Bangalore lectures, June 2013

Stochastic thermodynamics

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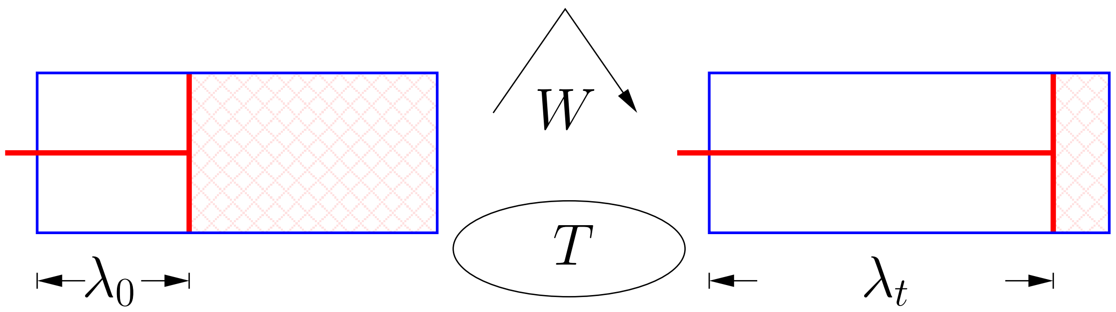
LECTURE I

- Classical vs. stochastic thermodynamics
- First law
- General fluctuation theorem and Jarzynski relation
- Optimization

- Perspective

1820 $\simeq$ 1850	classical thermodynamics	$dW = dU + dQ$ $dS \geq 0$
$\simeq$ 1900	eq stat phys	$p_i = \exp[-(E_i - F)/k_B T]$
1930 $\simeq$ 1960	non-eq: linear response	Onsager Green-Kubo, FDT
$\geq$ 1993	non-eq: beyond linear response stochastic thermodynamics	Fluctuation theorem Jarzynski relation

- Thermodynamics of macroscopic systems [19^{th} cent]



  - First law energy balance:

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

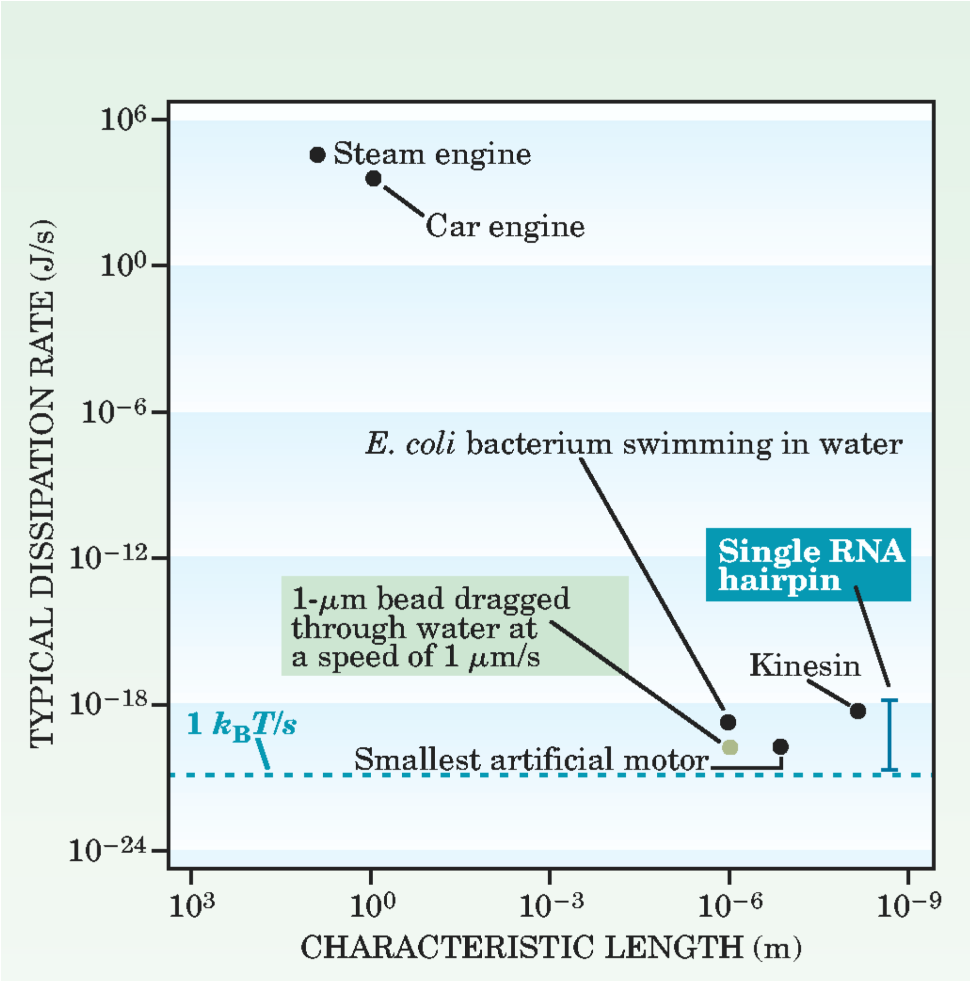
  - Second law:

$$\Delta S_{\text{tot}} \equiv \Delta S + \Delta S_M > 0$$

$$W > \Delta E - T \Delta S \equiv \Delta F$$

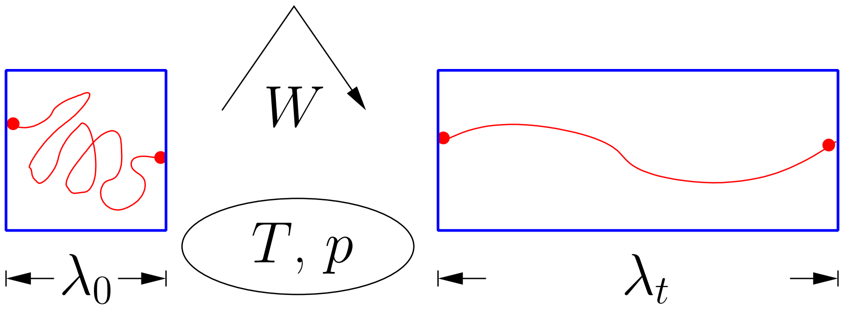
$$W_{\text{diss}} \equiv W - \Delta F > 0$$

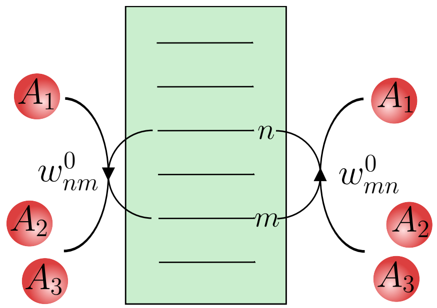
- Macroscopic *vs* mesoscopic *vs* molecular machines



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

- Stochastic thermodynamics for small systems

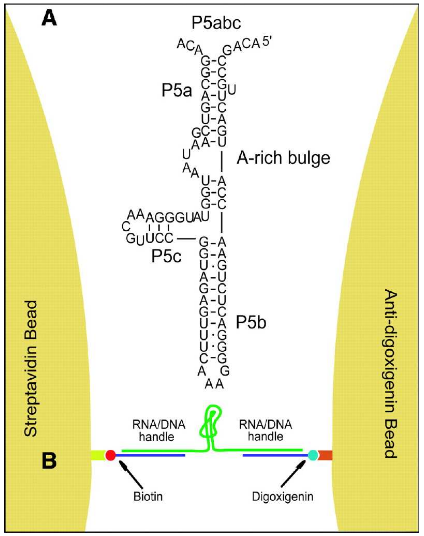


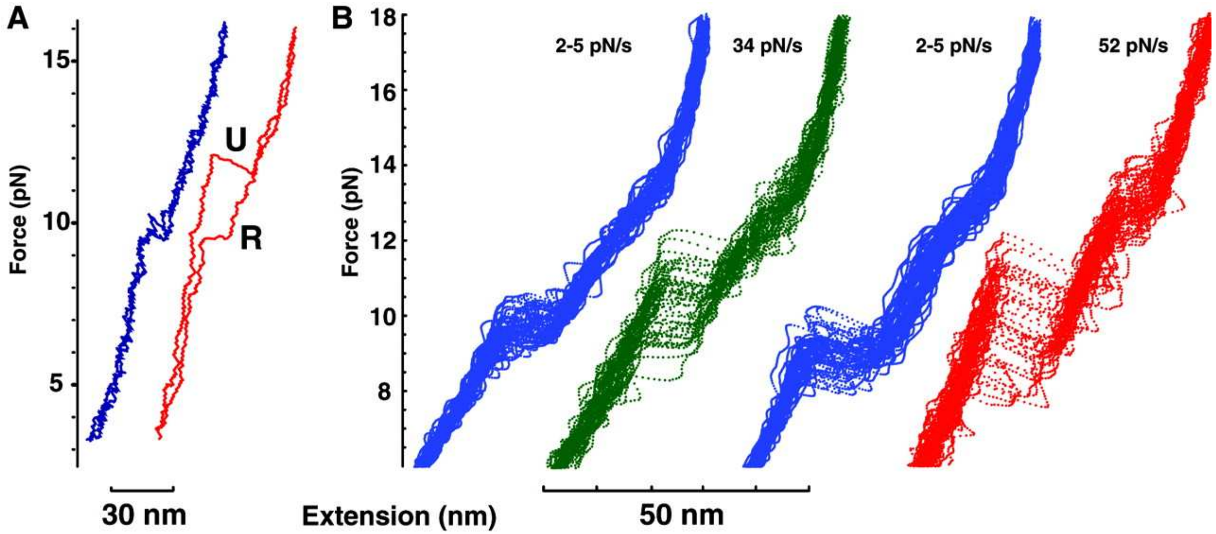


  - First law: how to define work, internal energy and exchanged heat?
  - fluctuations imply distributions: $p(W; \lambda(\tau))$ ...
  - entropy: distribution as well?

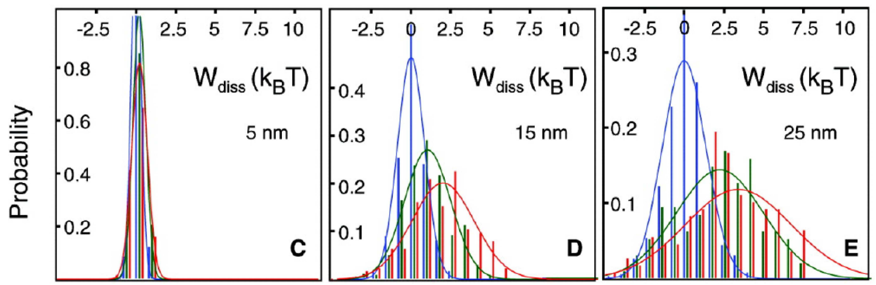
• Nano-world Experiment: Stretching RNA

[Liphardt et al, Science **296** 1832, 2002.]

