + f(\lambda)] + \zeta$$

	λ	V	f	
equilibrium	const	$V(x)$	$f = 0$	Gibbs-Boltzmann
NESS	const	$V(x)$	$f \neq 0$	F'theorem
from eq_1 to eq_2	$\lambda(\tau)$	$V(x,\lambda)$	$f = 0$	Jarzynski
from NESS_1 to NESS_2	$\lambda(\tau)$	$V(x)$	$f(\lambda) \neq 0$	Hatano-Sasa
periodic driving	$\lambda(\tau)$	$V(x,\lambda)$	$f(\lambda)$	Stuttgart expt's
arbitrary	$\lambda(\tau)$	$V(x,\lambda)$	$f(\lambda)$	

First law for a single trajectory [Sekimoto, 1997]



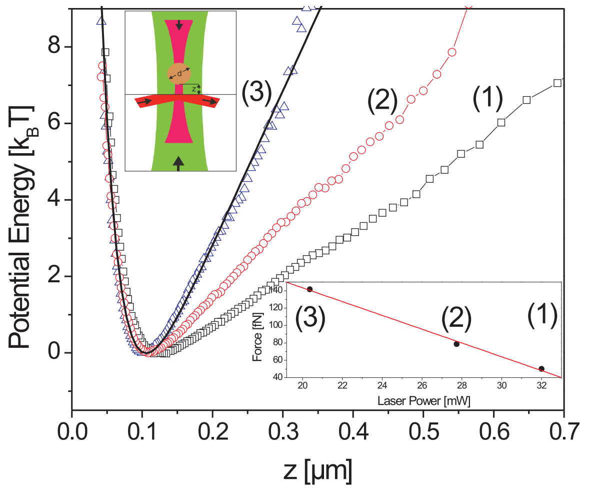
- Langevin equation

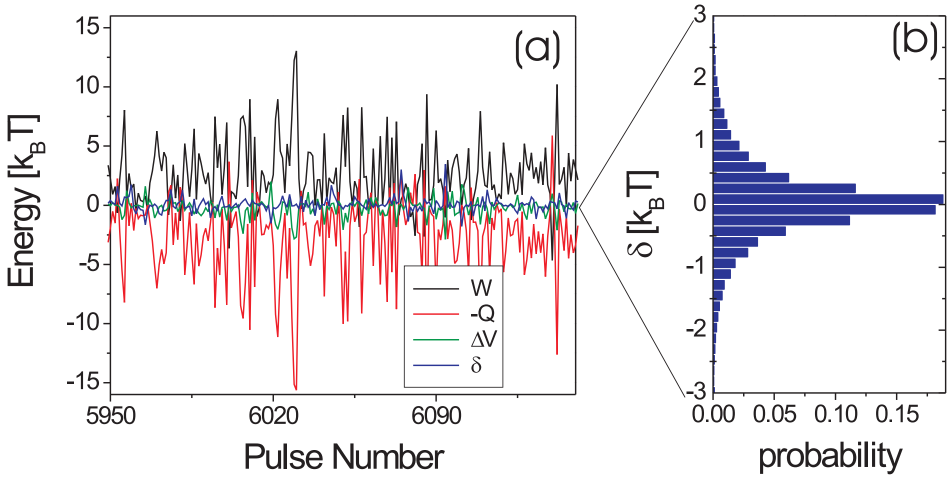
  $\dot{x} = \mu F(x,\lambda) + \zeta = \mu[-\partial_x V(x,\lambda) + f(\lambda)] + \zeta,$

- $dw = du + dq$
  - applied work: $dw = f dx + \partial_\lambda V(x,\lambda) d\lambda$
  - internal energy: $du = dV$
  - dissipated heat: $dq = dw - du = F dx = (1/\mu)(\dot{x} - \zeta) dx = T ds_{\mathrm{m}}$

