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

A coherent approach within stochastic dynamics

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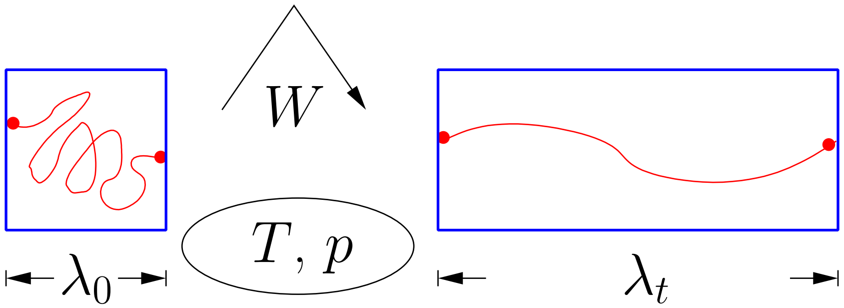
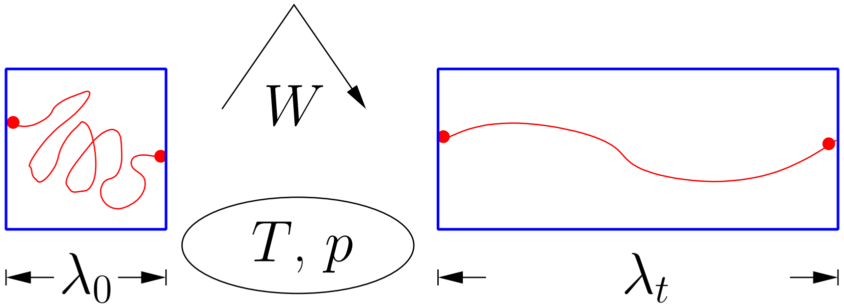
- Second law for small systems $(k_B T = 1)$



  - 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

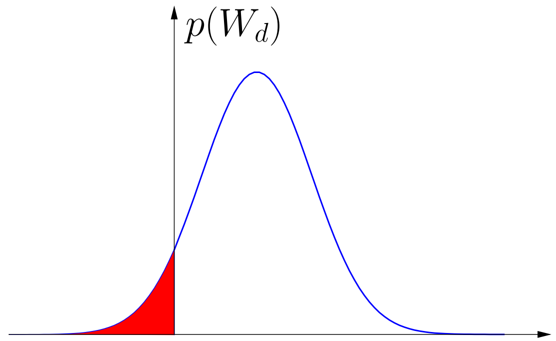
  – valid for any protocol $\lambda(\tau)$

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

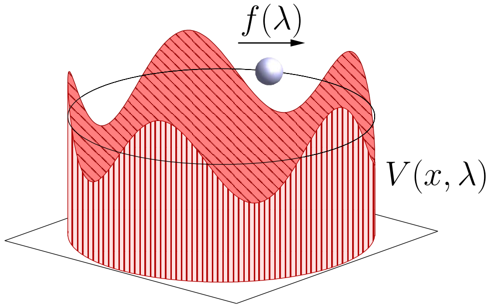


  - red events "violate the second law" (??)

  - 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

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

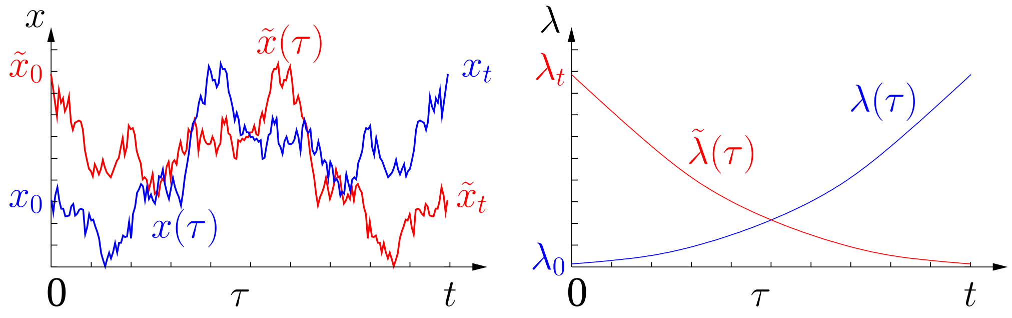
  - Stochastic entropy for a single trajectory $x(\tau)$

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

  - equation of motion

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

- "Time reversal"



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

- Ratio of forward to reversed path

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

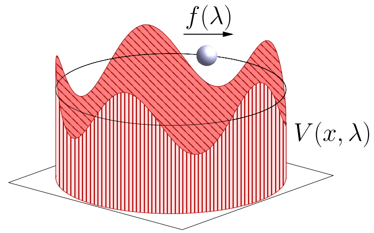
- General fluctuation theorem (cf. Jarzynski, Crooks, Maes)