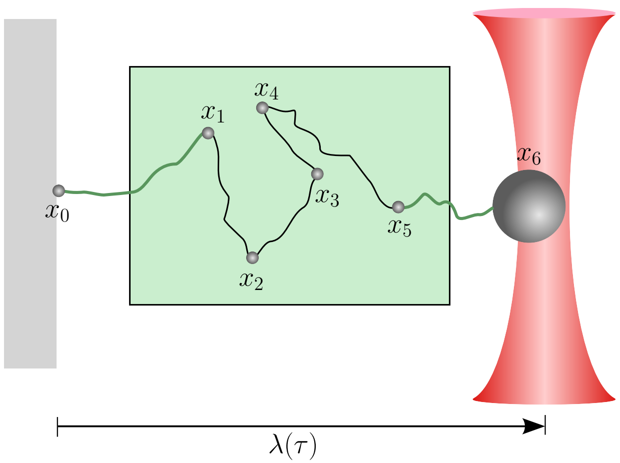




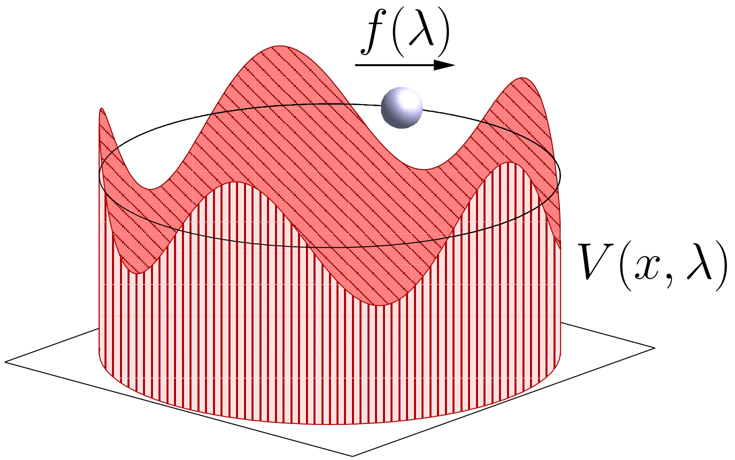
– distributions of W_{diss}:



- Mechanically driven systems

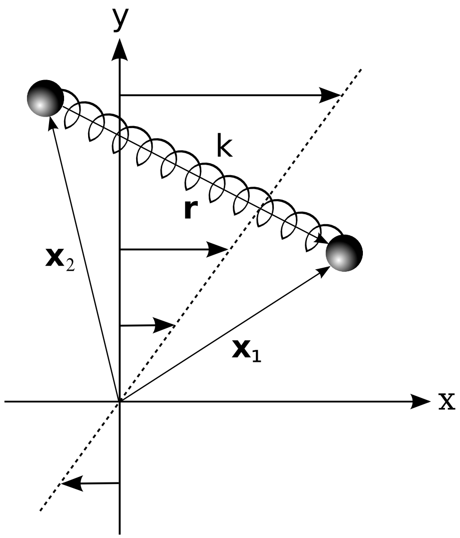


Pulling a biomolecule

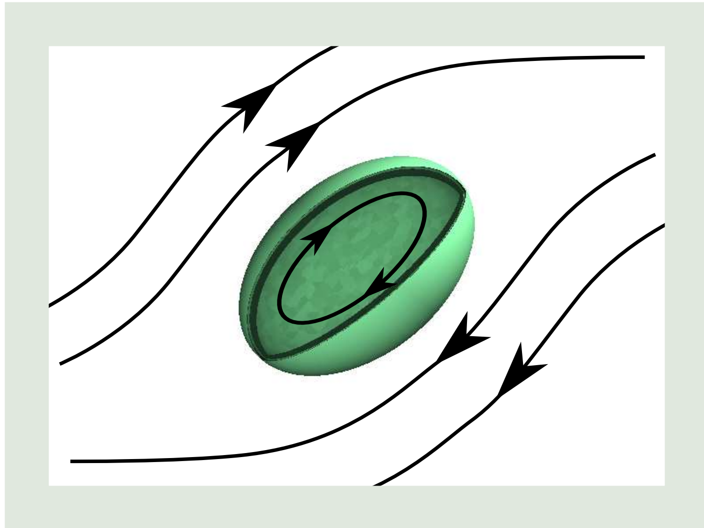


Colloidal partical in a laser trap

- Flow driven systems

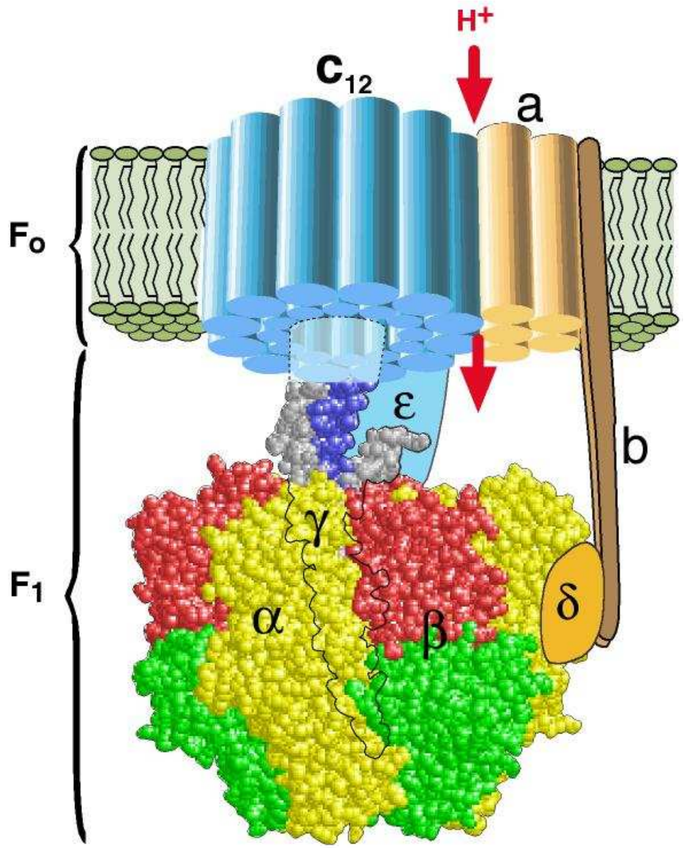


Stretching a polymer (dumbbell)

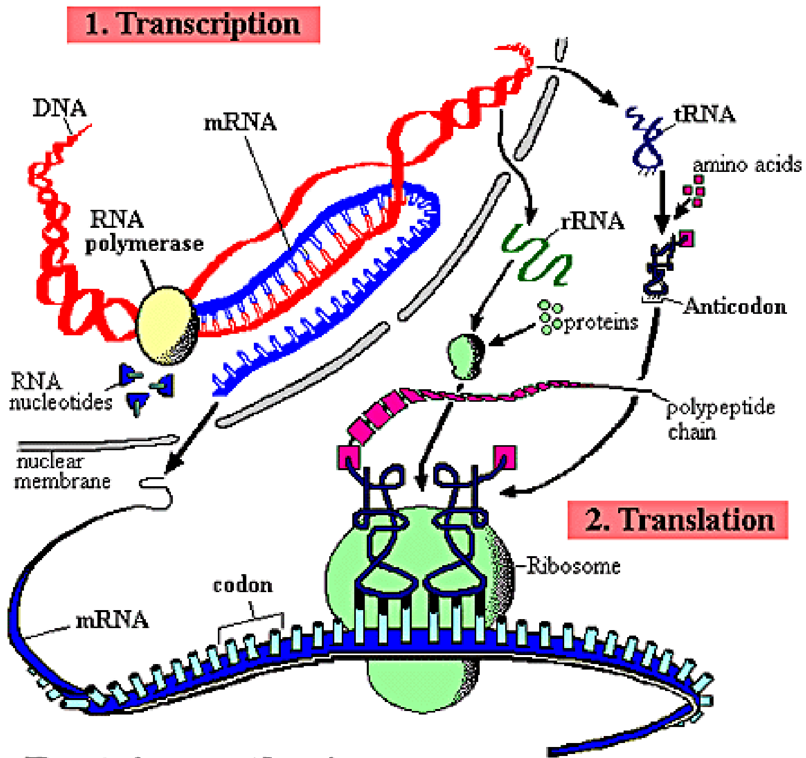


Tank-treading vesicle in shear flow

- (Bio)chemically driven systems



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



Protein synthesis

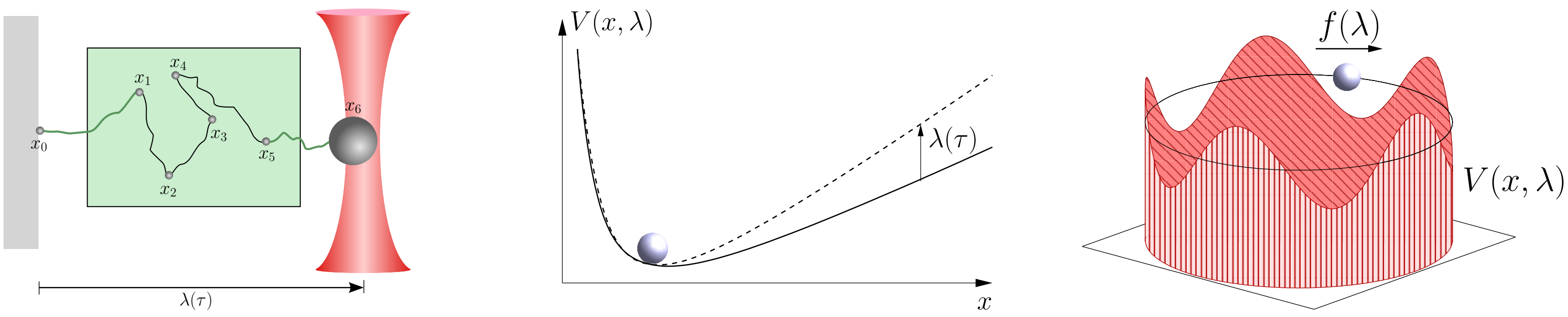
F1-ATPase

- **Stochastic thermodynamics** applies to such systems where
  - non-equilibrium is caused by mechanical or chemical forces
  - ambient solution provides a thermal bath of well-defined T
  - fluctuations are relevant due to small numbers of involved molecules

- Main idea: Energy conservation (1^{st} law) and entropy production (2^{nd} law) along a single stochastic trajectory

- Precursors:
  - notion "stoch th'dyn" by Nicolis, van den Broeck mid '80s (ensemble level)
  - stochastic energetics (1^{st} law) by Sekimoto late '90s
  - work theorem(s): Jarzynski, Crooks late '90s
  - fluct'theorem: Evans, Cohen, Galavotti, Kurchan, Lebowitz & Spohn '90s
  - quantities like stochastic entropy by Crooks, Qian, Gaspard in early '00s
  - ...