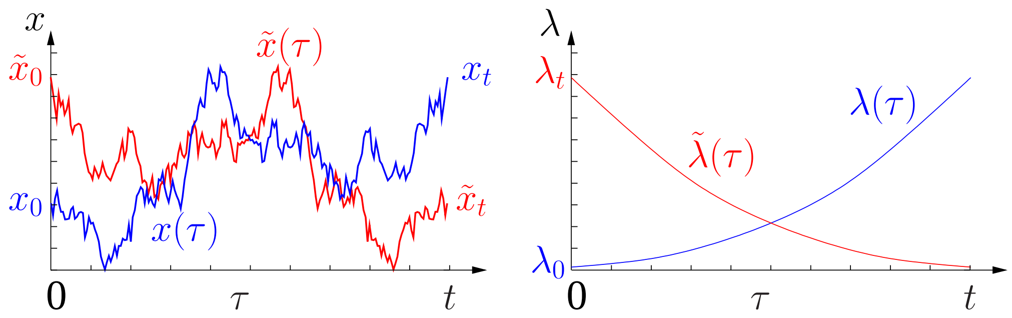
Experimental illustration: Colloidal particle in $V(x, \lambda(\tau))$

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





- Towards a second law: "Time reversal"



$\tilde{x}(\tau) \equiv x(t-\tau)$ and $\tilde{\lambda}(\tau) \equiv \lambda(t-\tau)$

- Ratio of forward to reversed path

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

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

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

- Fokker-Planck equation

$$\partial_\tau p(x,\tau) = -\partial_x j(x,\tau) = -\partial_x \left(\mu F(x,\lambda) - D\partial_x\right) p(x,\tau)$$

- Non-eq ensemble entropy

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

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

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

- equation of motion

$$\dot{s}(\tau) = \underbrace{-\frac{\partial_\tau p(x,\tau)}{p(x,\tau)}_{|x(\tau)} + \frac{j(x,\tau)}{Dp(x,\tau)}_{|x(\tau)}\dot{x}}_{\dot{s}_{\text{tot}}} - \underbrace{\frac{\mu F(x,\lambda)}{D}_{|x(\tau)}\dot{x}}_{\dot{s}_{\text{m}}} .$$

- General integral fluctuation theorem (cf. Jarzynski, Crooks, Maes)

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

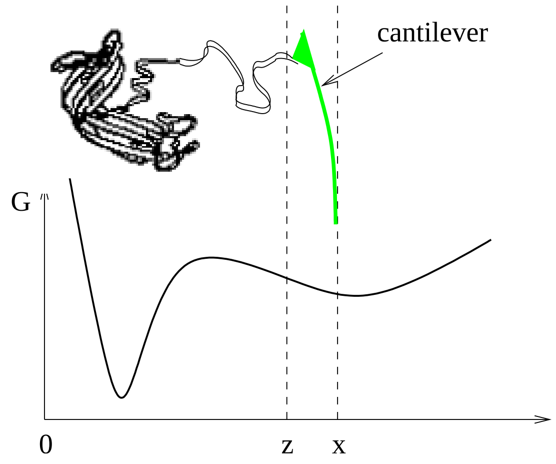
  - for any (normalized) $p_1(x_t)$
  - with $p_1(x_t) = p(x,t) = \exp[-s(t)]$
- $\boxed{\langle \exp[-\Delta s_{\rm tot}] \rangle = 1} \Rightarrow \boxed{\langle \Delta s_{\rm tot} \rangle \geq 0}$
  - integral fluctuation theorem for total entropy production
  - arbitrary initial state, driving, length of trajectory
- $\langle f(x_t) \exp[-\Delta s_{\rm tot}] \rangle = \langle f(x_t) \rangle$

- Jarzynski relation (1997)

  - $f \equiv 0$
  - $p_0(x_0) \equiv \exp[-\beta(V(x_0, \lambda_0) - F(\lambda_0)]$
  - $p_1(x_t) \equiv \exp[-\beta(V(x_t, \lambda_t) - F(\lambda_t)]$
  - $\boxed{\langle \exp[-\beta W] \rangle = \exp[-\beta \Delta F]}$
  - within stochastic dynamics an identity!