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

  - for any (normalized) $p_1(x_t)$
  - with $p_1(x_t) = p(x,t) = \exp[-s(\tau)]$

- $\boxed{\langle \exp[-\Delta s_{\rm tot}] \rangle = 1} \Rightarrow \boxed{\langle \Delta s_{\rm tot} \rangle \geq 0}$
  - integral fluctuation theorem for total entropy production
  - arbitrary initial state, driving, length of trajectory

- Jarzynski relation (1997)



  – $f = 0$, drive potential from λ_0 to λ_t

  – detailed balance for any fixed λ

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

  – $p_0(x_0) \equiv \exp[-\beta(V(x_0, \lambda_0) - G(\lambda_0)]$

  – $p_1(x_t) \equiv \exp[-\beta(V(x_t, \lambda_t) - G(\lambda_t)]$

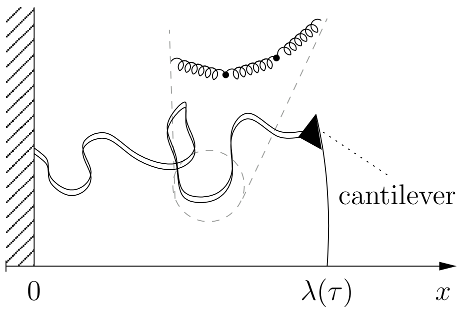
  – $\boxed{\langle \exp[-\beta W] \rangle = \exp[-\beta \Delta G]}$

  – within stochastic dynamics an identity!

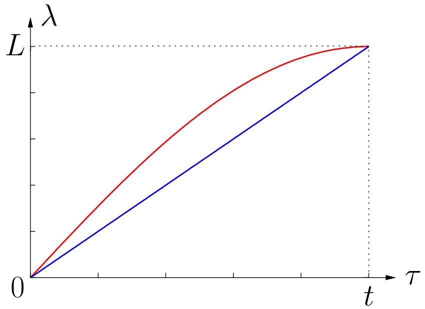
Generalization to many coupled Langevin equations obvious

- Gaussian distribution for W_d for slow driving of any process ($\dot{\lambda} t_{\rm rel} << 1$) [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]



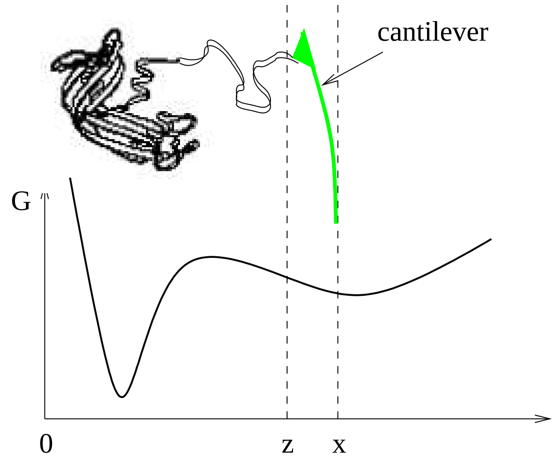
  - different protocols



    * 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]

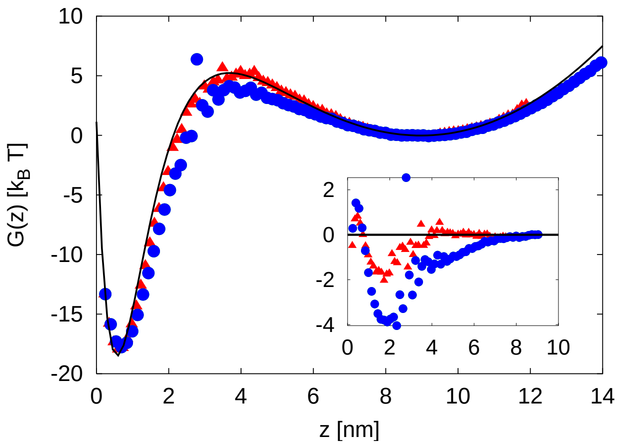


  - $H(z,\tau) = G(z) + (k/2)(\lambda(\tau) - z)^2$
  - Simulation using a Langevin equation

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

- Reconstruction of energy profile by z-resolved Jarzynski relation

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

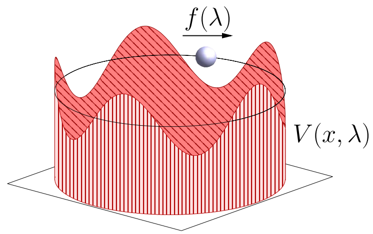


– linear loading: $\lambda(\tau) = x_0 + vt$

– 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

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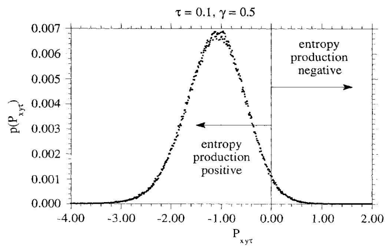
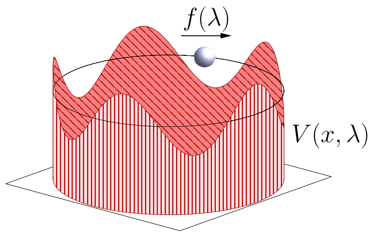


