# Stochastic thermodynamics

Udo Seifert

II. Institut für Theoretische Physik, Universität Stuttgart

thanks to:

- F. Berger, J. Mehl, T. Schmiedl and Th. Speck (theory)
- V. Blickle and C. Bechinger (expt's on colloidal particles)
- C. Tietz, S. Schuler and J. Wrachtrup (expt's on single atoms)

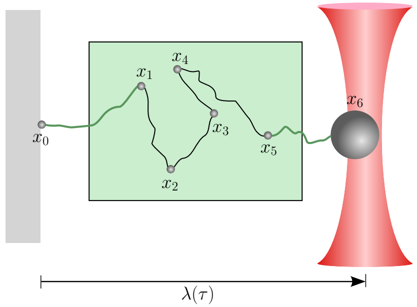
Review: U.S., Eur. Phys. J. B, 64 : 423-431, 2008.

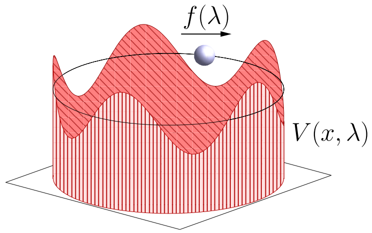
LECTURE II

- Stochastic entropy

- Non-equilibirum steady states (NESSs)

- 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** $x(\tau)$

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

  – equation of motion

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

  – $\Delta s = \Delta s_{\mathrm{tot}} - \Delta s_{\mathrm{m}} (= \Delta q/T)$

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

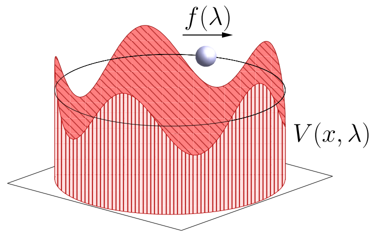
- $\boxed{\langle \exp[-\Delta s_{\mathrm{tot}}]\rangle = 1} \Rightarrow \boxed{\langle \Delta s_{\mathrm{tot}}\rangle \geq 0}$

  - 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 $\quad p^s(x) \equiv \exp[-\phi(x)]$ with $\phi(x) \neq V(x)/T$

  - broken detailed balance $\quad p(x_2(t)|x_1(0))p^s(x_1) \neq p(x_1(t)|x_2(0))p^s(x_2)$

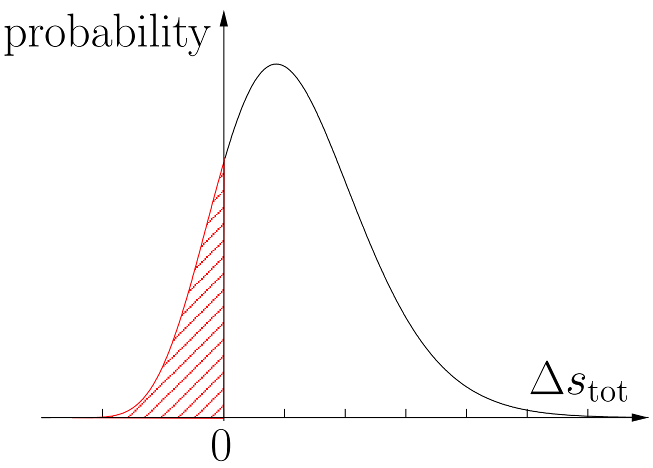
  - mean global velocity $\quad v_s = \langle \nu_s(x) \rangle = j_s$

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

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

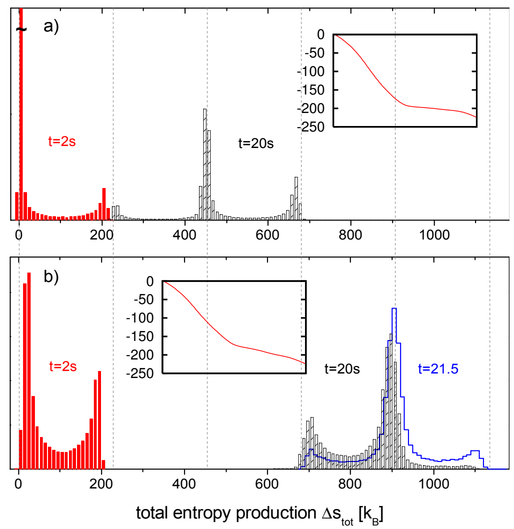
long-time limit: Evans et al (1993), Gallavotti & Cohen (1995), Kurchan (1998), Lebowitz & Spohn (1999) ... finite times: U.S., PRL'05