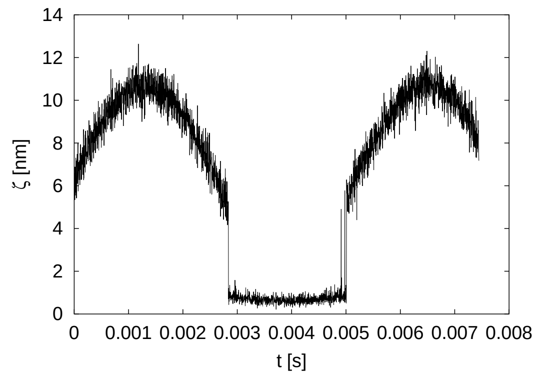
- Probing energy profiles by periodic loading

  [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

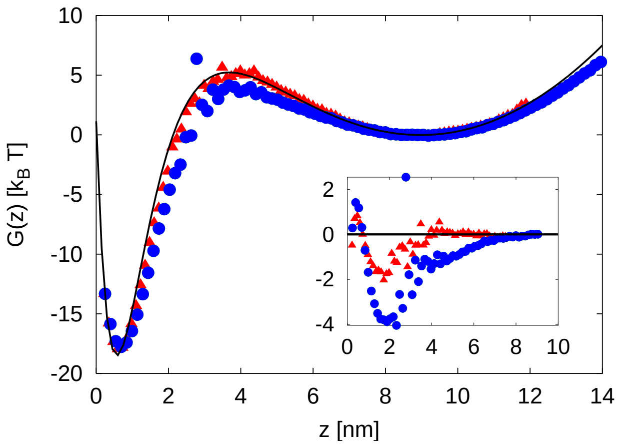


$$\dot{z} = \mu(-dV/dz) + \zeta$$

- Reconstruction of energy profile by z-resolved Jarzynski relation

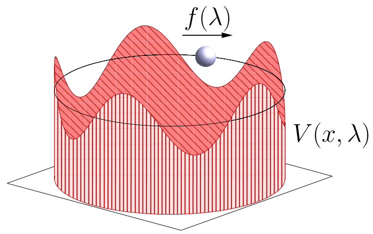
$$p_1(z) = \delta(z(t) - z) \quad \Rightarrow \quad e^{-G(z)} = \langle \delta[z - z(t)] e^{-W(t)} \rangle \;\; e^{(k/2)(z - \lambda(\tau))^2}$$

[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

- Non-equilibrium steady states (NESS): Detailed FT



  - $f = \text{const} \neq 0$

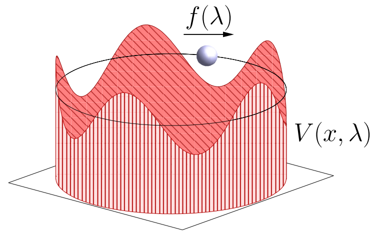
  - broken detailed balance

$$\boxed{p(-\Delta s_{\text{tot}})/p(\Delta s_{\text{tot}}) = \exp(-\Delta s_{\text{tot}})}$$

  - generalization of Evans et al (1993), Gallavotti & Cohen (1995), Kurchan (1998), Lebowitz & Spohn (1999) ... to finite times

- NESS II: FDT violation and restoration

  [T. Speck and U.S., cond-mat 0511696, Europhys Lett, in press]



  – $\dot{x} = \mu[-\partial_x V(x,\lambda) + f(\lambda)] + \zeta \equiv \mu F(x,\lambda) + \zeta,$

  – stat distribution $p^s(x) = \exp[-\phi(x)]$ with current j_s

  – local velocity $\nu_s(x) \equiv \langle \dot{x}|x\rangle = j_s/p^s(x) = \mu F + D\phi'(x)$

- FDT violation and restoration in NESS (cont'd)
  - FDT in eq:

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

  - violation of FDT in non-eq: (cf Harada + Sasa, PRL 2005)

$$T \frac{\delta \langle \dot{x}(t) \rangle}{\delta f(\tau)}_{|f \neq 0} = \langle \dot{x}(t) \dot{x}(\tau) \rangle_{\text{neq}} - \underbrace{\langle \dot{x}(t) \nu_s(x(\tau)) \rangle_{\text{neq}}}_{\leq \; \mu \langle \dot{q} \rangle}$$

    bounded by mean ent prod rate (cf Culgiandolo et al, PRL'97)
  - restoration of FDT in non-eq for renormalized velocity: $v(\tau) \equiv \dot{x}(\tau) - \nu_s(x(\tau))$

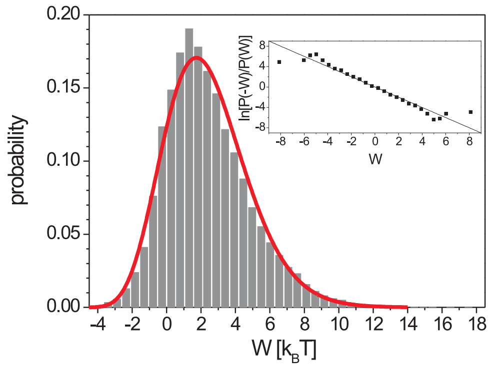
$$T \frac{\delta \langle v(t) \rangle}{\delta f(\tau)}_{|f \neq 0} = \langle v(t) v(\tau) \rangle_{\text{neq}}$$

    (spontaneous fluct decay like induced ones)

- Transitions between NESSs [Oono and Paniconi, Hatano and Sasa]
  - $V(x)$ time-independent, $f = f(\lambda(\tau))$ switches from f_1 to f_2
  - housekeeping heat: $\Delta s_{\text{m}} = q_{\text{tot}} \equiv q_{\text{ex}} + q_{\text{hk}}$
    - $\langle \exp[-\underbrace{(\Delta s_{\text{m}} - q_{\text{hk}} + \Delta\phi)}_{Y}] \rangle = 1$
    - $\tilde{S} \equiv -\int dx\, p^s(x,\lambda) \ln p^s(x,\lambda) \quad \Rightarrow \Delta \tilde{S} \geq -\langle q_{\text{ex}} \rangle$ ("2nd law for NESSs")
  - Further FTs: (T. Speck, U.S, J Phys A 38, L581, 2005)
    - $\langle \exp(-q_{\text{hk}}) \rangle = 1$
    - $\langle \exp[-\underbrace{\Delta s_{\text{m}} + \Delta\phi)}_{R}] \rangle = 1$ (generalized JR)

	General	DBS	NESS
		$Q_{\text{hk}} = 0$, $R = Y = \beta W_{\text{dis}}$	$Y = 0$, $R = \beta Q_{\text{hk}}$
(1)	$\langle \exp[-Y] \rangle = 1$	$\langle \exp[-\beta W_{\text{dis}}] \rangle = 1$	$1 = 1$
(2)	$\langle \exp[-\beta Q_{\text{hk}}] \rangle = 1$	$1 = 1$	$\langle \exp[-\beta Q_{\text{hk}}] \rangle = 1$
(3)	$\langle \exp[-R] \rangle = 1$	$\langle \exp[-\beta W_{\text{dis}}] \rangle = 1$	$\langle \exp[-\beta Q_{\text{hk}}] \rangle = 1$

- Periodic driving $\lambda(\tau) = \lambda(\tau + 2\pi\omega\tau)$
  - detailed F'th holds for p(W) for symmetric protocols with $\lambda(\tau) = \lambda(t - \tau)$
  - experimental test

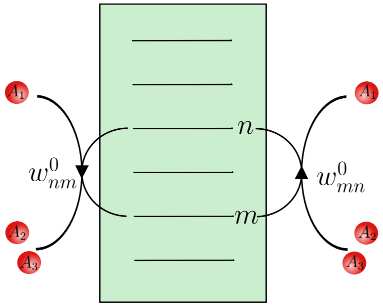


[Blickle et al, PRL '06]

