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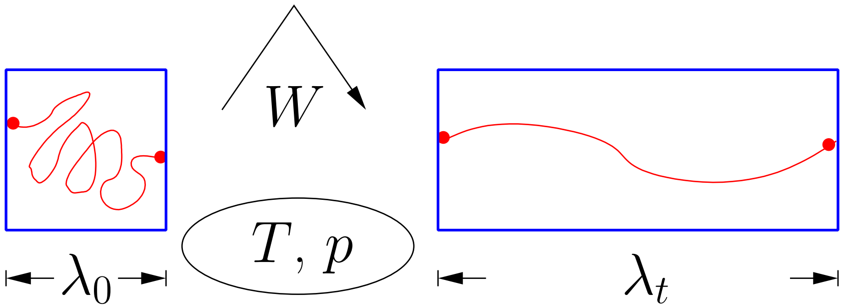
Fluctuation theorems, Jarzynski relation, and non-equilibrium entropy:

A coherent approach within stochastic dynamics

Udo Seifert

II. Institut für Theoretische Physik, Universität Stuttgart

- Second law for small systems $(k_B T = 1)$

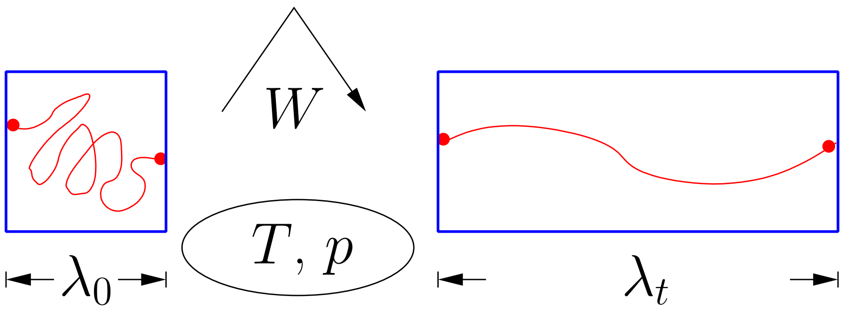


  - for small systems a distribution of work spent: $p(W; \lambda(\tau))$

  - Second law: $\boxed{\langle W \rangle_{|\lambda(\tau)} \geq \Delta G \equiv G(\lambda_t) - G(\lambda_0)}$

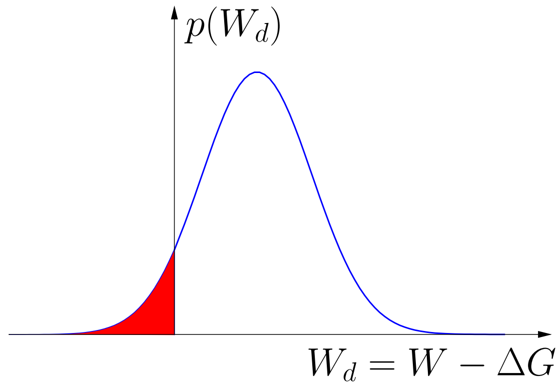
    * equality for infinitly slow processes $p(W) = \delta(W - \Delta G)$
    * Gaussian for slow pulling

- Jarzynski relation (1997)



  - $$\boxed{\langle e^{-W}\rangle_{|\lambda(\tau)} \equiv \int dW \;\, p(W;\lambda(\tau))e^{-W} \stackrel{!}{=} e^{-\Delta G}}$$
  - start with initial thermal distribution
  - valid for any protocol $\lambda(\tau)$
  - valid beyond linear response
  - allows to extract free energy differences from non-eq data
  - "implies" the second law (since $\langle e^{x}\rangle \geq e^{\langle x\rangle}$)

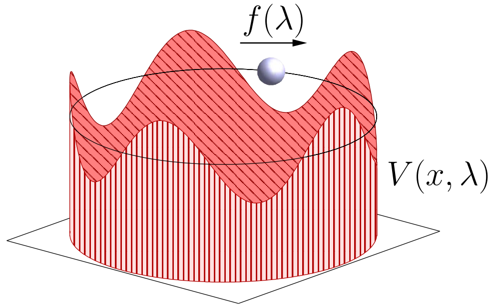
- Dissipated work $W_d \equiv W - \Delta G$
  - $\langle \exp[-W_d] \rangle \equiv \int_{-\infty}^{+\infty} dW_d \; p(W_d) \exp[-W_d] = 1$