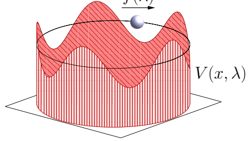
– violation of the $2^{nd}$ law ??




– experimental data

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





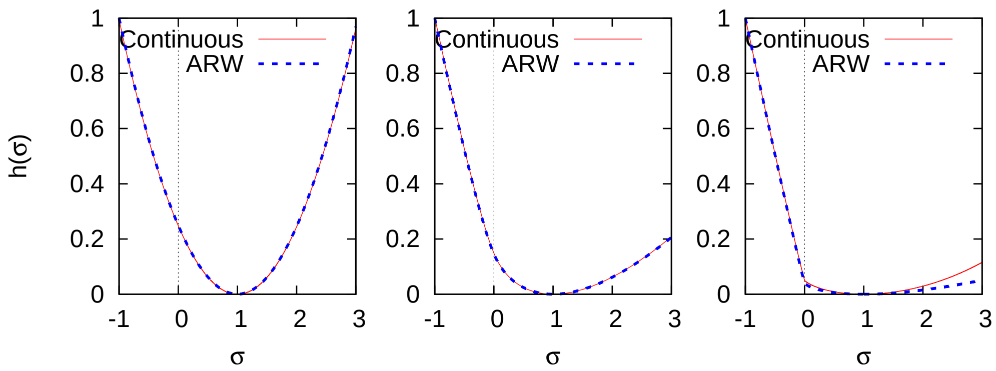

- Long time: Large deviation form

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

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

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

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




– mapping to asymm random walk

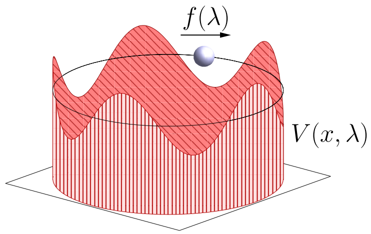
- Proof of finite time DFT [ U.S., PRL 95, 040602, 2005]
  - steady state distribution $p^s(x)$
  - total entropy production $\Delta s_{\mathrm{tot}} = \ln \frac{p[x(\tau)|x_0]\ p^s(x_0)}{p[\tilde{x}(\tau)|\tilde{x}_0]\ p^s(\tilde{x}_0)}$
  - for any function $g(\Delta s_{\mathrm{tot}})$

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

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

- NESS II: FDT violation and restoration

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




– 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:

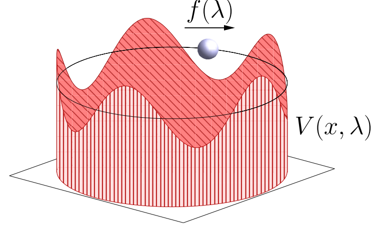
$$T\frac{\delta\langle\dot{x}(t)\rangle}{\delta f(\tau)}_{|f\neq 0} = \langle\dot{x}(t)\dot{x}(\tau)\rangle_{\text{neq}} - \langle\dot{x}(t)\nu_s(x(\tau))\rangle_{\text{neq}}$$