- Paradigm for mechanical driving:



  – Langevin dynamics $\dot{x} = \mu \underbrace{[-V'(x,\lambda) + f(\lambda)]}_{F(x,\lambda)} + \zeta \quad \langle\zeta\zeta\rangle = 2\mu \underbrace{k_B T}_{(\equiv 1)} \delta(...)$

  – external protocol $\lambda(\tau)$

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

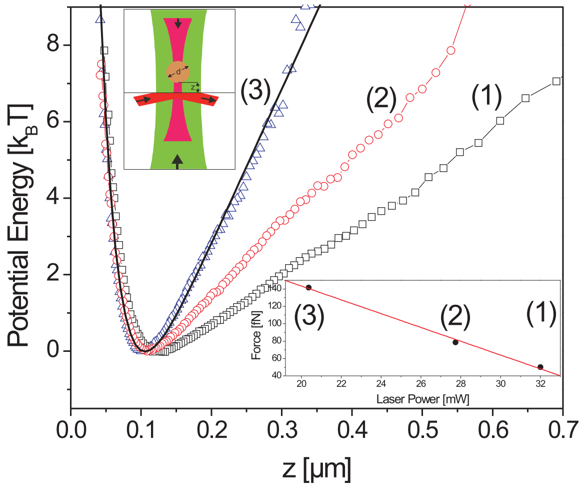
  – applied work: $dw = \partial_\lambda V(x,\lambda) d\lambda + f(\lambda) dx$

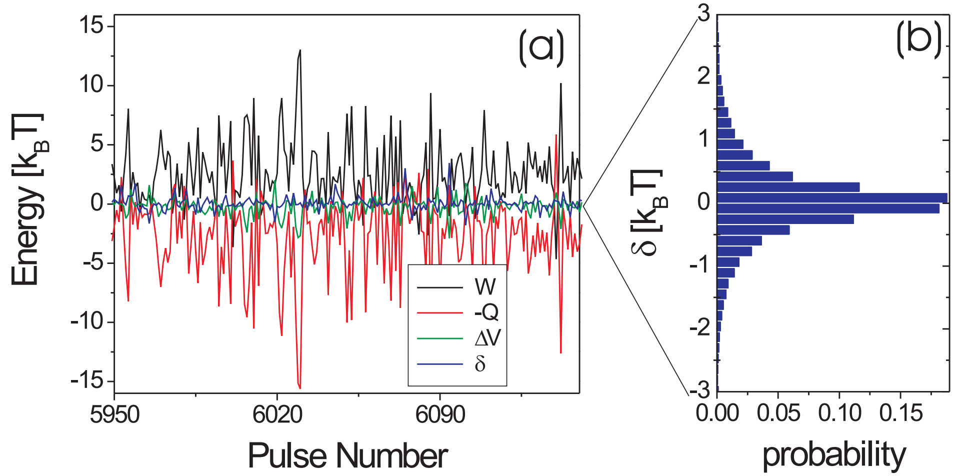
  – internal energy: $du = dV$

  – dissipated heat: $dq = dw - du = F(x,\lambda) dx = T ds_{\mathrm{m}}$

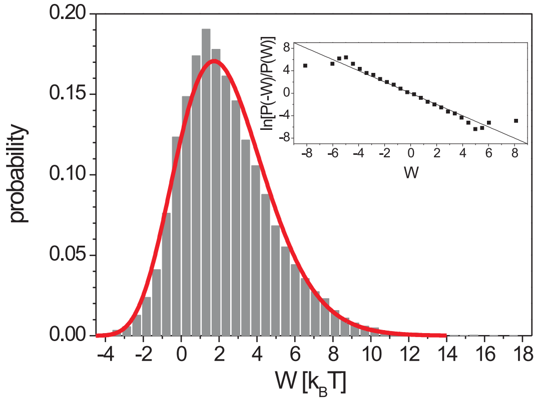
- Experimental illustration: Colloidal particle in $V(x, \lambda(\tau))$

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





– work distribution



– non-Gaussian distribution $\Rightarrow$

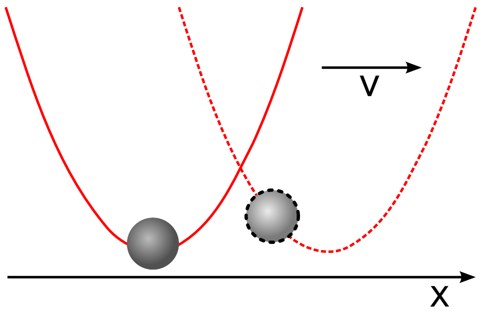
– Langevin valid beyond lin response

[T. Speck and U.S., PRE 70, 066112, 2004]

- Role of external flow and frame invariance

  [T. Speck, J. Mehl and U.S., PRL **100** 178302, 2008]

Lab frame



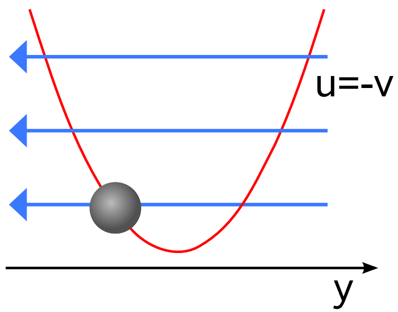
$$V(x,\tau) = k(v\tau - x)^2/2$$

$$\dot{x} = \mu k(v\tau - x) + \zeta$$

$$\dot{w} = \partial_\tau V = kv(v\tau - x(\tau)) \neq 0$$

comoving frame:

$y \equiv x(\tau) - v\tau$



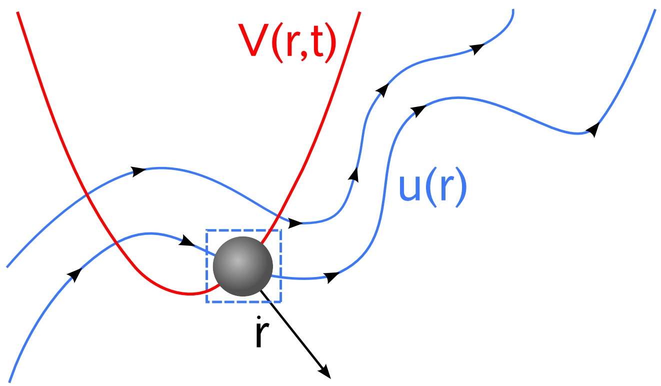
$$V(y) = ky^2/2$$

$$\dot{y} = -\mu k y - v + \zeta$$

$$\dot{w} = \partial_\tau V = 0 \quad ??$$

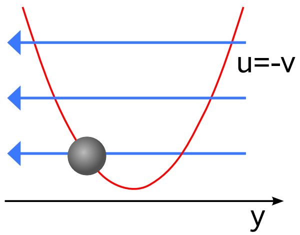
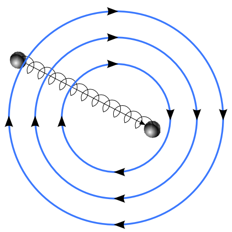
det balance satisfied: equilibrium ??

- Correct definitions of th'dynamic quantities



no flow	flow $\quad u(\mathbf{r}) \neq 0$	
$dw = \partial_t V + \mathbf{f}\, d\mathbf{r}$	$dw \equiv D_t V + \mathbf{f}[d\mathbf{r} - \mathbf{u}dt]$	$(D_t \equiv \partial_t + \mathbf{u}\nabla)$
$dq = (-\nabla V + \mathbf{f})d\mathbf{r}$	$dq \equiv (-\nabla V + \mathbf{f})(d\mathbf{r} - \mathbf{u}dt)$	

- Equilibrium vs. non-equilibrium for flow driven systems

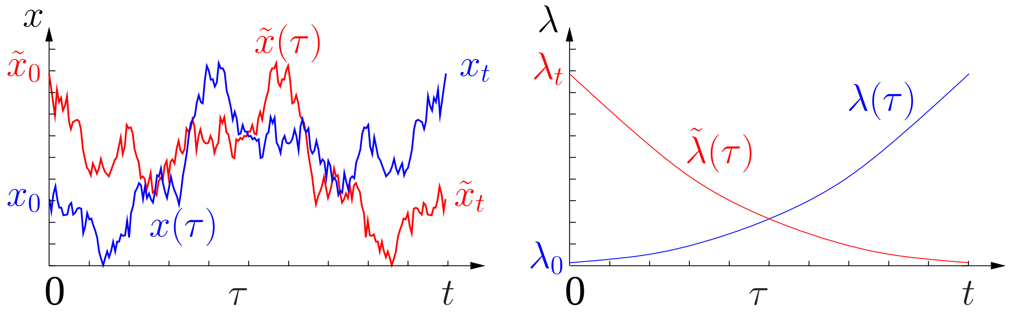
system	det bal	prob currents	
 particle trapped in flow	fulfilled	zero	non-eq
 dumbbell in pure rot flow	broken	non-zero	eq

- better criterion for eq: $\boxed{dw = 0 = D_t V + \mathbf{f}[d\mathbf{r} - \mathbf{u}dt]}$

- Path integral representation
  - "Boltzmann factor for a whole trajectory"

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

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



  - "time reversal" $\tilde{x}(\tau) \equiv x(t-\tau)$ and $\tilde{\lambda}(\tau) \equiv \lambda(t-\tau)$
  - Ratio of forward to reversed path

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

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

- General fluctuation theorem

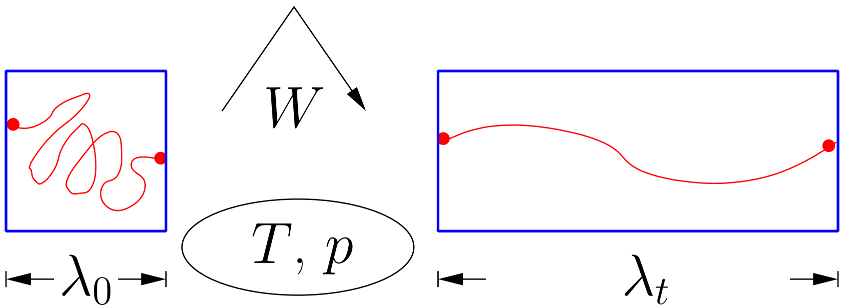
  [U.S., PRL **95**, 040602, 2005; generalizing Jarzynski, Crooks, Maes]

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

  – for arbitrary initial condition $p_0(x)$

  – for arbitrary (normalized) function $p_1(x_t)$

- Jarzynski relation (PRL, 1997)



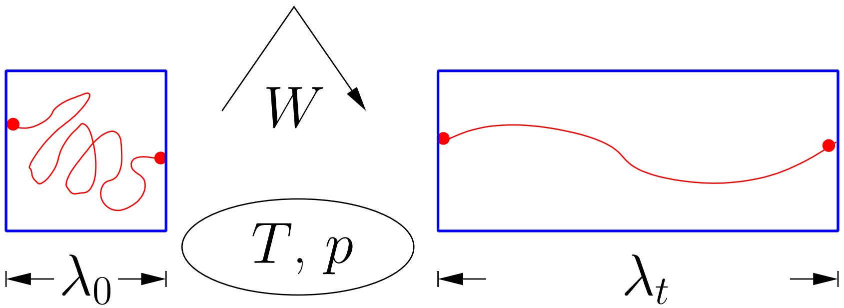
2^{nd} law:
$\langle W \rangle_{|\lambda(\tau)} \geq \Delta F \equiv F(\lambda_t)) - F(\lambda_0)$

  - $\boxed{\langle \exp[-W] \rangle = \exp[-\Delta F]}$ $\quad (k_B T = 1)$

  - Short proof: $1 = \langle \exp[\underbrace{-q[x(\tau)]}_{-\Delta s_m} + \ln p_1(x_t)/p_0(x_0)] \rangle$
    - $p_0(x_0) \equiv \exp[-(V(x_0, \lambda_0) - F(\lambda_0)]$
    - $p_1(x_t) \equiv \exp[-(V(x_t, \lambda_t) - F(\lambda_t)]$

  - within stochastic dynamics an identity!