  - red events "violate the second law" (??)
  - Special case: Gaussian distribution

$$p(W_d) \sim \exp[-(W_d - \langle W_d \rangle)^2/2\sigma^2] \qquad \text{with} \qquad \langle W_d \rangle = \sigma^2/2$$

Paradigm: Colloidal particle



- Langevin equation

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

  - Gaussian noise: $\langle \zeta(\tau)\zeta(\tau')\rangle = 2D\delta(\tau - \tau')$ with $D = k_B T \mu$
  - Total force

    $F(x,\lambda) = -\partial_x V(x,\lambda) + f(\lambda)$

    depends on external driving or protocol $[\lambda(\tau)]$

- First law: $dw = du + dq$ [(Sekimoto, 1997)]:
  - applied work: $dw = f dx + \partial_\lambda V(x,\lambda) d\lambda$
  - internal energy: $du = dV$
  - dissipated heat: $dq = dw - du = F dx = (1/\mu)(\dot{x} - \zeta) dx = T\Delta s_{\mathrm{m}}$

- Towards a refinement of the second law: 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

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

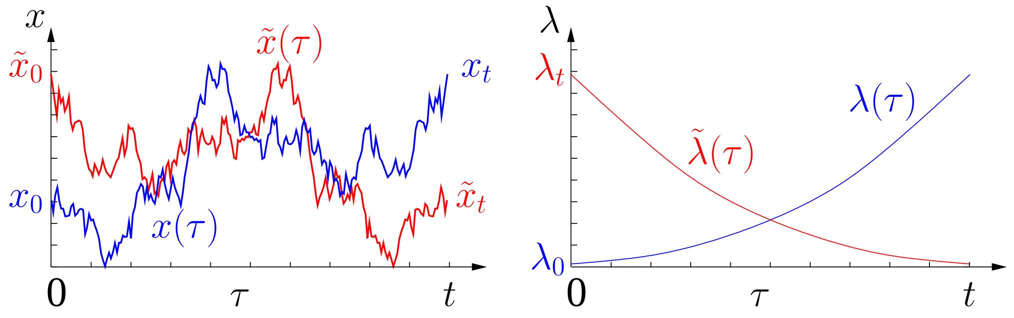
  - Stochastic entropy for a single trajectory $x(\tau)$

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

  - equation of motion

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

- "Time reversal"



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

- Ratio of forward to reversed path

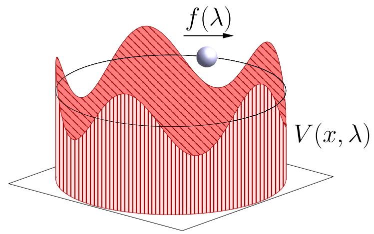
$$\frac{p[x(\tau)|x_0]}{\tilde{p}[\tilde{x}(\tau)|\tilde{x}_0]} = \exp\ \beta \int_0^t d\tau\ \dot{x}F = \exp\ \beta q[x(\tau)] = \exp \Delta s_m$$

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

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

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

- Jarzynski relation (1997)



  - $f = 0$, drive potential from λ_0 to λ_t
  - detailed balance for any fixed λ

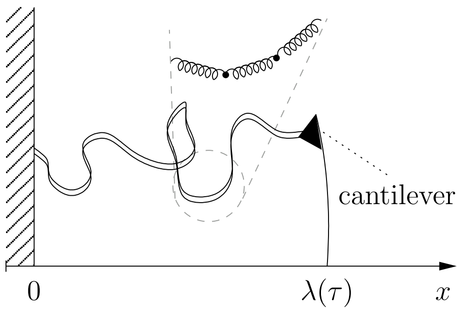
    $$1 = \langle \exp[\underbrace{-\beta q[x(\tau)]}_{-\Delta s_{\rm m}} + \ln p_1(x_t)/p_0(x_0)] \rangle$$