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

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

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

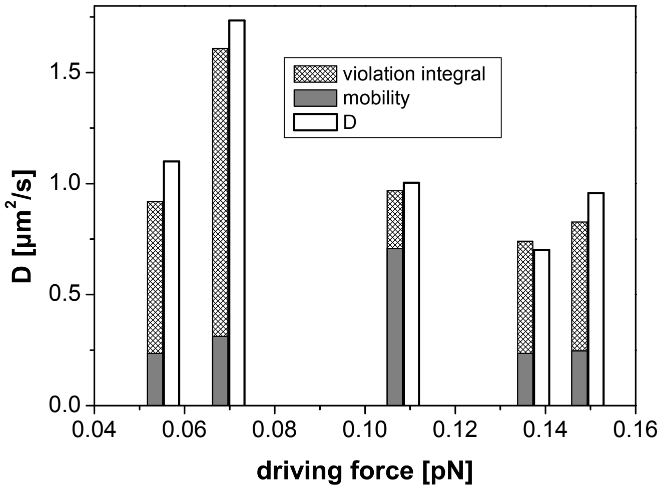
- NESS III: Generalized Einstein relation




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

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

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

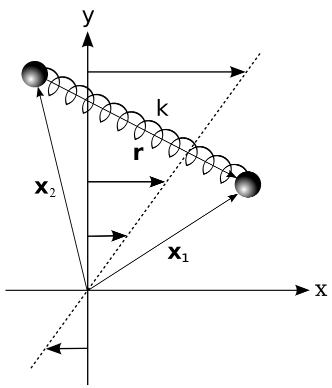



cf giant diffusion [Reimann et al 2001]

$$\neq \ D_{\text{eff}}(f) = \ T_{\text{eff}}(f)\ \mu_{\text{eff}}(f)$$

- NESS IV: : Entropy production for dumbbell in shear flow

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



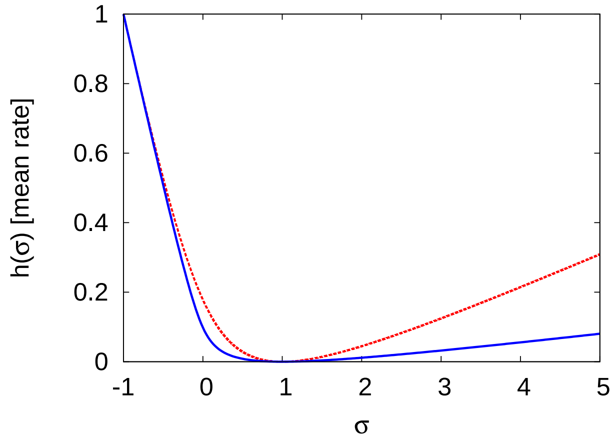

- Scaled entropy production rate

  $\sigma \equiv \Delta s_{\mathrm{m}} / \langle \dot{s_{\mathrm{m}}} \rangle t$

- "Large deviation" for $t \to \infty$

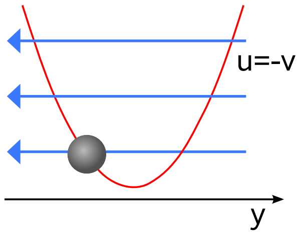
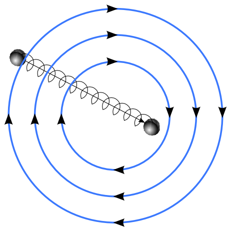
  $p(\Delta s_{\mathrm{m}}, t) \sim \exp[-t \; h(\sigma)]$

- Rate function $h(\sigma)$



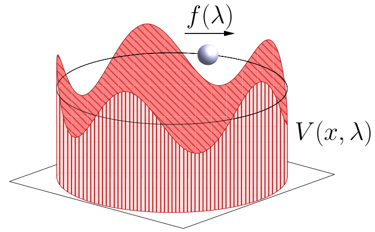

[cf. Turitsyn et al, PRL 2007]

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

- Transitions between NESSs (SST) [Oono and Paniconi, Hatano and Sasa]
  - $V(x)$ time-independent, $f = f(\lambda(\tau))$ switches from $f_1$ to $f_2$
  - $\phi(x,\lambda) \equiv -\ln p^s(x,\lambda)$ $\quad (\neq s(\tau))$