- Jarzynski (cont'd) $(k_B T = 1)$

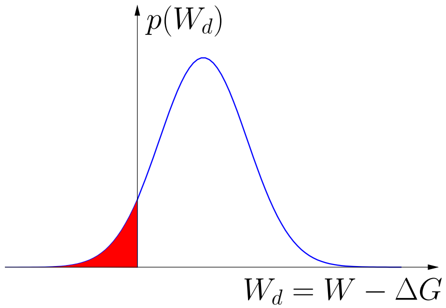


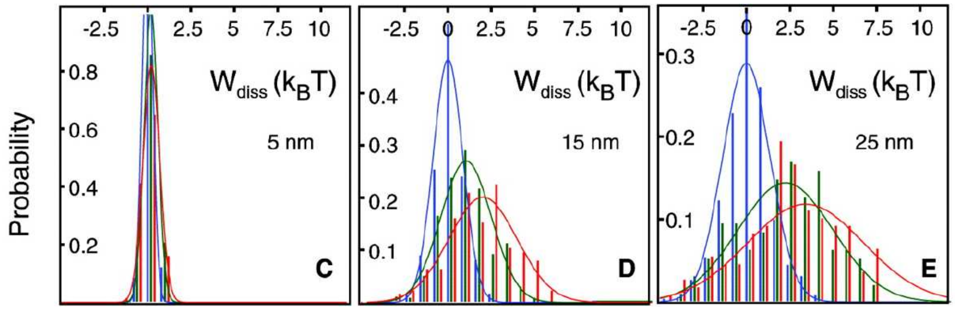
- $\boxed{\langle e^{-W} \rangle_{|\lambda(\tau)} \stackrel{!}{=} e^{-\Delta F}}$
- start with initial thermal distribution
- valid for any protocol $\lambda(\tau)$
- valid beyond linear response
- allows to extract free energy differences from non-eq data
- "implies" a variant of the second law

  $\langle e^x \rangle \geq e^{\langle x \rangle} \quad \Rightarrow \quad \langle W \rangle \geq \Delta F$

- 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

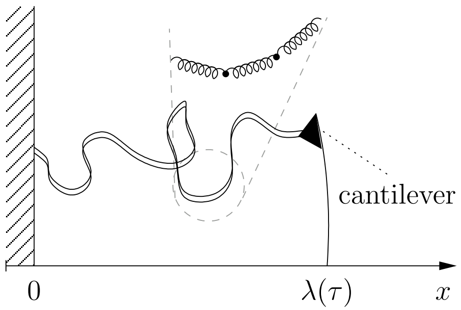
$$p(W_d) \sim \exp[-(W_d - \langle W_d \rangle)^2 / 2\sigma^2] \qquad \text{with} \qquad \langle W_d \rangle = \sigma^2/2$$

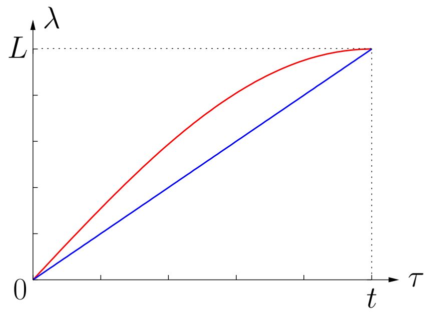
  ∗ scenario 1: slow driving of any process

    [T. Speck and U.S., Phys. Rev E **70**, 066112, 2004]

- Scenario 2: linear equations of motion and arbitrary driving

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



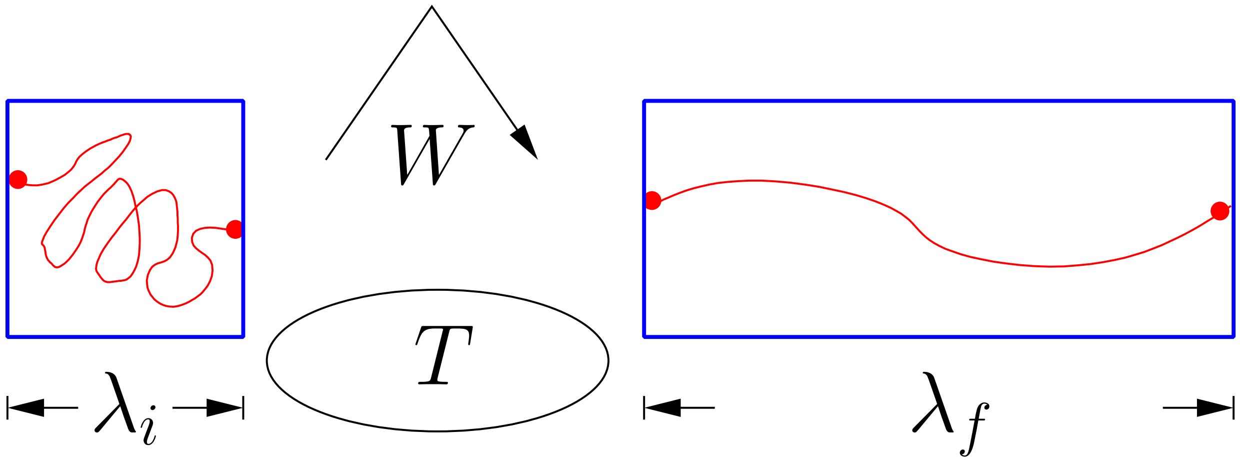


  – different protocols

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

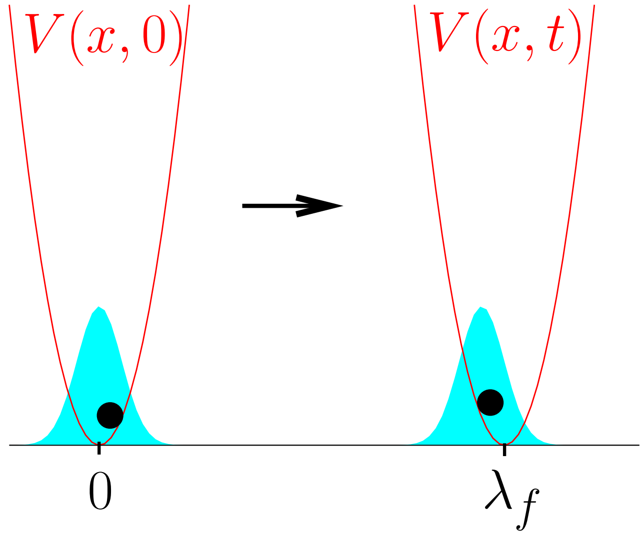
- Optimal finite-time processes in stochastic thermodynamics

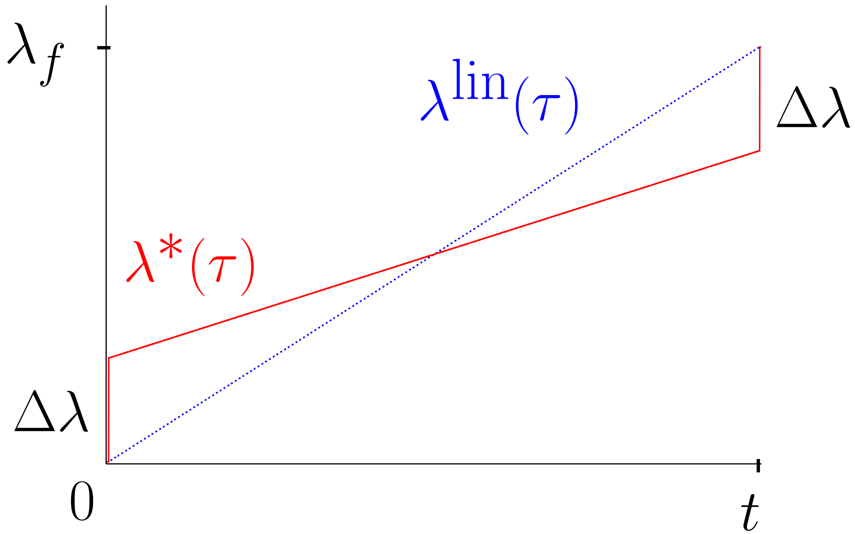
  [T. Schmiedl and U.S., PRL 98, 108301, 2007]



  – optimal protocol $\lambda^*(\tau)$ minimizes $\langle W \rangle$ for given λ_i, λ_f and finite t

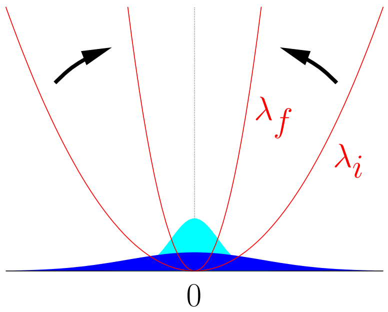
- Ex 1: Moving a laser trap $V(x, \lambda) = (x - \lambda(\tau))^2/2$



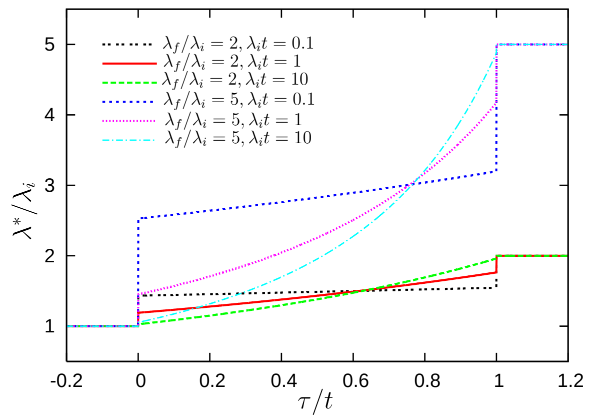


  - $\lambda^*(\tau)$ requires jumps at beginning and end $\qquad \Delta\lambda = \lambda_f/(t+2)$
  - gain $\qquad 1 \geq W^*(t)/W^{lin}(t) \geq 0.88$

- Ex 2: Stiffening trap $\qquad V(x,\lambda) = \lambda(\tau)x^2/2$



(a)



  - jumps are generic

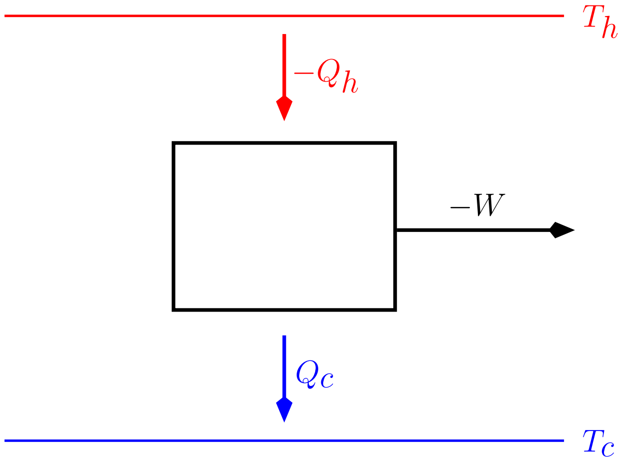
  - should help to improve convergence of $\langle \exp(-W) \rangle$

  - generalization: underdamped dynamics $\Rightarrow$ delta-peaks

    [A. Gomez-Marin, T.Schmiedl , U.S., J. Chem. Phys., 129 : 024114, 2008]

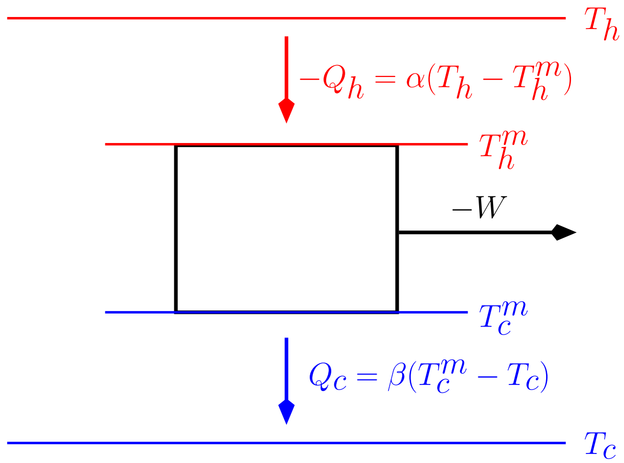
- Heat engines at maximal power

  – Carnot (1824)



