Universal features of current fluctuations

of driven and active systems

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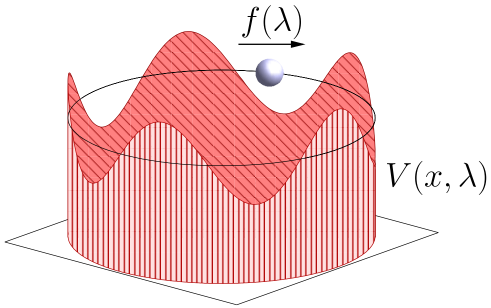
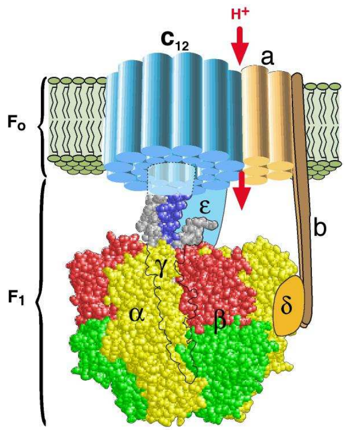
- Stochastic th'dynamics of NESSs*: Fluct'theorem and hidden slow degrees of freedom
- Thermodynamic unc'relation and implications
- Entropy production of active particles
- Extreme fluctuations of active particles

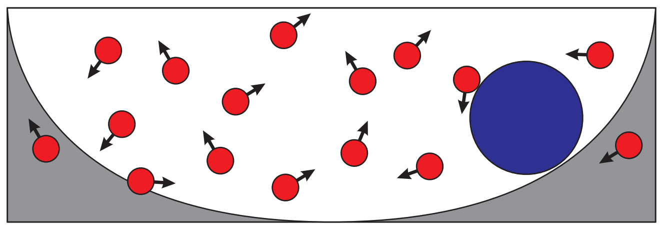
*Review: U.S., Rep. Prog. Phys. **75** 126001, 2012.

- NESSs: Examples and common characteristics





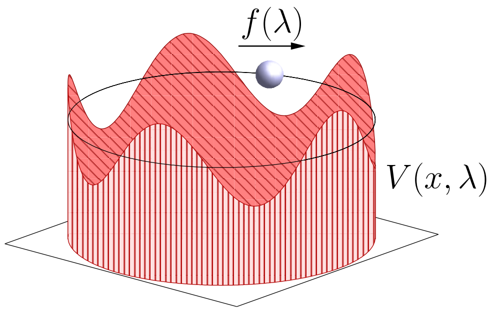
H. Wang and G. Oster (1998). Nature 396:279-282.



  - Time-independent driving beyond linear response regime
  - Broken detailed-balance
  - Persistent "currents" with permanent dissipation
  - Stationary (non-Boltzmann) distribution

- Stochastic thermodynamics of NESSs: Colloidal particle as paradigm

  [Review: U.S., Rep. Prog. Phys. **75** 126001, 2012]



  – Langevin dynamics $\dot{x} = \mu[-V'(x) + f] + \zeta$ with $\langle \zeta_1 \zeta_2 \rangle = 2\mu k_B T \delta_{12}$

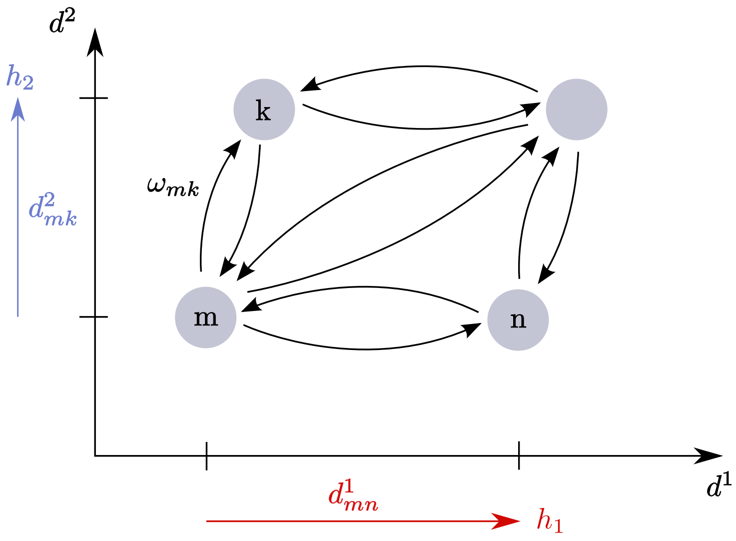
  – first law [(Sekimoto, 1997)]: $\boxed{dw = du + dq}$