  - non-Gaussian distribution indicates existence of a "Langevin regime beyond linear response" since
    - $*$ p(W) is always Gaussian for "slow" driving
      [T. Speck and U.S., PRE 70, 066112, 2004]

- Stochastic thermodynamics of biochemical reactions

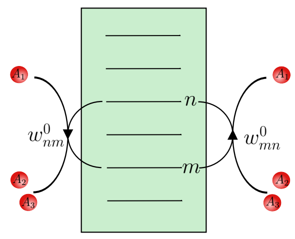
  [T. Schmiedl, T, Speck and U.S., cond-mat 0601636]



$$\sum_\alpha r_\alpha^{nm} A_\alpha + n \underset{w_{mn}}{\overset{w_{nm}}{\rightleftharpoons}} m + \sum_\alpha s_\alpha^{nm} A_\alpha.$$

  - mass action law kinetics $\frac{w_{nm}}{w_{mn}} = \frac{w^0_{nm}}{w^0_{mn}} \prod_\alpha (c_\alpha)^{r_\alpha^{nm} - s_\alpha^{nm}}$
  - externally controlled (clamped) $\mu_\alpha \equiv E_\alpha + \ln c_\alpha$
  - in hypothetical eq $\frac{w^{\text{eq}}_{nm}}{w^{\text{eq}}_{mn}} = \frac{w^0_{nm}}{w^0_{mn}} \prod_\alpha (c_\alpha^{\text{eq}})^{r_\alpha^{nm} - s_\alpha^{nm}} = \frac{p^{\text{eq}}_m}{p^{\text{eq}}_n} = \exp(-\Delta G)$

    with $\Delta G \equiv -[E_n - E_m + \sum_\alpha (r_\alpha^{nm} - s_\alpha^{nm}) \mu_\alpha^{\text{eq}}]$
  - ratio of int rates: $\frac{w^0_{nm}}{w^0_{mn}} = \exp[E_n - E_m + \sum_\alpha (r_\alpha^{nm} - s_\alpha^{nm}) E_\alpha]$



- First law along stochastic trajectory

$w = \Delta E + q$ for a single step

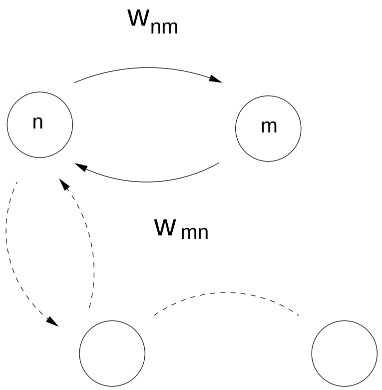
  - chemical work: $w_{\text{chem}}^{nm} \equiv \sum_\alpha (r_\alpha^{nm} - s_\alpha^{nm})\mu_\alpha$

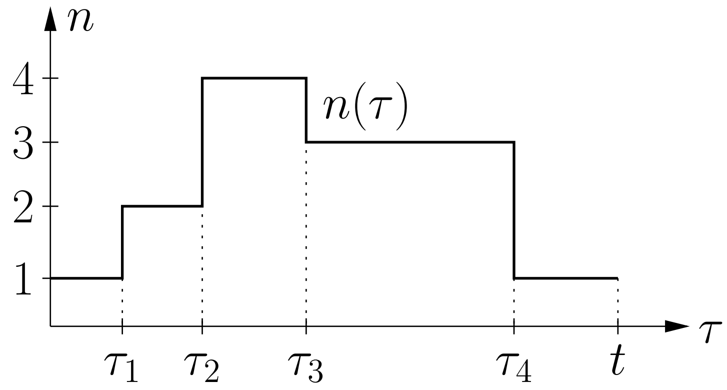
  - internal energy: $\Delta E^{nm} \equiv E_m - E_n$

  - dissipated heat: $q^{nm} = \ln \frac{w_{nm}}{w_{mn}} \equiv T\Delta s_{\text{m}}^{nm}$