  – $\eta_c \equiv 1 - T_c/T_h$
    but zero power

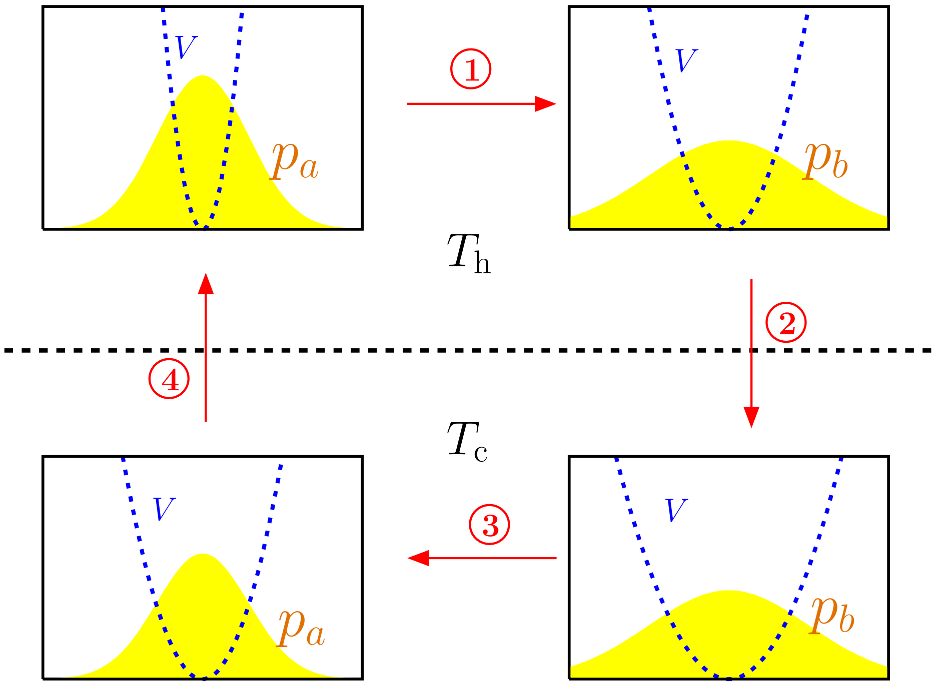
  – Curzon-Ahlborn (1975)

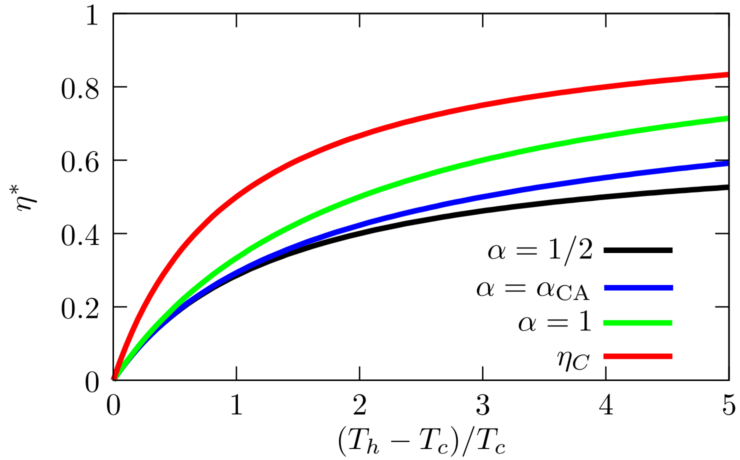


  – efficiency at maximum power
    $\eta_{ca} \equiv 1 - \sqrt{T_c/T_h}$
  – recent claims for universality(?)
  – what about fluctuations?

- Brownian heat engine at maximal power

  [T. Schmiedl and U.S., EPL **81**, 20003, (2008)]



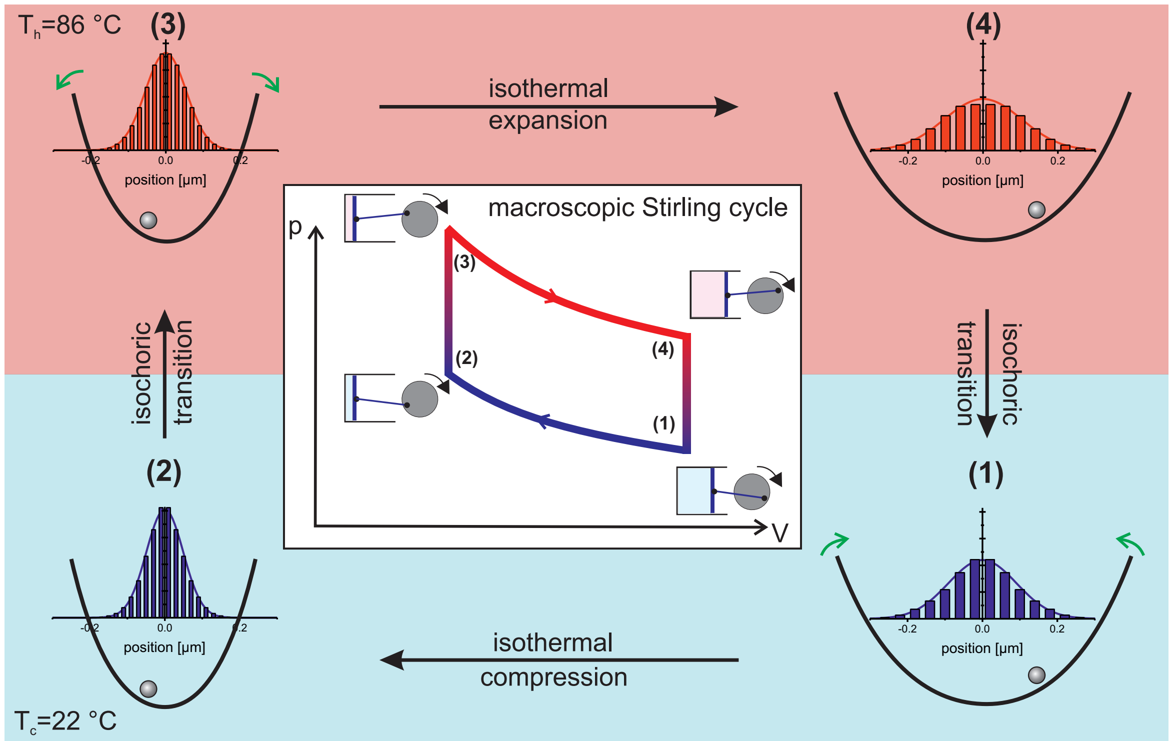


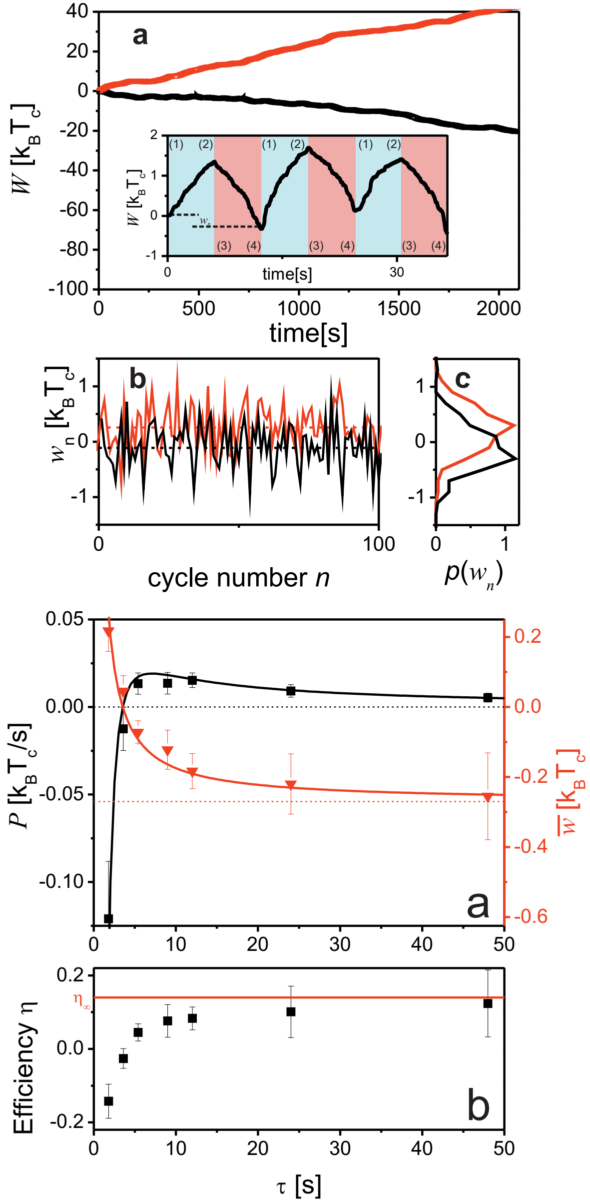
  – $\eta^* = \frac{\eta_c}{2-\alpha\eta_c}$ with $\alpha = 1/2$ for temp-independent mobility

  – Curzon-Ahlborn neither universal nor a bound

• Experimental realization in the Stirling version

[V. Blickle and C. Bechinger, Nature phys. 8, 143, 2012]

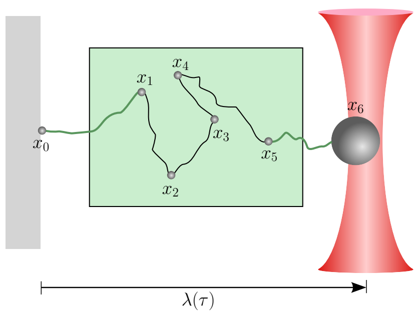


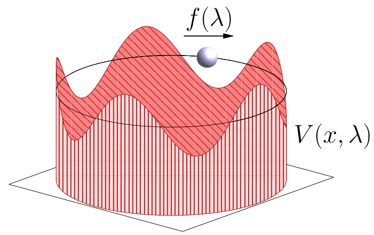


LECTURE II

- Stochastic entropy
- Stochastic dynamics on discrete states
- Non-equilibrium steady states (NESSs)
- FDT in NESS

- Recap: Paradigm for mechanical driving:





  - Langevin dynamics: $\dot{x} = \mu F(x, \lambda) + \zeta,$
  - Total force: $F(x, \lambda) = -\partial_x V(x, \lambda) + f(\lambda)$ depends on $[\lambda(\tau)]$
  - Gaussian noise: $\langle \zeta(\tau)\zeta(\tau') \rangle = 2D\delta(\tau - \tau')$ with $D = k_B T \mu$
  - Fokker-Planck equation:

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

- Stochastic entropy [U.S., PRL 95, 040602, 2005]
  - Fokker-Planck equation
    $$\partial_\tau p(x,\tau) = -\partial_x j(x,\tau) = -\partial_x \left(\mu F(x,\lambda) - D\partial_x\right) p(x,\tau)$$
  - Common 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
    $$\dot{s}(\tau) = \underbrace{-\left.\frac{\partial_\tau p(x,\tau)}{p(x,\tau)}\right|_{x(\tau)} + \left.\frac{j(x,\tau)}{Dp(x,\tau)}\right|_{x(\tau)} \dot{x}}_{\dot{s}_{\mathrm{tot}}} \underbrace{- \left.\frac{\mu F(x,\lambda)}{D}\right|_{x(\tau)} \dot{x}}_{\dot{s}_{\mathrm{m}}}.$$
  - $\Delta s = \Delta s_{\mathrm{tot}} - \Delta s_{\mathrm{m}} (= \Delta q/T)$

- Integral fluctuation theorem for entropy

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

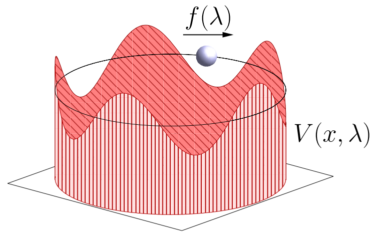
  - for any (normalized) $p_1(x_t)$
  - with $p_1(x_t) = p(x,t) = \exp[-s(t)]$

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

- Unification through a general integral fluctuation theorem

$$\boxed{\langle \exp[-\Delta s_{\mathrm{m}}]\ p_1(x_t)/p_0(x_0)\rangle = 1}$$ for any (normalized) $p_1(x_t)$

$p_1(x)$	Integral F'theorem	
$p(x,t)$	$\langle \exp[-\Delta s_{\mathrm{tot}}]\rangle = 1$	U.S. '05
$p_{\mathrm{eq}}(x,\lambda_t)$	$\langle \exp[-W]\rangle = \exp[-\Delta F]$	Jarzynski '97
$p_{\mathrm{eq}}(x,\lambda_0)$	$\langle \exp[-W_0]\rangle = 1$	Bochkov-Kuzovlev '81
$f(x)p_{\mathrm{eq}}(x,\lambda_t)/\mathcal{N}$ ...	$\langle f(x_t)\exp[-W_d]\rangle = \langle f(x)\rangle_{\mathrm{eq}(\lambda_t)}$	Crooks '00 ...