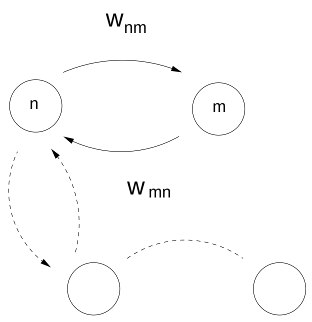
FIG. 1. The probability distribution of segment averages, $\langle P_{xy,i}\rangle_\tau$, of the xy element of the pressure tensor for 56 WCA disks at $H_0/N = 1.56032$, $n = 0.8$, a shear rate $\gamma = 0.5$, and a segment time $\tau = 0.1$. For those states where $\langle P_{xy,i}\rangle_\tau = P_{xy\tau}$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

- Transitions between different NESS



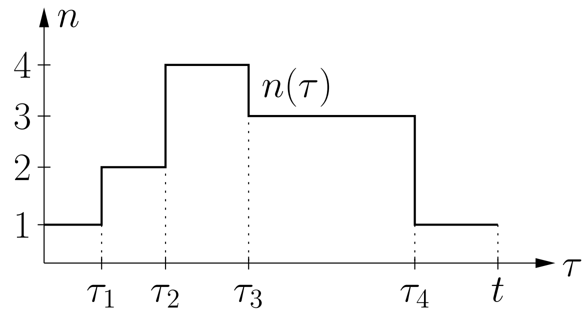
  - $V(x)$ time-independent, $f = f(\lambda(\tau))$ switches from f_1 to f_2
  - $\phi(x,\lambda) \equiv -\ln p^s(x,\lambda) \qquad (\neq s(\tau))$
  - Hatano + Sasa, PRL 2001: $\Delta s_{\rm m} = q_{\rm tot} \equiv q_{\rm ex} + q_{\rm hk}$
    * $\langle \exp[-(q_{\rm ex} + \Delta\phi)] \rangle = 1$
    * $S \equiv -\int dx\, p^s(x,\lambda) \ln p^s(x,\lambda) \;\; \Rightarrow \Delta S \geq -\langle q_{\rm ex} \rangle$ ("2nd law for NESSs")
  - Further FTs: (T. Speck, U.S, J Phys A 38, L581, 2005)
    * $\langle \exp(-q_{\rm hk}) \rangle = 1$
    * $\langle \exp(-\Delta s_{\rm m} + \Delta\phi) \rangle = 1$ (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]

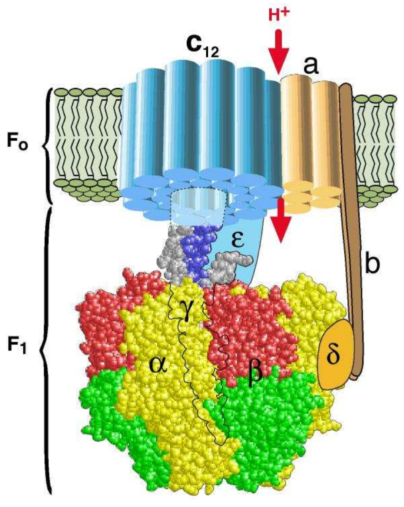
  - Integral FT for total entropy production for arbitrary driving

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

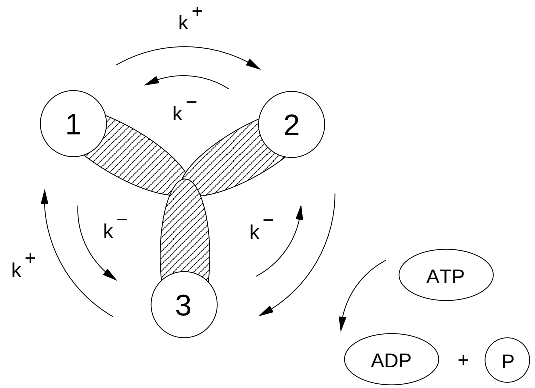
  - Detailed FT for total entropy production in a NESS

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

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



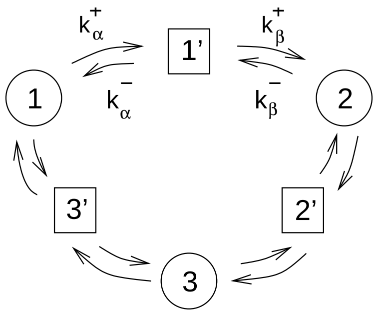
H. Wang and G. Oster (1998). Nature 396:279-282.