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

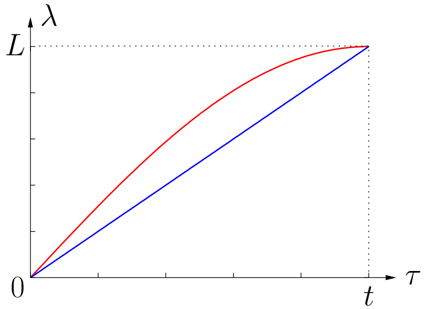
Generalization to many coupled Langevin equations obvious

- Gaussian distribution for W_d for slow driving of any process ($\dot{\lambda} t_{\text{rel}} << 1$) [T. Speck and U.S., Phys. Rev E 70, 066112, 2004]

- Stretching of Rouse polymer [T. Speck and U.S., EPJ B 43, 521, 2005]



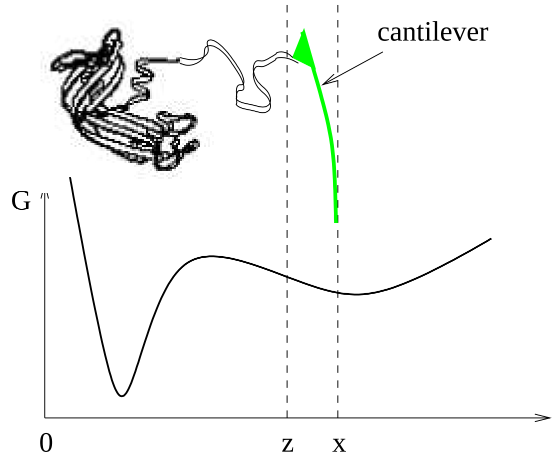
  - different protocols



    * linear: $\lambda(\tau) = \tau L/t \quad \Rightarrow \quad \langle W_d \rangle = (N\gamma/3)L^2/t$
    * periodic: $\lambda(\tau) = L \sin \pi\tau/2t \quad \Rightarrow \langle W_d \rangle = [\pi^2/8](N\gamma/3)L^2/t$

- Probing energy profiles by periodic loading

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

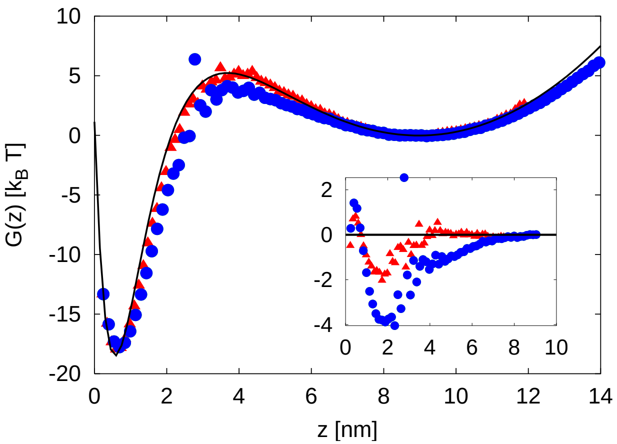


  - $H(z,\tau) = G(z) + (k/2)(\lambda(\tau) - z)^2$
  - Simulation using a Langevin equation

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

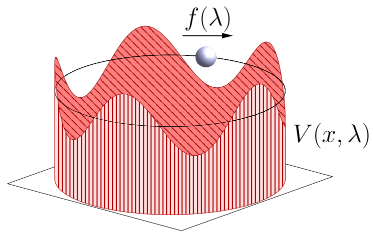
- Reconstruction of energy profile by z-resolved Jarzynski relation

$$e^{-G(z_0)} = \langle \delta[z_0 - z(t)] e^{-W(t)} \rangle \quad e^{(k/2)(z_0-\lambda(\tau))^2}$$