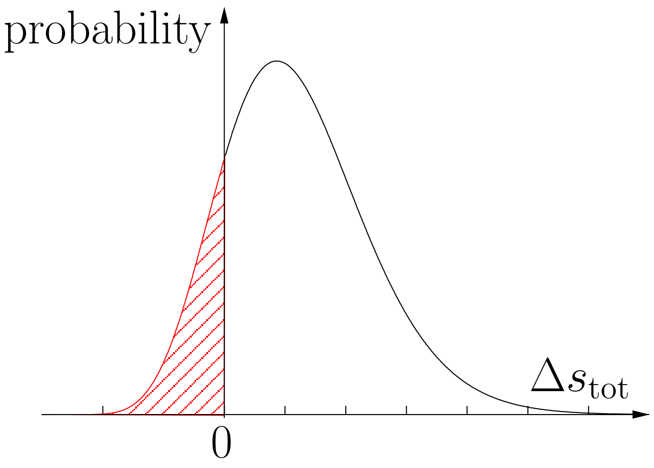


- Non-equilibrium steady state (NESS)
  - $\dot{x} = \mu[-\partial_x V(x) + f] + \zeta \equiv \mu F(x) + \zeta,$
  - stat distribution $p^s(x) \equiv \exp[-\phi(x)]$ with $\phi(x) \neq V(x)/T$
  - broken detailed balance $p(x_2(t)|x_1(0))p^s(x_1) \neq p(x_1(t)|x_2(0))p^s(x_2)$
  - mean global velocity $v_s = \langle \nu_s(x) \rangle = j_s$
  - mean local velocity $\nu_s(x) \equiv \langle \dot{x}|x \rangle = j_s/p^s(x) = \mu F(x) + D\phi'(x)$

- NESS I: Fluct'n theorem $\boxed{p(-\Delta s_{\mathrm{tot}})/p(\Delta s_{\mathrm{tot}}) = \exp(-\Delta s_{\mathrm{tot}})}$

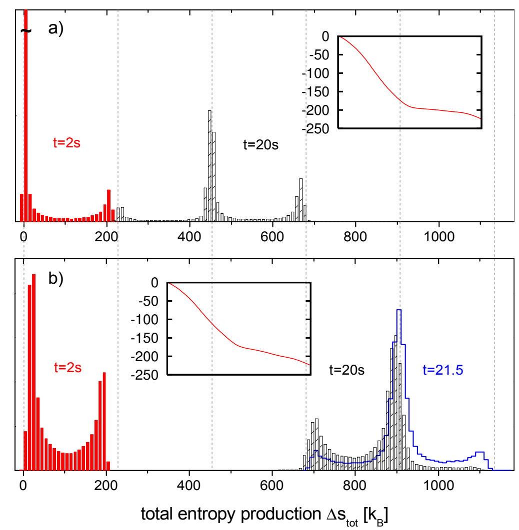
long-time limit: Evans et al (1993), Gallavotti & Cohen (1995), Kurchan (1998), Lebowitz & Spohn (1999) ... finite times: U.S., PRL'05

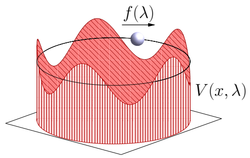
- violation of the 2^{nd} law ??



- experimental data

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





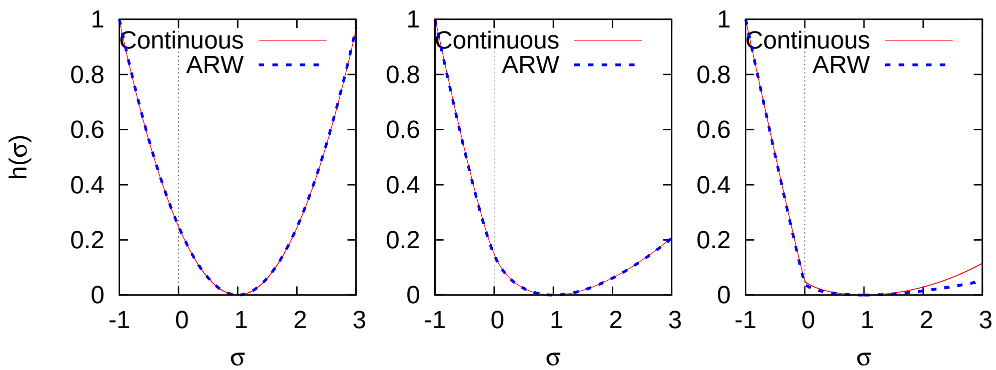
- Long time: Large deviation form

  [J. Mehl, T. Speck, U.S., Phys. Rev. E, 78 : 011123, 2008.]

  – Scaled entropy production rate $\quad \sigma \equiv \Delta s_{\mathrm{m}}/\langle \dot{s}_{\mathrm{m}} \rangle t$

  – "Large deviation" for $t \to \infty \quad p(\Delta s_{\mathrm{m}}, t) \sim \exp[-t\, h(\sigma)]$

  – Rate function $\quad h(\sigma) = h(-\sigma) - \sigma$



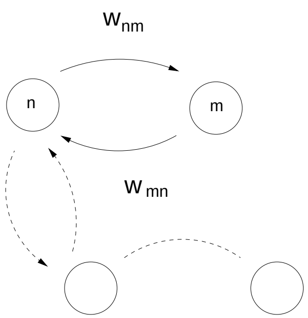
  – mapping to asymm random walk

- Proof of finite time DFT [U.S., PRL 95, 040602, 2005]
  - steady state distribution $p^s(x)$
  - total entropy production $\Delta s_{\text{tot}} = \ln \frac{p[x(\tau)|x_0]\ p^s(x_0)}{p[\tilde{x}(\tau)|\tilde{x}_0]\ p^s(\tilde{x}_0)}$
  - for any function $g(\Delta s_{\text{tot}})$

$$
\begin{aligned}
\langle g(\Delta s_{\text{tot}})\rangle &= \sum_{x(\tau),n_0} p[x(\tau)|x_0]\ p^s(x_0)\ g(\Delta s_{\text{tot}}) \\
&= \sum_{x(\tau),x_0} p[\tilde{x}(\tau)|\tilde{x}_0]\ p^s(\tilde{x}_0) \exp \Delta s_{\text{tot}}\ g(\Delta s_{\text{tot}}) \\
&= \sum_{\tilde{x}(\tau),\tilde{x}_0} p[\tilde{x}(\tau)|\tilde{x}_0]\ p^s(\tilde{x}_0) \exp \Delta s_{\text{tot}}\ g(\Delta s_{\text{tot}}) \\
&= \sum_{x(\tau),n_0} p[x(\tau)|x_0]\ p^s(x_0) \exp(-\Delta s_{\text{tot}})\ g(-\Delta s_{\text{tot}}) \\
&= \langle \exp(-\Delta s_{\text{tot}})\ g(-\Delta s_{\text{tot}})\rangle
\end{aligned}
$$

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

- Master equation dynamics on discrete states



states $\{n\}$ could be

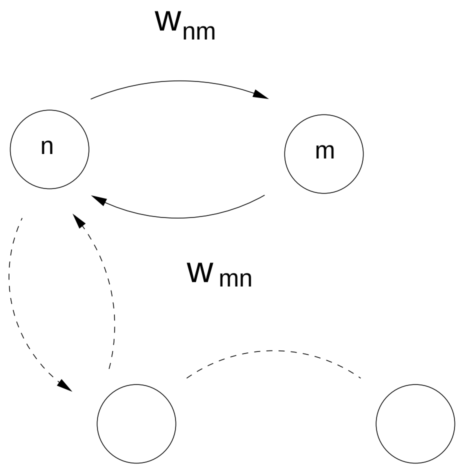
- internal states of a protein
- number of a species
- discrete spatial coordinate
- ....

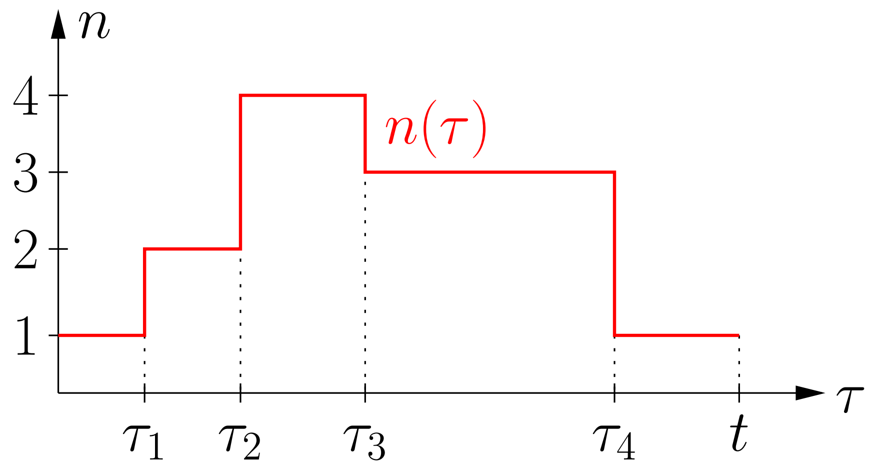
- time-dependent rates given by a "protocol" $\lambda(\tau)$
- $\partial_\tau p_n = \sum_m [w_{mn}(\lambda) p_m - w_{nm}(\lambda) p_n]$
- solution $p_n(\tau)$ depends on initial $p_n(0)$
- unique stationary solution $p_n^s(\lambda)$ for any fixed λ
  * detailed balanced

    $p_n^s w_{nm} = p_m^s w_{mn} \to \frac{w_{nm}}{w_{mn}} = \exp(E_n - E_m)$ with $E_n \equiv -\ln p_n^s$
  * persistent cycle currents

    $p_n^s w_{nm} \neq p_m^s w_{mn}$

- Stochastic trajectory





– jumps at τ_j from n_j^- to n_j^+

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

- Non-equilibrium ensemble entropy

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

- Stochastic (trajectory-dependent) entropy of the system

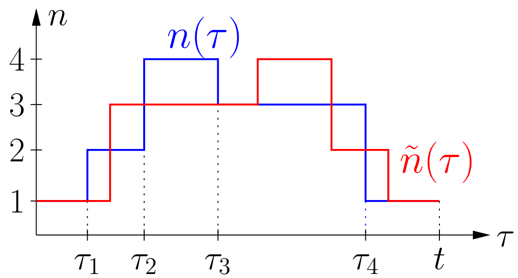
  $s(\tau) \equiv -\ln p_{n(\tau)}(\tau)$