    * applied work: $dw = f \; dx$
    * internal energy : $du = dV$
    * dissipated heat: $dq = dw - du = [-\partial_x V(x) + f]dx = T ds_\mathrm{m}$

  – stochastic entropy: $\boxed{ds \equiv -d\ [\ln p(x,t)] \ \Rightarrow \langle \exp[-\Delta(s + s_\mathrm{m})] \rangle = 1}$

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

- Paradigm II: discrete states [U.S., PRL **95**, 040602 (2005)]



– rates must obey local detailed balance

$$\frac{w_{mn}(h)}{w_{nm}(h)} = \frac{w_{mn}}{w_{nm}}\Big|_{|h=0} \exp\ (h_\alpha d^\alpha_{mn}/k_BT)$$

with "fields" $h_\alpha \sim$ force or $\Delta\mu$ of a reaction

– currents

– mean currents $j^s_{mn} \equiv p_m w_{mn} - p_n w_{nm}$

– empirical/fluctuating currents $j_{mn}(t) \equiv [n_{mn}(t) - n_{nm}(t)]/t$

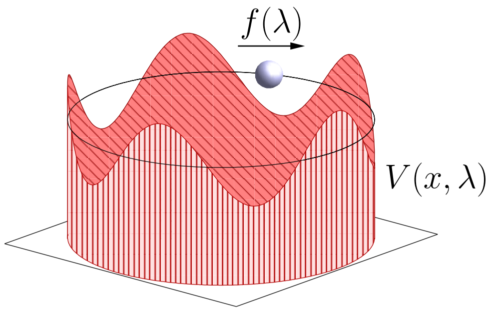
– entropy production

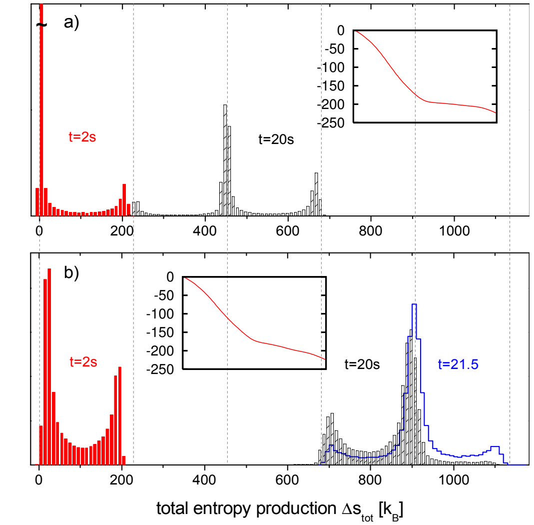
$$\dot{s}_{\text{tot}}(\tau) = \underbrace{-\sum_j \delta(\tau-\tau_j) \ln \frac{p^s_{n_j^+}}{p^s_{n_j^-}}}_{\equiv\ \dot{s}(\tau)} + \underbrace{\sum_j \delta(\tau-\tau_j) \ln \frac{w_{n_j^+ n_j^-}}{w_{n_j^- n_j^+}}}_{\equiv\ \dot{s}_{\text{m}}(\tau)}$$

- Fluctuation theorem $\boxed{p(-\Delta s_{\rm tot})/p(\Delta s_{\rm tot}) = \exp(-\Delta s_{\rm tot})}$

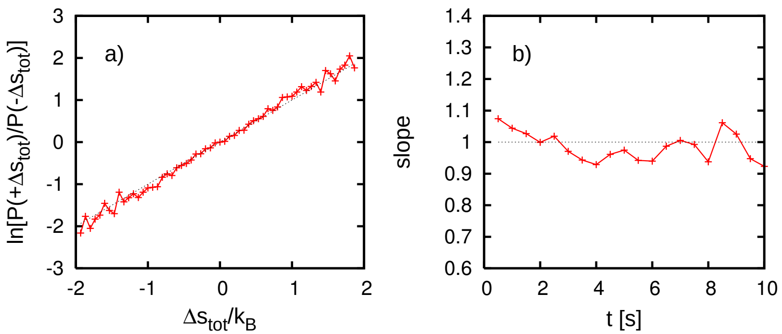
  Evans et al (1993), Gallavotti & Cohen (1995), Kurchan (1998), Lebowitz & Spohn (1999), U.S. (2005)

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





  – FT-representation:



- F'theorem and slow hidden degrees of freedom

  [J. Mehl, B. Lander, C. Bechinger, V. Blickle and U.S., PRL 108, 220601, 2012]