  - sum over all reaction events between 0 and t

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





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

– Stochastic trajectory $n(\tau)$ jumps at τ_j from n_j^- to n_j^+

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

– equation of motion

$$\dot{s}(\tau) = \underbrace{-\frac{\partial_\tau p_n(\tau)}{p_n(\tau)}\Big|_{n(\tau)} - \sum_j \delta(\tau - \tau_j) \ln \frac{p_{n_j^+} w_{n_j^+ n_j^-}}{p_{n_j^-} w_{n_j^- n_j^+}}}_{\equiv \ \dot{s}_{\text{tot}}(\tau)} + \underbrace{\sum_j \delta(\tau - \tau_j) \ln \frac{w_{n_j^+ n_j^-}}{w_{n_j^- n_j^+}}}_{\equiv \ -\dot{s}_{\text{m}}(\tau)}$$

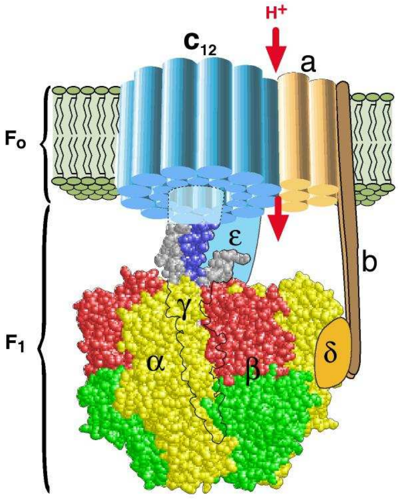
- Two fluctuation theorems for finite times
  - Integral FT for total entropy production for arbitrary driving

$$\boxed{\langle \exp(-\Delta s_{\text{tot}}) \rangle = 1}$$

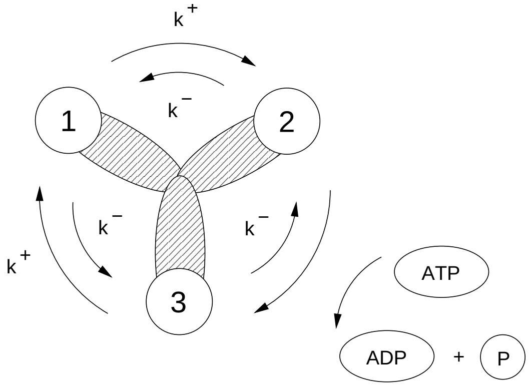
  - Detailed FT for total entropy production in a NESS

$$\boxed{p(-\Delta s_{\text{tot}})/p(\Delta s_{\text{tot}}) = \exp(-\Delta s_{\text{tot}})}$$

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



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

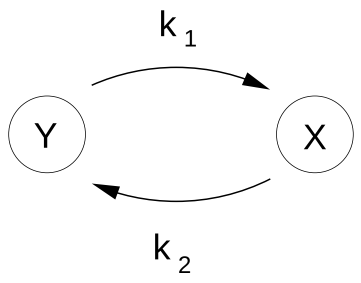


- $\partial_\tau p_1 = -(k^+ + k^-)p_1 + k^+ p_2 + k^- p_3$ & cyc
- $\Delta s_{\text{tot}} = n \ln(k^+/k^-) = n[\mu_{ATP} - \mu_{ADP} - \mu_P]/T$
- $\boxed{p(-n)/p(n) = \exp[-n \ln(k^+/k^-)]}$

Illustration: Birth-death or chemical master equations

[U.S., J Phys A 37, L517, 2004]