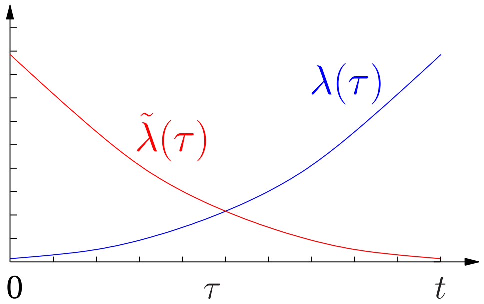
- equation of motion

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

- $\langle \dot{s}_{\mathrm{tot}}(\tau) \rangle \geq 0$

- "Time reversal"





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

- Ratio of backward to forward path

$$\frac{\tilde{p}[\tilde{n}(\tau)|\tilde{n}_0]}{p[n(\tau)|n_0]} = \exp[-\Delta s_m]$$

- general fluctuation theorem

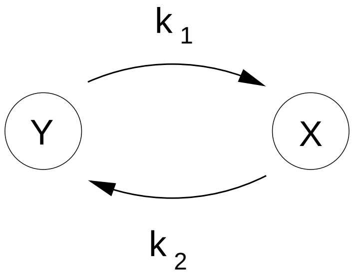
$$
\begin{aligned}
1 &= \sum_{\tilde n(\tau),\tilde n_0} \tilde p[\tilde n(\tau)|\tilde n_0]\ p_1(\tilde n_0) \\
&= \sum_{n(\tau),n_0} p[n(\tau)|n_0]\ p_0(n_0) \frac{\tilde p[\tilde n(\tau)|\tilde n_0]\ p_1(\tilde n_0)}{p[n(\tau)|n_0]\ p_0(n_0)} \\
&= \langle \exp[-\Delta s_{\rm m} + \ln p_1(n_t)/p_0(n_0)] \rangle
\end{aligned}
$$

- choice 1: $p_1(n) = p(n,t) \quad \Rightarrow \quad \boxed{\langle \exp[-\Delta s_{\rm tot}] \rangle = 1 \quad \Rightarrow \langle \Delta s_{\rm tot} \rangle \geq 0}$
  - arbitrary initial distribution, arbitrary driving, finite times
- choice 2: $p_1(n) = p^s(n,\lambda_t) \quad \Rightarrow \langle \exp(-R) = 1 \rangle$
  - with $R = -\int_0^t \partial_\tau \ln p^s_n(\lambda(\tau))_{|n(\tau)}$
  - athermal discrete generalization of the Jarzynski relation
- similarly for a NESS: DFT $\boxed{p(-\Delta s_{\rm tot})/p(\Delta s_{\rm tot}) = \exp(-\Delta s_{\rm tot})}$

Illustration: Birth-death or chemical master equations

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

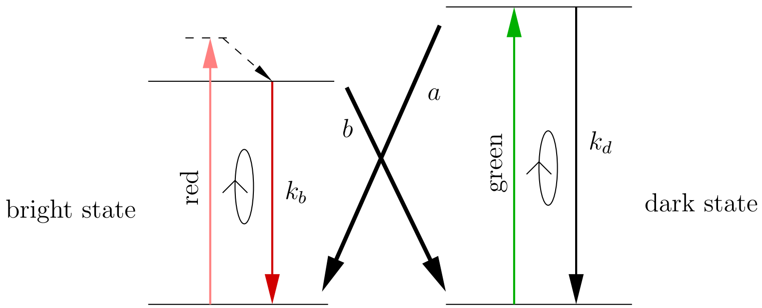
- Simplest case: Isomerization

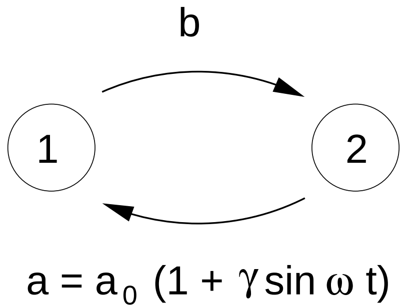


  - $n_X \equiv n = N - n_Y$
  - $q(\tau) \equiv k_1(\tau)/k_2(\tau)$
  - stationary distribution: $p^s(n) = [q/(1+q)]^N \binom{N}{n}$
  - stationary mean $n^s = Nq/(1+q)$
  - $\boxed{\langle \exp\{\int_0^t d\tau \, \underbrace{[n(\tau) - n^s(\tau)]}_{\text{non−eq lag}} \frac{d}{d\tau} \ln q(\tau)\}\rangle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

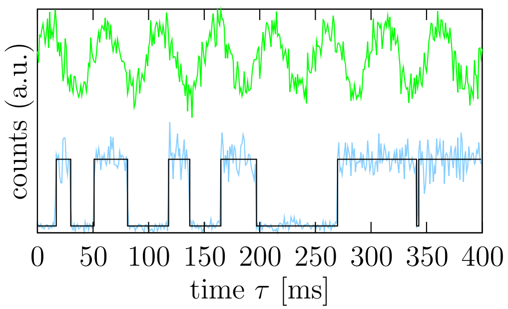
Periodically driven system: Optically active defect center in diamond

[S. Schuler, T. Speck, C. Tietz, J. Wrachtrup and U.S., PRL **94**, 180602, 2005
C. Tietz, S. Schuler, T. Speck, U. S., and J. Wrachtrup, PRL **97** 050602, 2006]



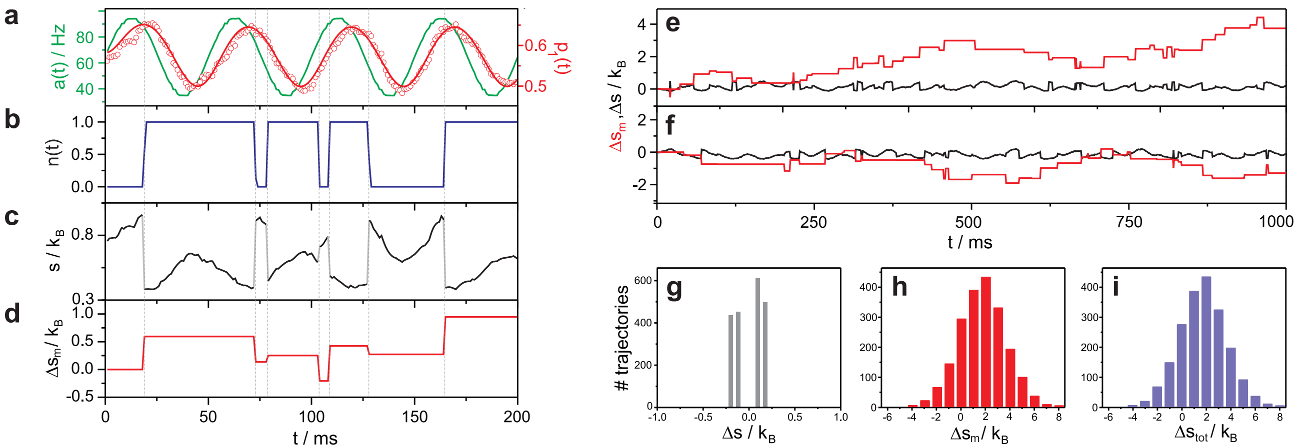


- Trajectories



- Entropy production along a single trajectory

Figure 1



- Int FT

Det FT

Figure 2

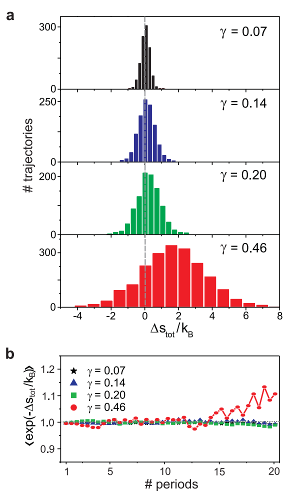
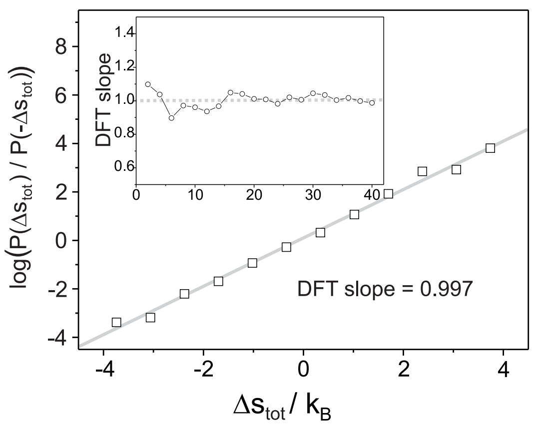


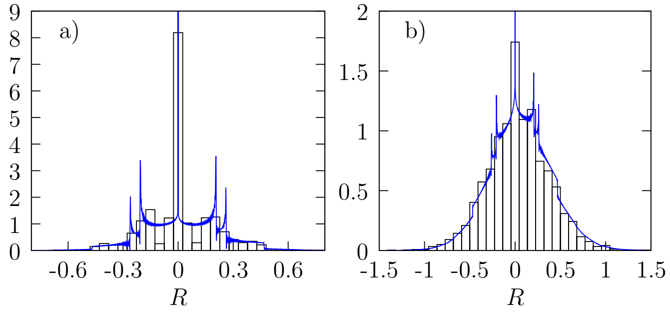
Figure 3



- Generalized JR:

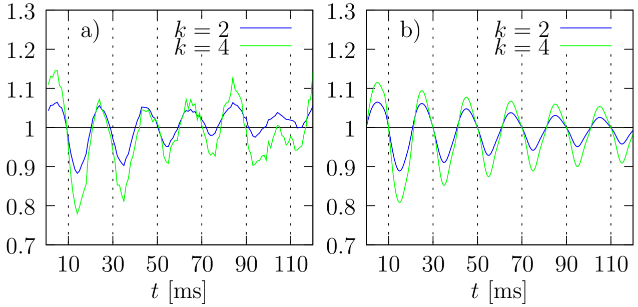
$\langle \exp[-R] \rangle = 1$ for $R[n(\tau)] \equiv -\int_o^t d\tau \dot{\lambda} \partial_\lambda \ln p^s_{n(\tau)}(\lambda)$ $(= W - \Delta F)$

probability distribution $p(R)$



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

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



- 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

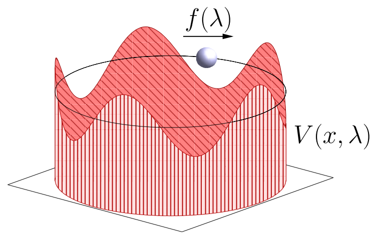
  - often (phenomenologically) modified by an effective temp:

    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:

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

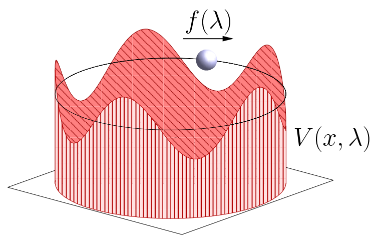
– extended FDT in non-eq:

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

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

– 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

- General FDT in a NESS

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

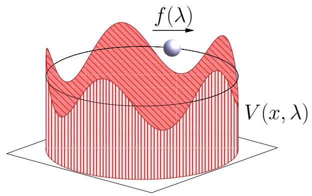
$$\text{NESS}: \quad \frac{\langle \delta A(t_2)\rangle}{\delta f(t_1)} = \langle A(t_2)\partial_f \dot{s}(t_1)\rangle$$