  – total entropy production in the NESS

$$\Delta s_{\text{tot}} \equiv \int_0^t d\tau [\dot{x}_1 \nu_1(x_1, x_2) + \dot{x}_2 \nu_2(x_1, x_2)]$$

  with $\nu_1(x_1, x_2) \equiv \langle \dot{x}_1 | x_1, x_2 \rangle$

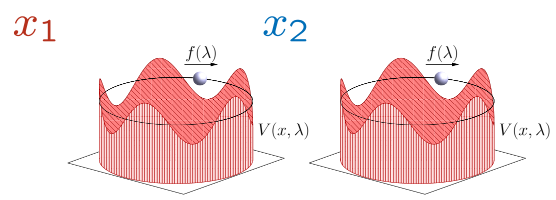
  obeys FT $\quad p(\Delta s_{\text{tot}})/p(-\Delta s_{\text{tot}}) = \exp \Delta s_{\text{tot}}$

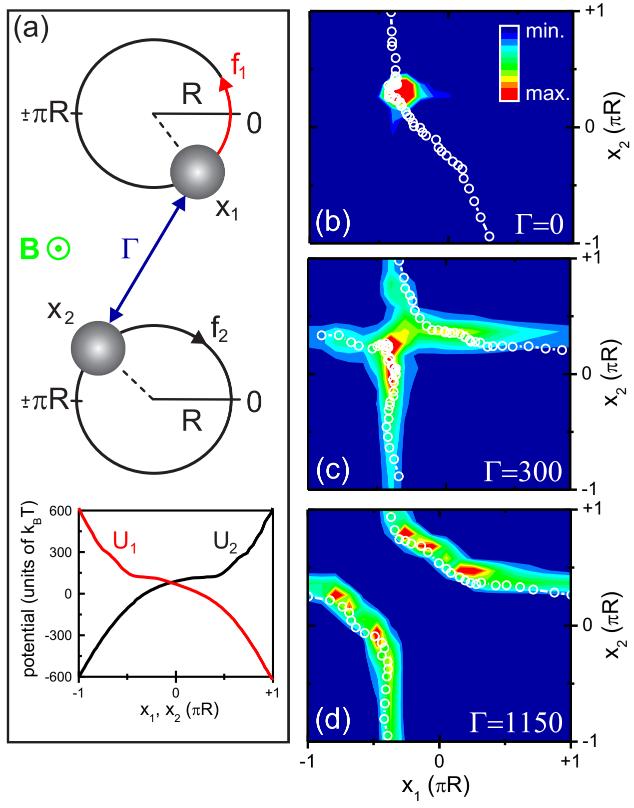
  – suppose x_2 is hidden:

$$\tilde{\nu}_1(x_1) \equiv \int \nu(x_1, x_2) p(x_2 | x_1) dx_2$$

  – apparent entropy production

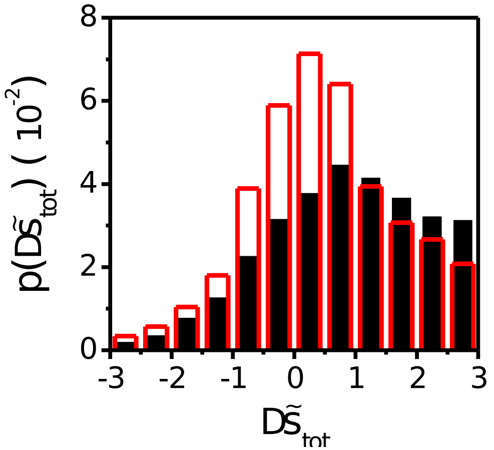
$$\Delta \tilde{s}_{\text{tot}} \equiv \int_0^t d\tau \dot{x}_1 \tilde{\nu}_1(x_1) \qquad \text{obeys FT ??}$$