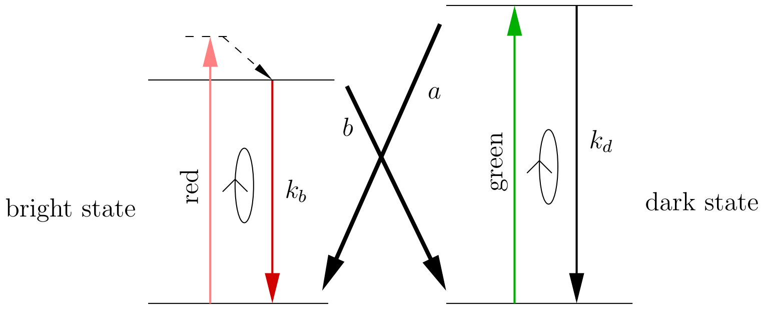
- Simplest case: Isomerization

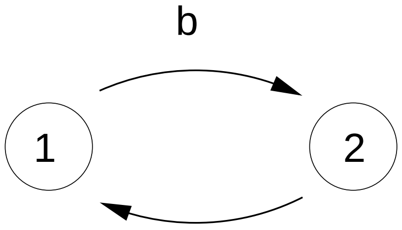


  - $n_X \equiv n = N - n_Y$
  - $q(\tau) \equiv k_1(\tau)/k_2(\tau)$
  - stationary distribution: $p^s(n) = [q/(1+q)]^N \binom{N}{n}$
  - stationary mean $n^s = Nq/(1+q)$
  - $\langle \exp\{\int_0^t d\tau \underbrace{[n(\tau) - n^s(\tau)]}_{\text{non−eq lag}} \frac{d}{d\tau} \ln q(\tau)\}\rangle = 1$
  - follow-up: C. Jarzynski, J. Phys. A. 38, L227, 2005

Periodically driven system: Optically active defect center in diamond

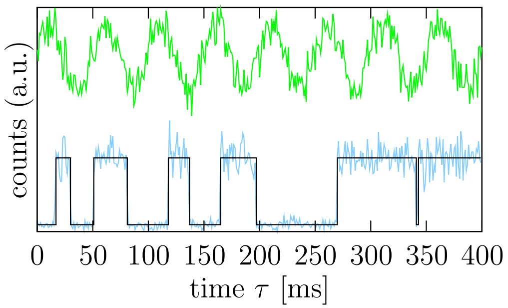
[S.Schuler, T. Speck, C. Tietz, J. Wrachtrup and U.S., PRL 94, 180602, 2005 and submitted]





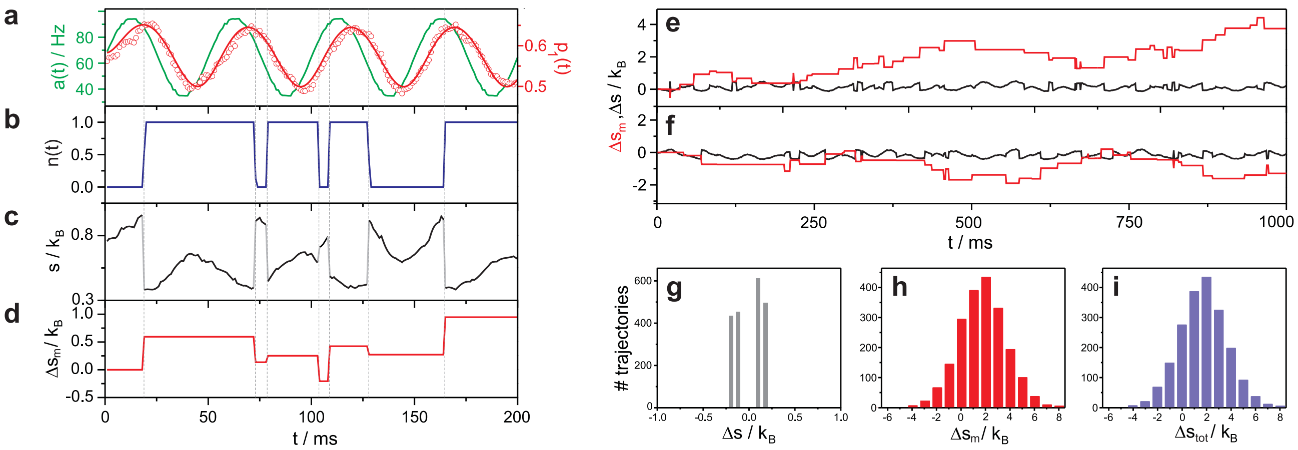
$a = a_0\,(1 + \gamma \sin \omega t)$

- Trajectories



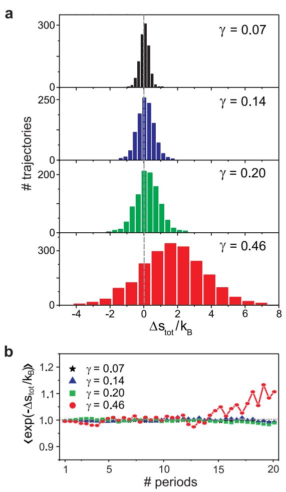
- Entropy production along a single trajectory