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

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

- 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

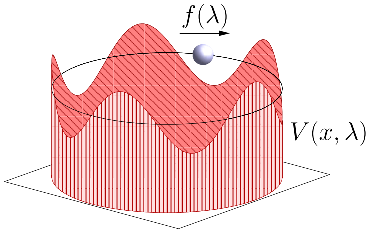
- "Non-uniqueness" of the FDT in a NESS: Three canonical forms



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

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

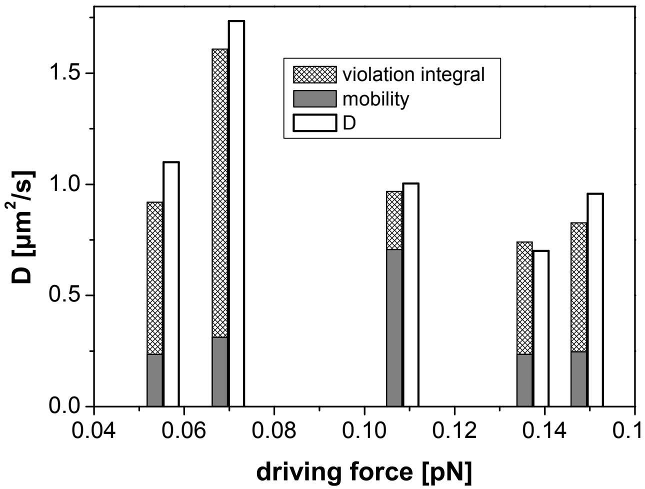
- Integrated version: Generalized Einstein relation



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

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

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

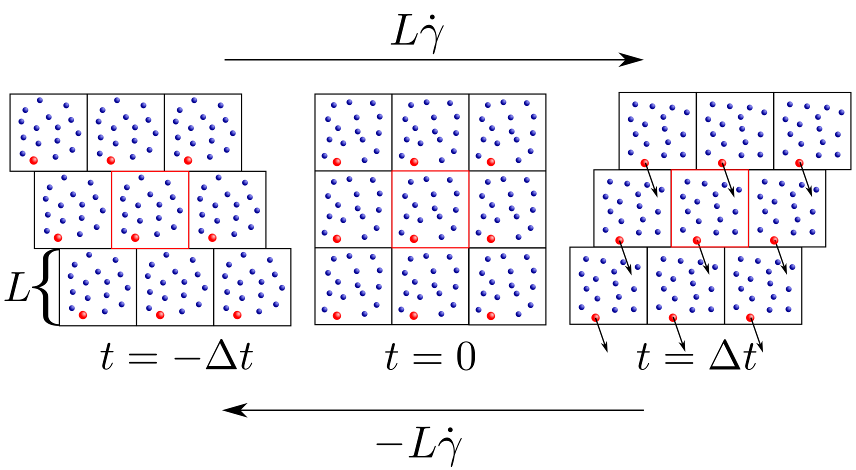


– cf giant diffusion [Reimann et al 2001]

- Sheared colloidal suspension with 3d Brownian dynamics

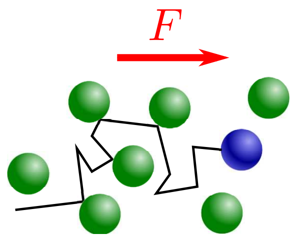
[B. Lander, U.S. and T. Speck, EPL **92** 58001, 2010; PRE 85, 021103, 2012]

driving:
- linear shear flow



perturbating field:

force on tagged particle



- velocity-force FDT in a NESS

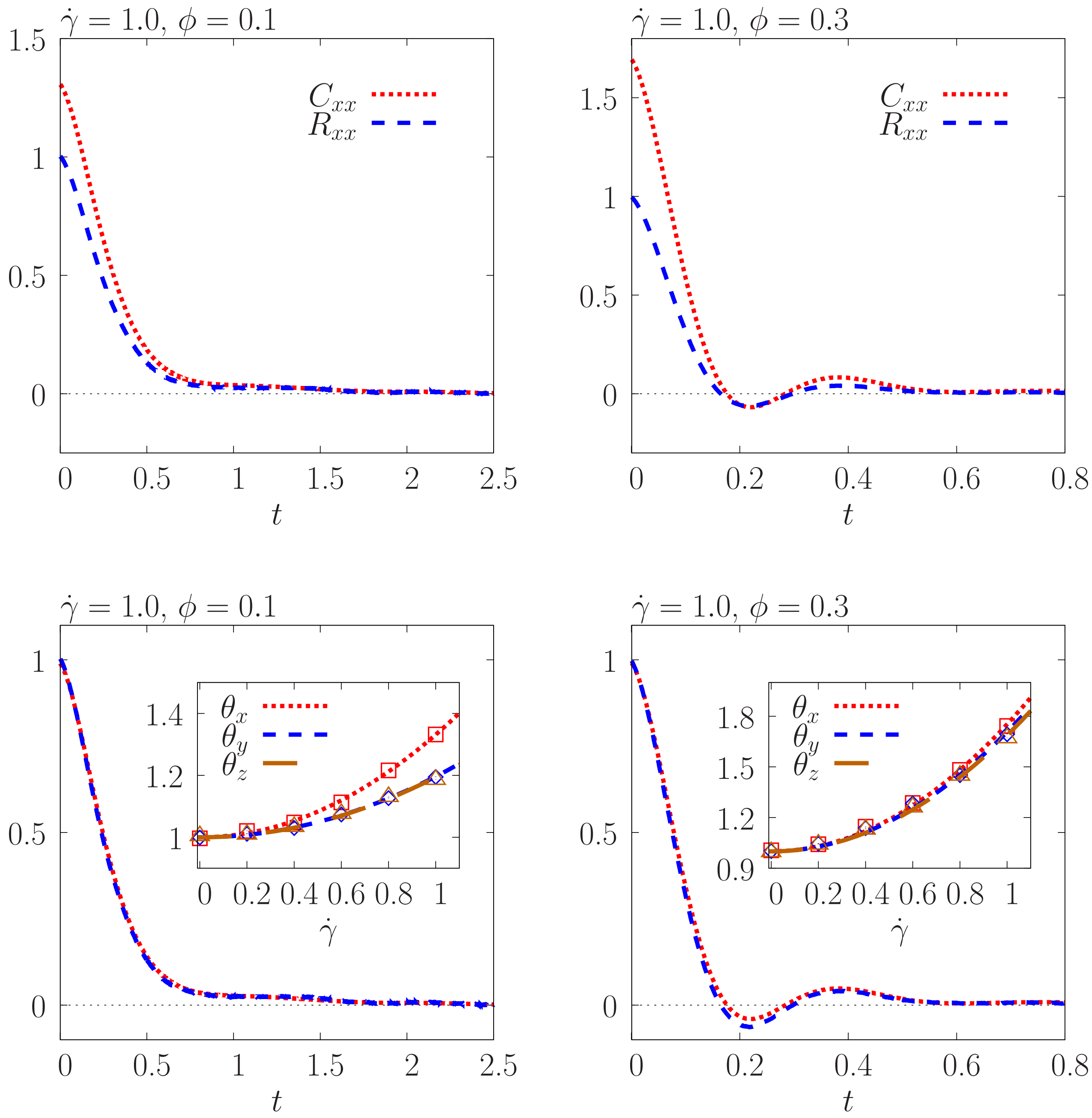
  – $R_{ij}(t) = \frac{\delta\langle v_i(t)\rangle}{\delta f_j(0)}$

  – $C_{ij}(t) = \left\langle v_i(t) v_j(0) \right\rangle$

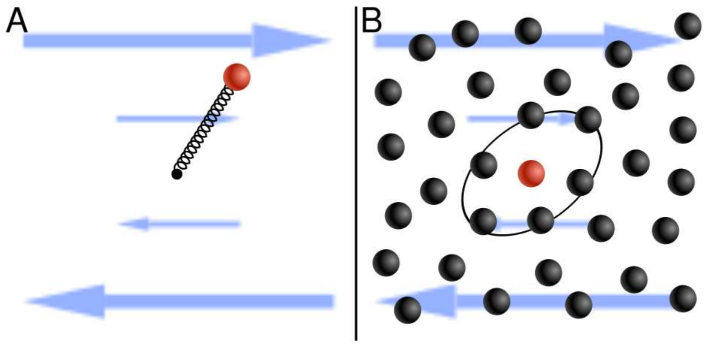
  – effective temperature?

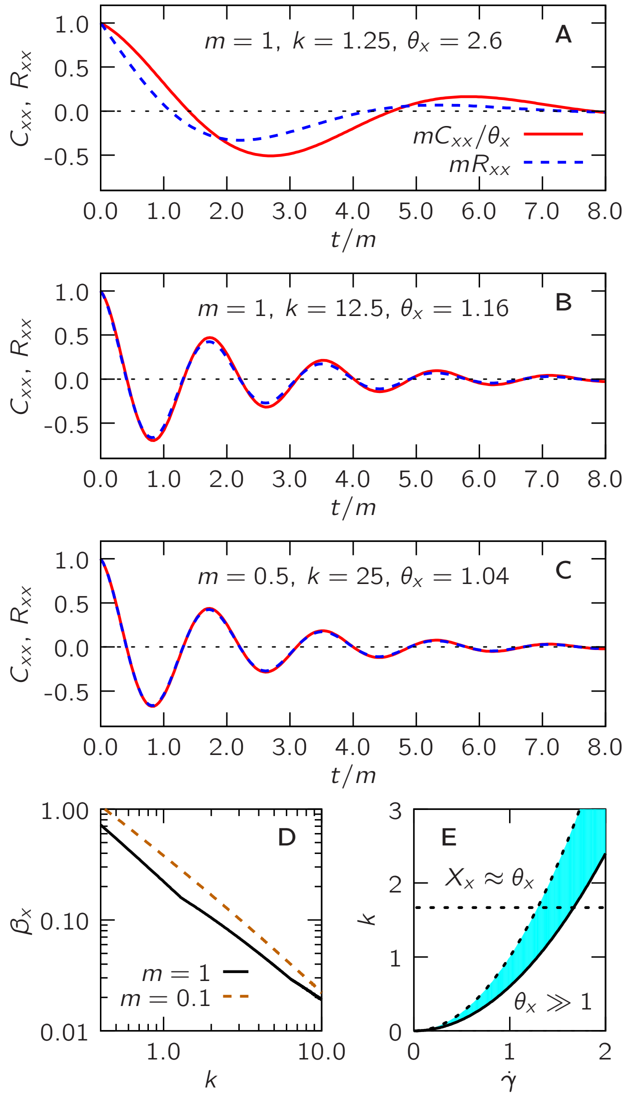
    $\theta_i \approx \frac{C_{ii}(t)}{R_{ii}(t)} \approx 1 + a\dot{\gamma}^2$

    works well at larger densities



- effective confinement for moderate/large densities





  – effective temperature also for trapped particle?

  – similar math. structure

    in confined suspensions

  – $C_{ii}(t) \simeq \theta_i R_{ii}(t) + \dot\gamma^2 \beta_i I_i(t)$

    with $\max |I_i(t)| = 1$

- **Stochastic thermodynamics** along single trajectories
  - formulation of the 1^{st} law
  - refinement of the 2^{nd} law
  - generalized FDT's

    * mechanically or flow driven: colloids, polymers, proteins
    * biochemically driven: single enzyms, motors, reaction networks
    * optically driven: defect centers, other quantum systems ....

  - generalizations

    * many interacting degrees of freedom
    * stochastic field theories (like KPZ-eq)
    * quantum systems (JR done, DFT open)
    * ...