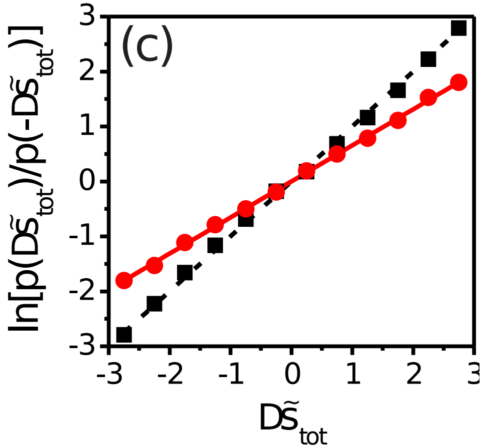


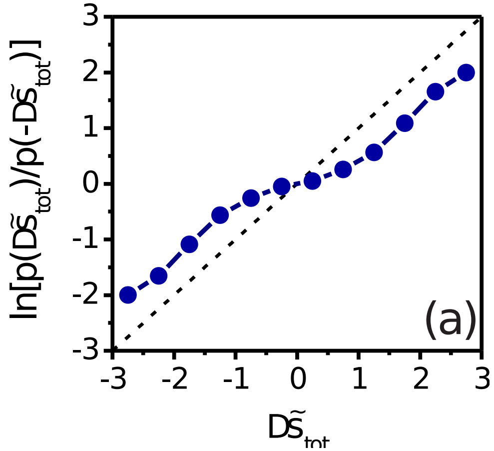


- Experimental data

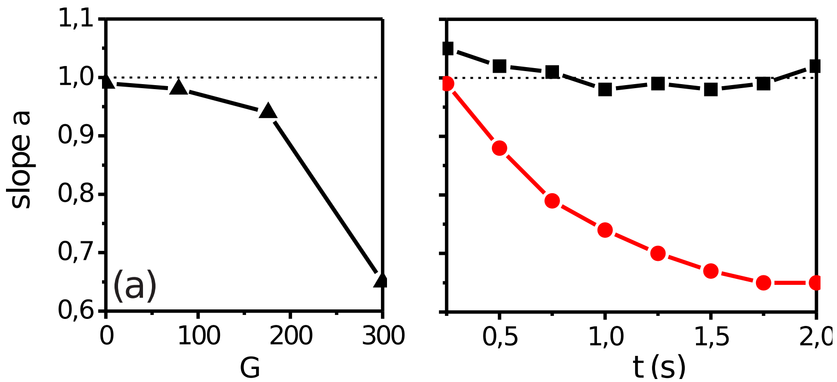
  - with and without coupling [rarely:]





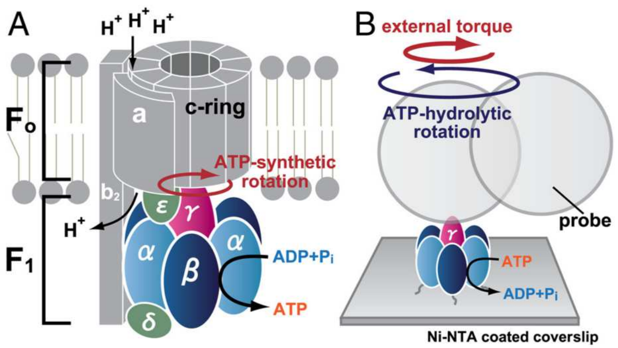


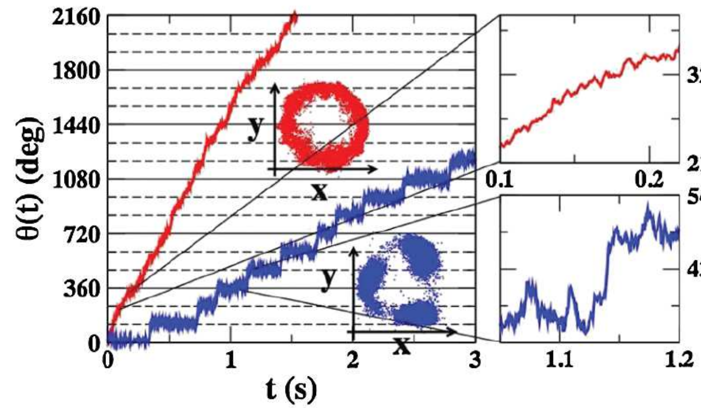
  - FT-slope

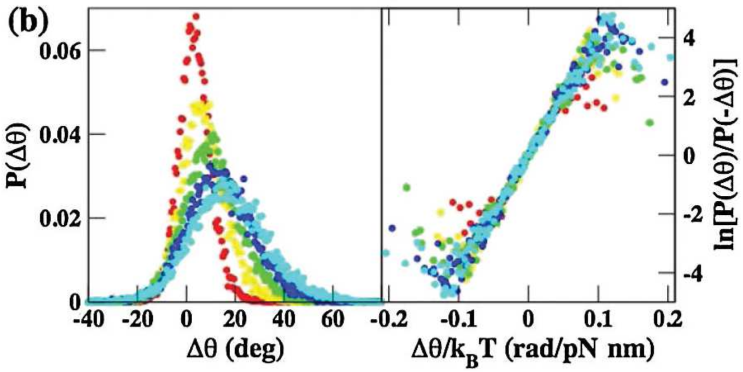


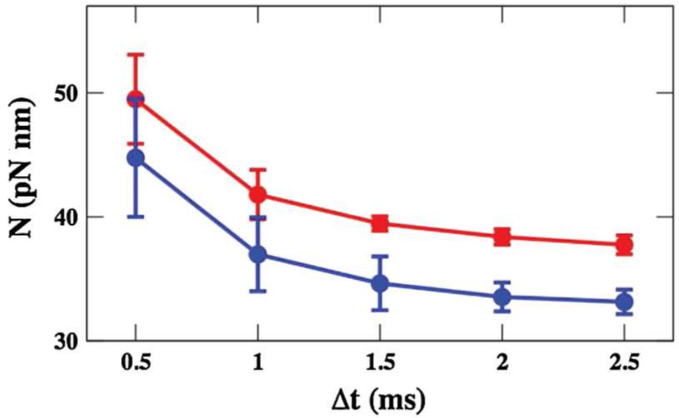
- $\Rightarrow$ hidden slow degrees of freedom spoil the FT