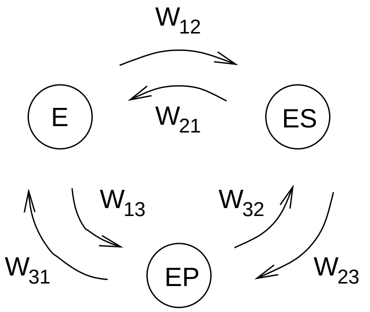
- $\partial_\tau p_1 = -(k^+ + k^-)p_1 + k^+ p_2 + k^- p_3$ & cyc
- $\Delta s_{\text{tot}} = n \ln(k^+/k^-) = n[\mu_{ATP} - \mu_{ADP} - \mu_P]/T$
- $\boxed{p(-n)/p(n) = \exp[-n \ln(k^+/k^-)]}$

- More complex schemes:

  - Intermediate steps

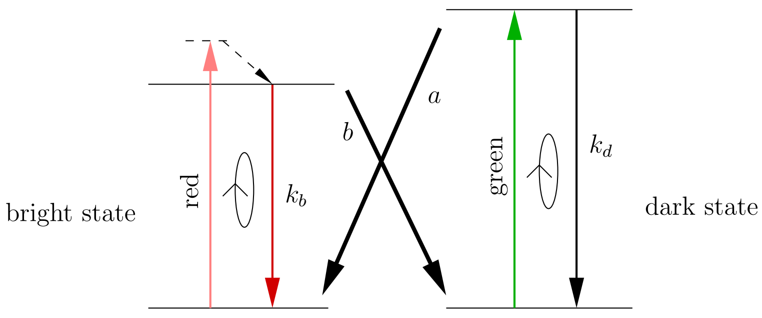


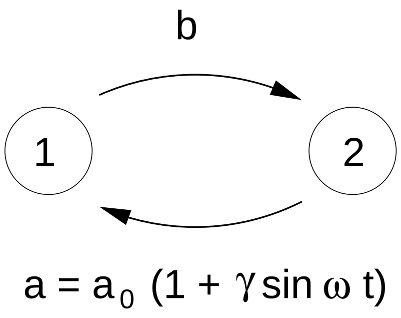
  - Michaelis Menten kinetics



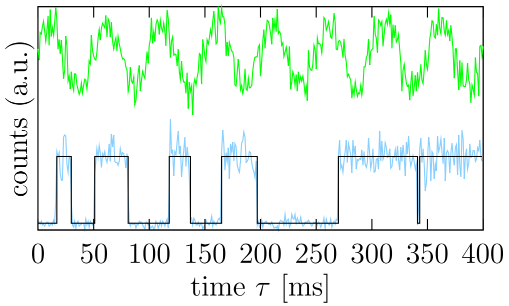
Periodically driven system: Optically active defect center in diamond

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





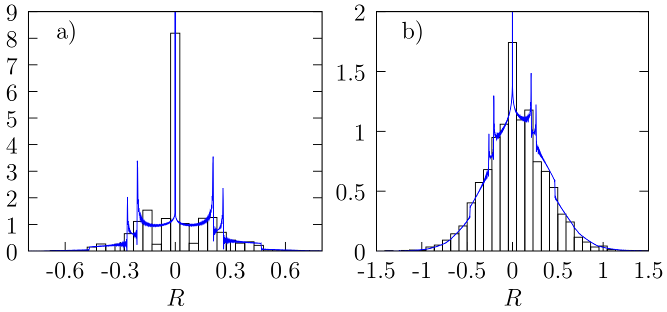
- Trajectories



- Integral theorem:

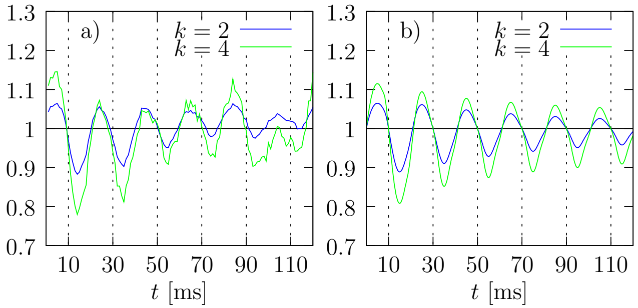
$\langle \exp[-R] \rangle = 1$ for $R[n(\tau)] \equiv -\int_o^t d\tau \dot{\lambda} \partial_\lambda \ln p^s_{n(\tau)}(\lambda) \quad (= W_d \sim \Delta s_{\text{tot}})$

$p(R)$



- 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