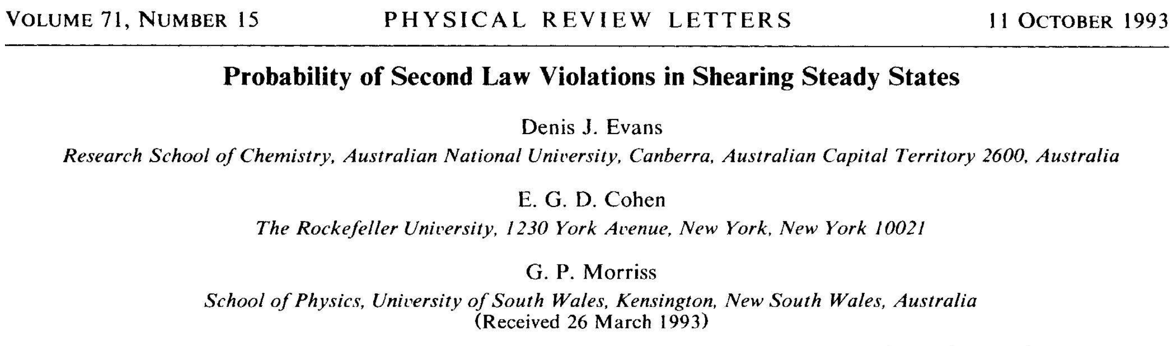


  – linear loading: $\lambda(\tau) = x_0 + vt$
  – periodic loading: $\lambda(\tau) = x_0 + a \sin \omega t$
  – Comparison: periodic forcing significantly better than linear

- Non-equilbrium steady states



  - $f = \text{const} \neq 0$
  - broken detailed balance
  - detailed fluctuation theorem: $$p(-\Delta s_{\text{tot}})/p(\Delta s_{\text{tot}}) = \exp(-\Delta s_{\text{tot}})$$
  - generalization of Evans et al (1993), Gallavotti & Cohen (1995), Lebowitz & Spohn (1999) ... to finite times



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Probability of Second Law Violations in Shearing Steady States

Denis J. Evans
Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory 2600, Australia

E. G. D. Cohen
The Rockefeller University, 1230 York Avenue, New York, New York 10021

G. P. Morriss
School of Physics, University of South Wales, Kensington, New South Wales, Australia
(Received 26 March 1993)

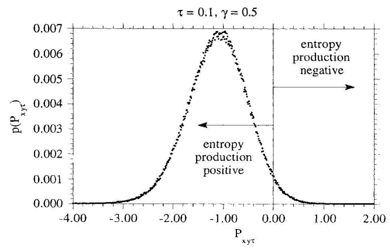
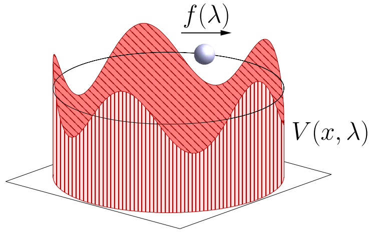


FIG. 1. The probability distribution of segment averages, $\langle P_{xy,i}\rangle_\tau$, of the xy element of the pressure tensor for 56 WCA disks at $H_0/N = 1.56032$, $n = 0.8$, a shear rate $\gamma = 0.5$, and a segment time $\tau = 0.1$. For those states where $\langle P_{xy,i}\rangle_\tau = P_{xy\tau}$ is positive the entropy production is negative for a period of time τ, counter to the second law of thermodynamics.

- Transitions between different NESS



  - $V(x)$ time-independent, $f = f(\lambda(\tau))$ switches from f_1 to f_2

  - $\phi(x,\lambda) \equiv -\ln p^s(x,\lambda) \qquad (\neq s(\tau))$

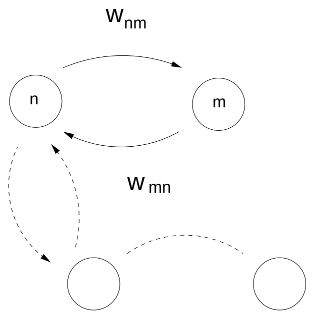
  - Hatano + Sasa, PRL 2001: $\qquad \Delta s_{\mathrm{m}} = q_{\mathrm{tot}} \equiv q_{\mathrm{ex}} + q_{\mathrm{hk}}$

    * $\langle \exp[-(q_{\mathrm{ex}} + \Delta\phi)] \rangle = 1$

    * $S \equiv -\int dx\, p^s(x,\lambda) \ln p^s(x,\lambda) \;\; \Rightarrow \Delta S \geq -\langle q_{\mathrm{ex}} \rangle$ ("2nd law for NESSs")