- F1-ATPase and the fluctuation theorem [K. Hayashi et al, PRL 104, 218103 (2010)]









$$-\Gamma\dot{\theta} = N + \zeta$$

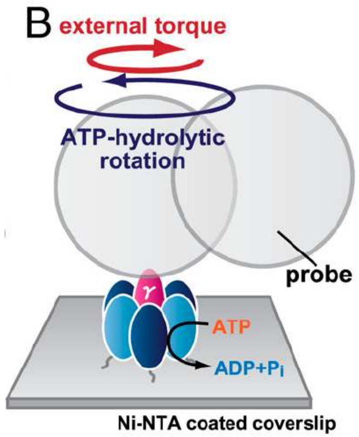
$$\Rightarrow \ln[p(\Delta\theta)/p(-\Delta\theta)] = N\Delta\theta/k_B T$$

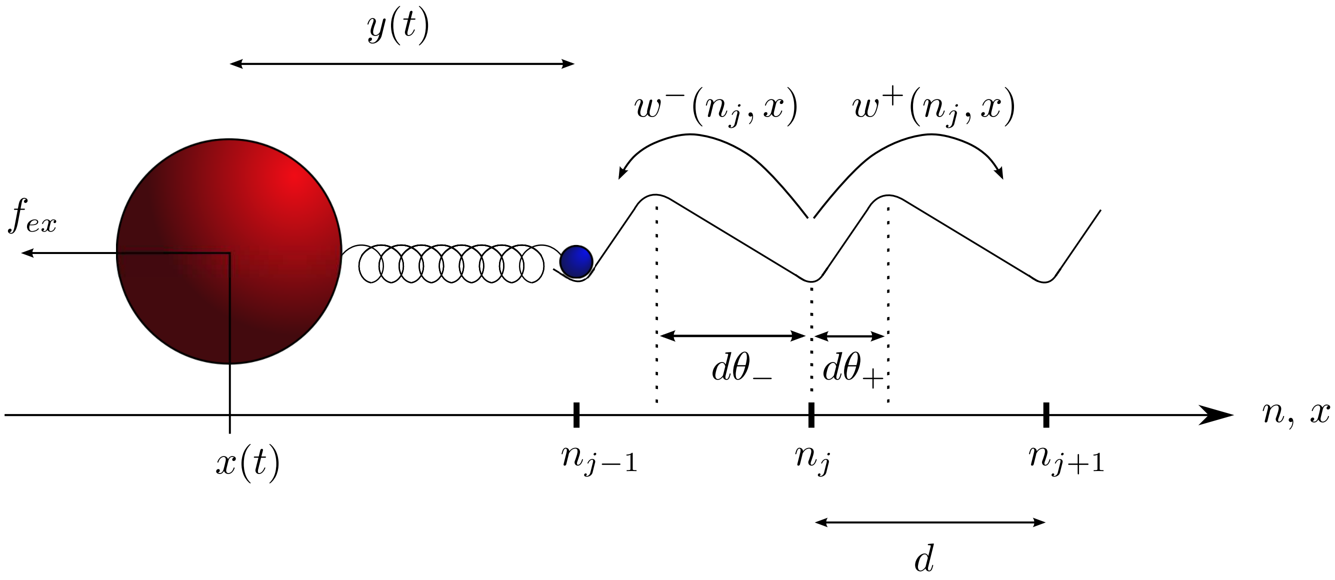
independent of friction coefficient Γ

time-dependence?

torque from $\Delta t \to \infty$?