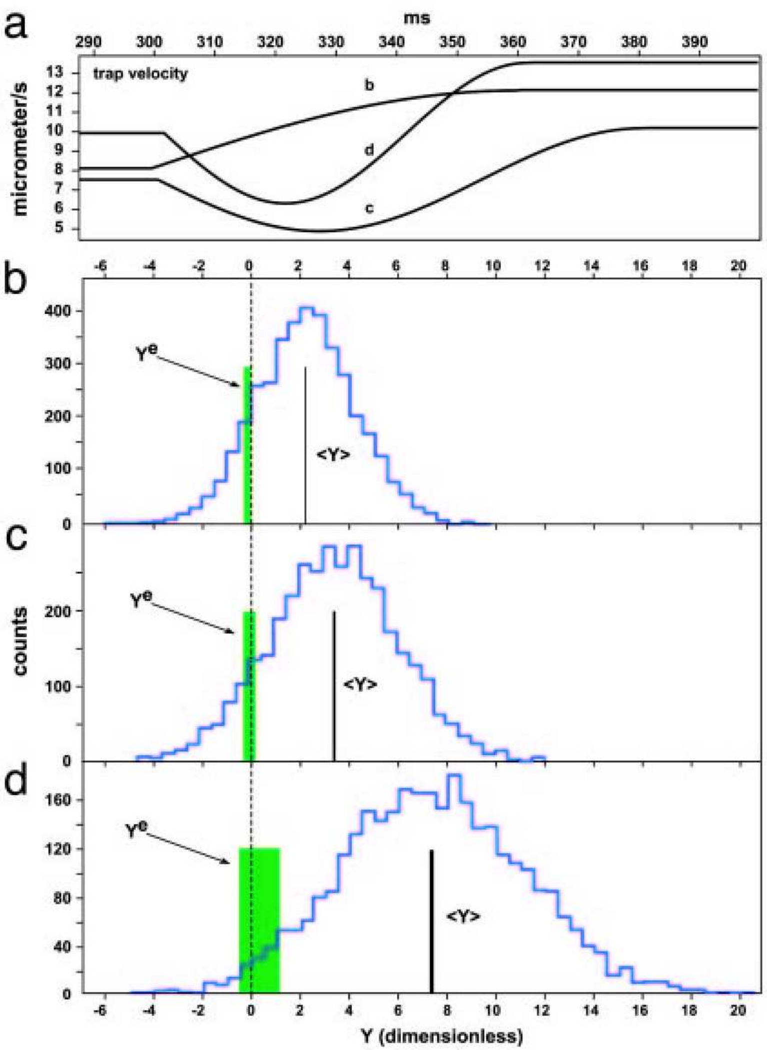

  - total heat

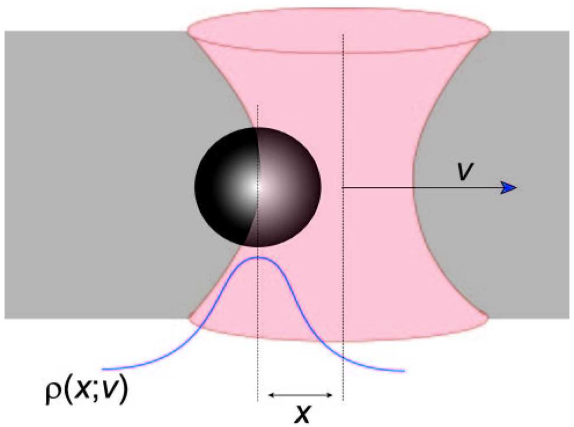
$$\begin{aligned} q &= \int_0^t d\tau F(x,\lambda)\dot{x} = \Delta s_m \\ &= \underbrace{\int_0^t \nu_s(x(\tau),\lambda)\dot{x}}_{q_{hk}} \underbrace{\underbrace{-D[(\phi(x_t,\lambda_t) - \phi(x_0,\lambda_0))]}_{\Delta S} + \underbrace{D\int \dot{\lambda}(\partial\phi/\partial\lambda)}_{\equiv Y}}_{q_{ex}} \end{aligned}$$

  - $\langle \exp[-Y] \rangle = 1 \quad \Rightarrow \boxed{\Delta S \geq -\langle q_{ex} \rangle}$ ("2nd law for NESSs")

- Experimental test of the Hatano-Sasa relation $\langle \exp -Y \rangle = 1$

[E.H. Trepagnier et al, PNAS 2004]



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

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