Figure 1



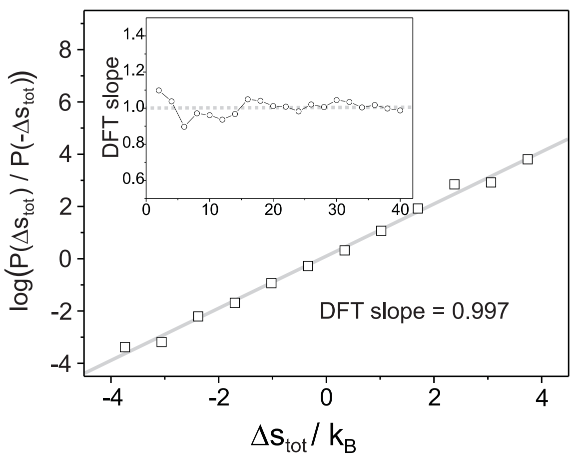
- Int FT

Figure 2



Det FT

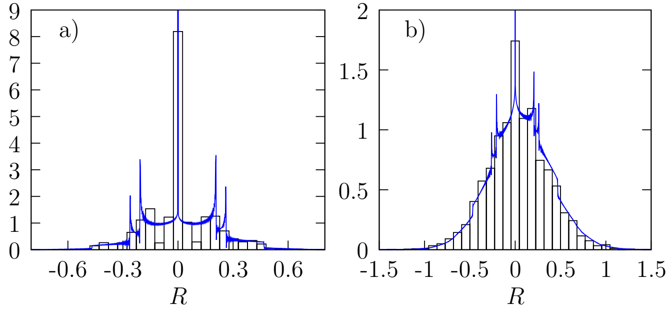
Figure 3



- Generalized JR:

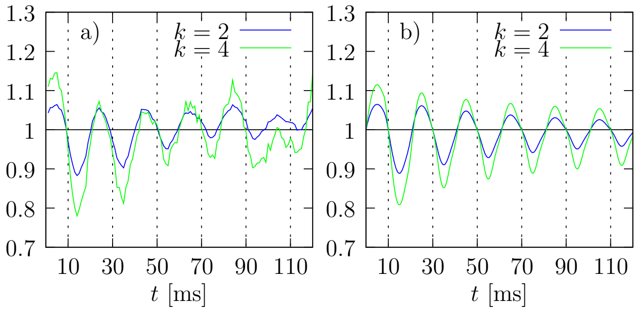
$\langle \exp[-R] \rangle = 1$ for $R[n(\tau)] \equiv -\int_o^t d\tau \dot{\lambda} \partial_\lambda \ln p^s_{n(\tau)}(\lambda) \quad (= W - \Delta F)$

probability distribution $p(R)$



- Detailed theorem for symmetric protocols $\lambda(\tau) = \lambda(t-\tau)$:

$p(-R)/p(R) = \exp(-R) \quad \Rightarrow \langle R^k \rangle = (-1)^k \langle R^k \exp(-R) \rangle$



Summary and Perspectives

- Stochastic thermodynamics of small biophysical systems
  - mechanically driven: colloids, polymers, proteins
  - biochemically driven: single enzyms, motors, switches, networks
  - paradigm for “physics of life” ?

- Non equilibrium statistical mechanics
  - exact relation beyond linear response
  - towards a comprehensive theory of NESS
  - transitions between different NESS, periodically driven systems
  - further implications of stochastic entropy ?