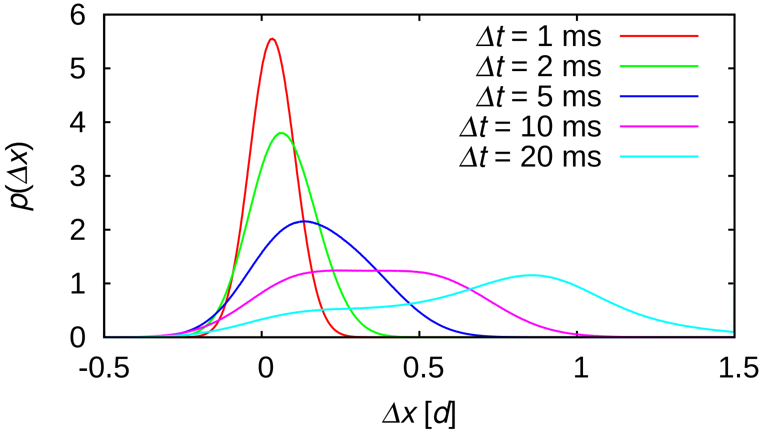
- Hybrid model [E. Zimmermann and U.S., New J. Phys. 14, 103023, 2012]

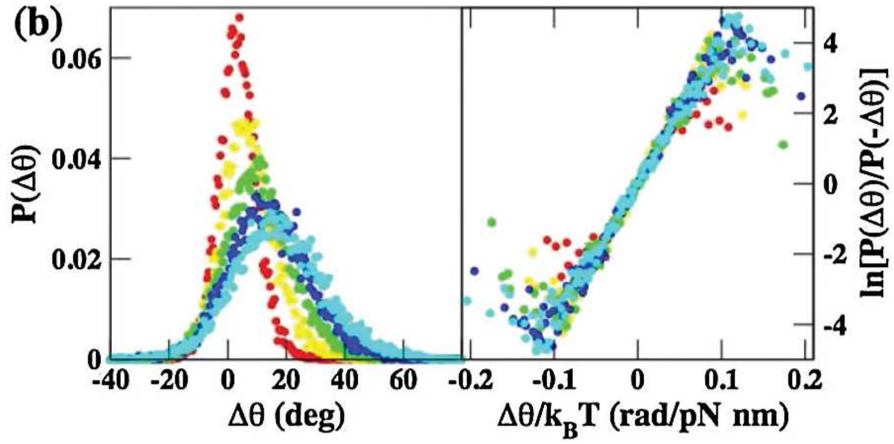


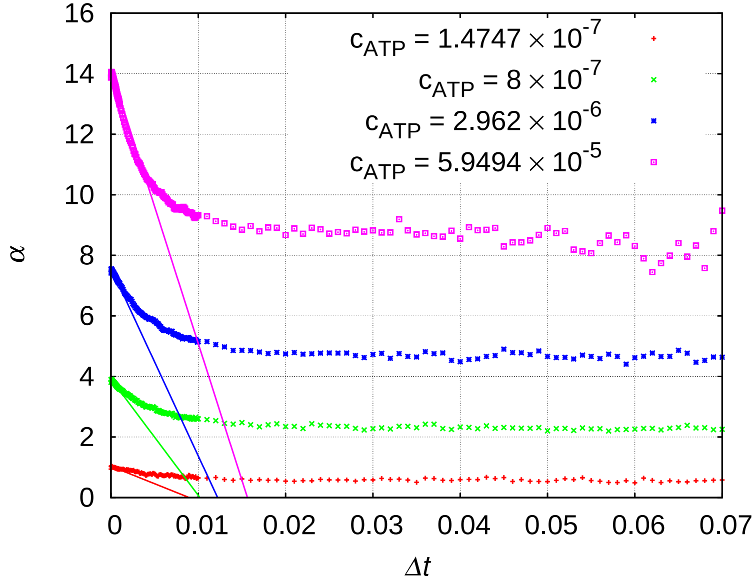


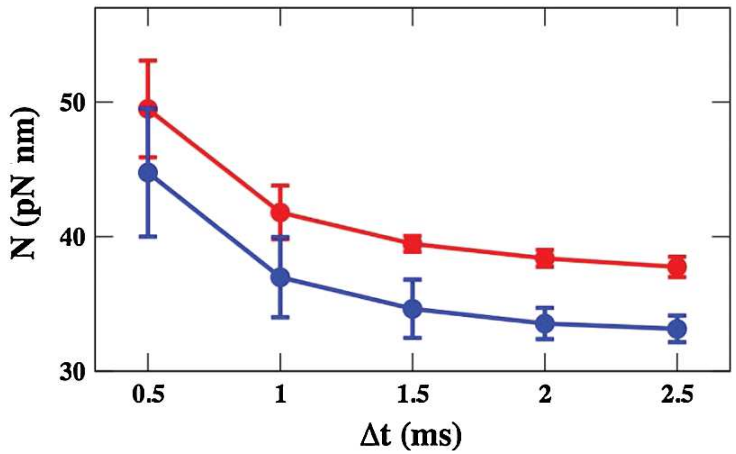
  - probe particle
    - $\dot{x} = \mu(-\partial_y V(y) + f^{\text{ex}}) + \zeta$ with $y(\tau) \equiv n(\tau) - x(\tau)$
  - motor
    - $w^+/w^- = \exp[\Delta\mu - V(n+d, x) - V(n, x)]$
    - local detailed balance condition