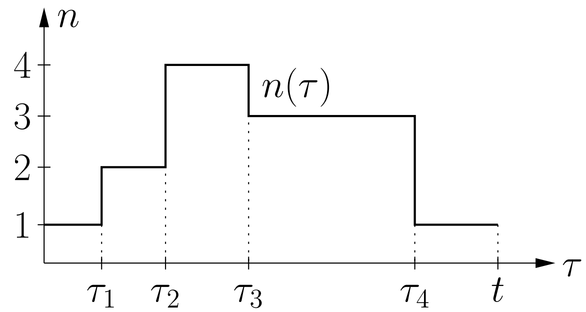
  - Further FTs: (T. Speck, U.S, J Phys A 38, L581, 2005)
    * $\langle \exp(-q_{\mathrm{hk}}) \rangle = 1$
    * $\langle \exp(-\Delta s_{\mathrm{m}} + \Delta\phi) \rangle = 1$ (generalized JR)

- Stochastic dynamics on discrete states



  - $\partial_t p_n = \sum_m [w_{mn}(\lambda)p_m - w_{nm}(\lambda)p_n]$
  - solution $p_n(\tau)$ depends on initial $p_n(0)$
  - stationary solution $p_n^s(\lambda)$ for any fixed λ

- Stochastic trajectory



Stochastic entropy

- Non-equilibrium ensemble entropy

  $S(\tau) \equiv -\sum_n p_n(\tau) \ln p_n(\tau) = -\langle \ln p_n(\tau) \rangle$

- Stochastic (trajectory-dependent) entropy of the system

  $s(\tau) \equiv -\ln p_{n(\tau)}$

- equation of motion

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

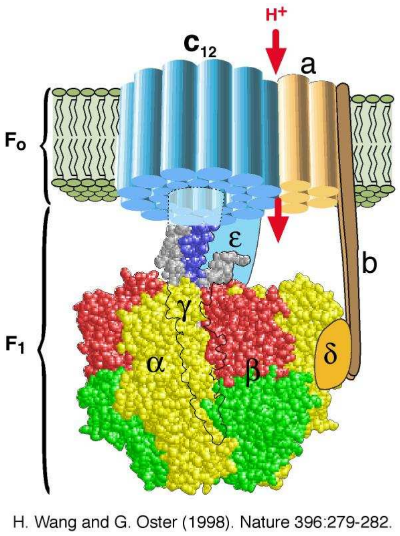
- Two fluctuation theorems [U.S., PRL 95, 040602, 2005]
  - Integral FT for total entropy production for arbitrary driving

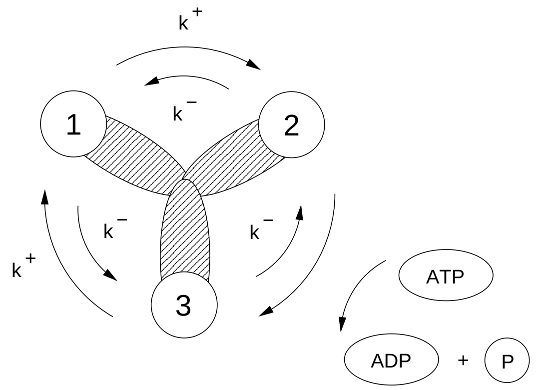
    $$\boxed{\langle \exp(-\Delta s_{\text{tot}}) \rangle = 1}$$

  - 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]

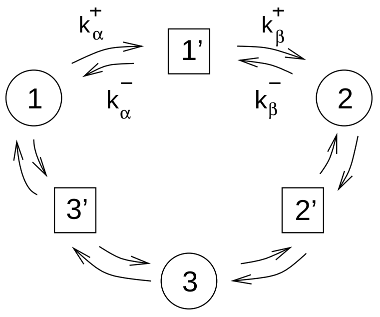




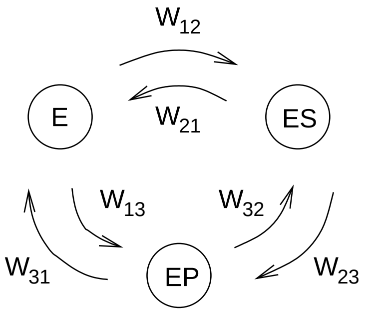
- $\partial_\tau p_1 = -(k^+ + k^-)p_1 + k^+ p_2 + k^- p_3$ & cyc
- $\Delta s_{\text{tot}} = n \ln(k^+/k^-) = n[\mu_{ATP} - \mu_{ADP} - \mu_P]/T$
- $\boxed{p(-n)/p(n) = \exp[-n \ln(k^+/k^-)]}$