- FT-slope from simulations vs experiment





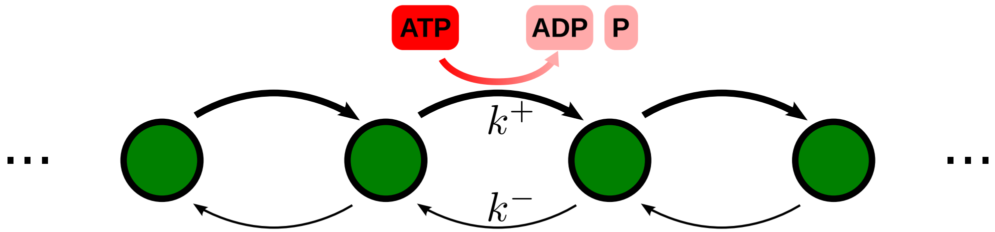




$\Delta t \to 0$ limit yields average force/torque

- From the asymmetric random walk to the th'dynamic uncertainty relation

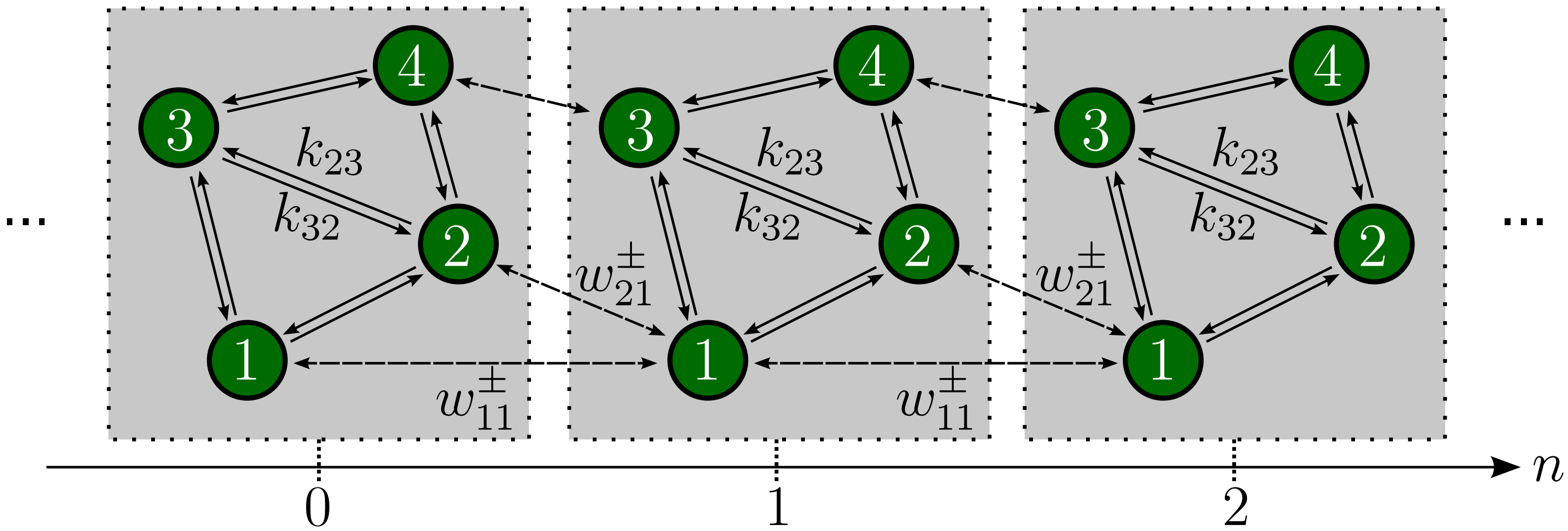
  [AC Barato and US, Phys. Rev. Lett. 114, 158101, 2015]



  - output $X(t)$ with $\langle X \rangle = Jt = (k^+ - k^-)t$
  - variance $\langle (X(t) - \langle X \rangle)^2 \rangle = 2Dt = (k^+ + k^-)t$
  - uncertainty $\epsilon^2 \equiv \text{var}/\text{output}^2 = 2D/J^2 t$
  - th'dyn cost $\mathcal{C} = \sigma t = J\mathcal{A}t$ with $\sigma \equiv$ rate of entropy production
  - with affinity $\mathcal{A} = k_B T \ln(k^+/k^-) = \mu_{\text{ATP}} - \mu_{\text{ADP}} - \mu_{\text{P}}$
  - $\boxed{\mathcal{C}\epsilon^2 = \mathcal{A} \coth[\mathcal{A}/2k_B T] \geq 2k_B T}$ independent of run time t