- More complex schemes:

  – Intermediate steps

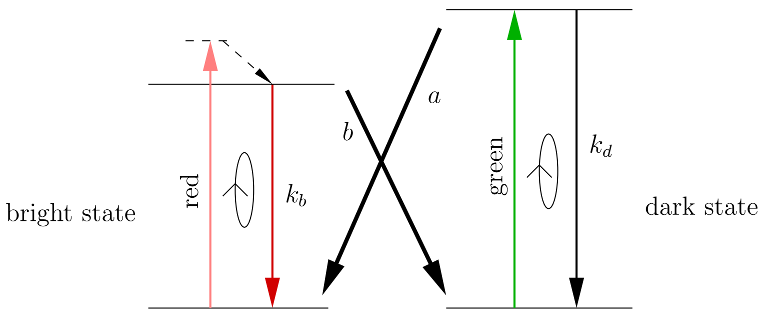


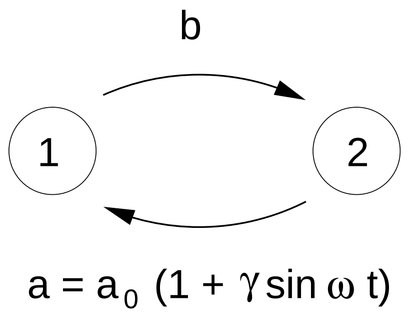
  – Michaelis Menten kinetics



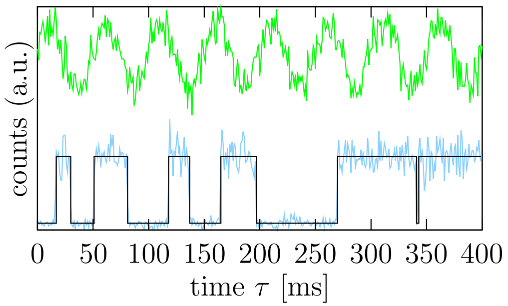
Periodically driven system: Optically active defect center in diamond

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





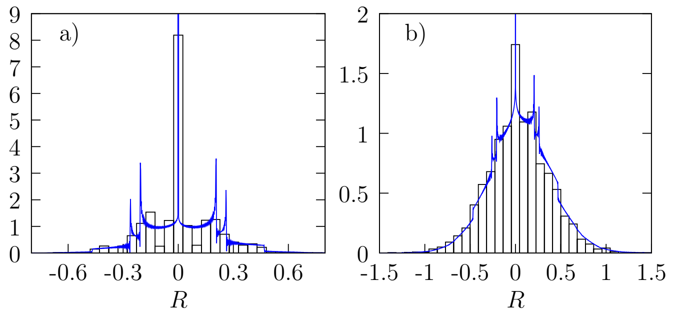
- Trajectories



- Integral theorem:

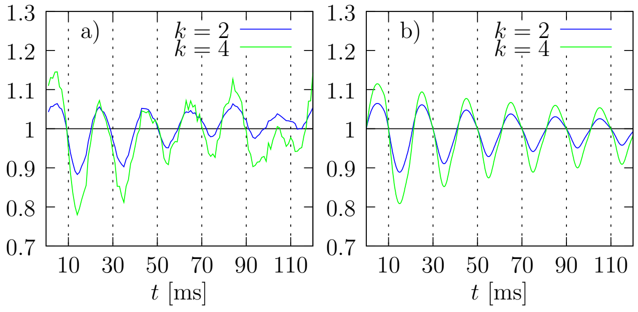
  $\langle \exp[-R] \rangle = 1$ for $R[n(\tau)] \equiv -\int_o^t d\tau \dot{\lambda} \partial_\lambda \ln p^s_{n(\tau)}(\lambda)$ $(= W_d \sim \Delta s_{\text{tot}})$

  $p(R)$



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

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



Perspectives

- Stochastic dynamics as a unifying concept for FT and JR
- Stochastic entropy leads (at least) to nice theorems for finite times
- Isothermal non-eq dynamics as emerging paradigm for small driven systems
  - mechanically driven: colloids, polymers, proteins
  - biochemically driven: single enzyms, motors, switches, networks