- Thermodynamic uncertainty relation holds for general multicyclic processes

  [AC Barato and US, Phys. Rev. Lett. 114, 158101, 2015; proof by Gingrich et al, PRL 2016]



  – $\mathcal{C} \geq 2k_BT/\epsilon^2$ for any th'dyn consistent process at finite T

  – a precision of 1% costs at least 20.000 k_BT

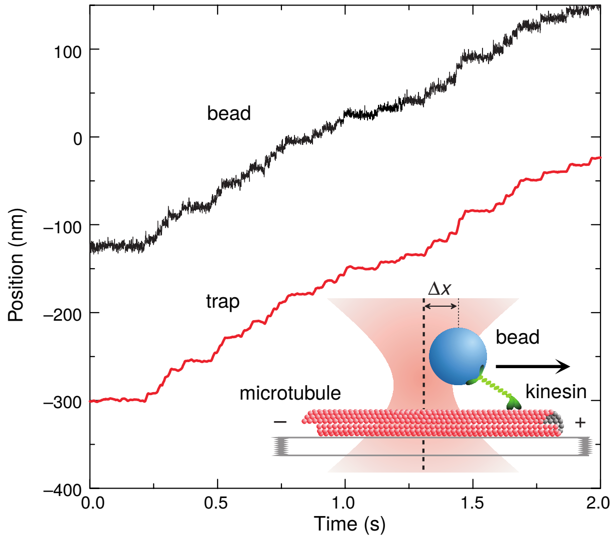
  – inhomogeneous rates and adding cycles increases fluctuations, i.e., uncertainty

- Uncertainty relation for general currents in a Langevin/stochastic field dynamics in a NESS
  - set of variables $\phi_\alpha(t)$, or fields $\phi_\alpha(\mathbf{r}, t)$
  - dynamics $\partial_t \phi_\alpha(t) = F_\alpha(\{\phi_\beta(t)\}) + \zeta_\alpha(t)$ with $\langle \zeta_\alpha(t)(t_2)\zeta_\beta(t)(t_1)\rangle = 2D_{\alpha\beta}\delta(t_2 - t_1)$
  - mean "velocity" $\nu_\beta(\{\phi_\alpha\}) \equiv \langle \partial_t \phi_\beta | \{\phi_\alpha\}\rangle$
  - mean entropy production rate $\sigma = \langle \nu_\alpha D^{-1}_{\alpha\beta} \nu_\beta \rangle$
  - α-current $j_\alpha(t) = \partial_t \phi_\alpha(t) = j^s_\alpha + \delta j_\alpha(t)$
  - dispersion $D_\alpha \equiv \int_0^\infty dt \langle \delta j_\alpha(t) \delta j_\alpha(0)\rangle$

$$\boxed{\sigma D_\alpha \geq {j^s_\alpha}^2}$$

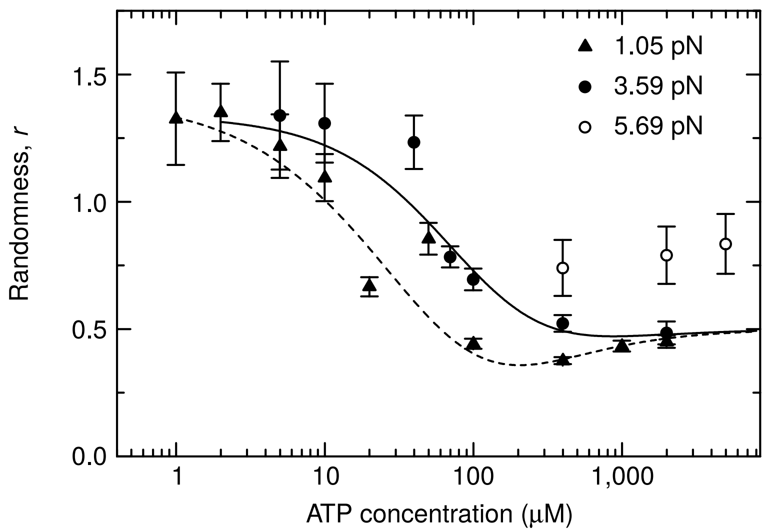
  - holds even for an arbitrary current $j(t) \equiv \int dr \sum_\alpha g_\alpha(r, \{\phi_\beta)\}\partial_t \phi_\alpha$
  - can be used to infer a bound on entr'prod from known current fluctuations

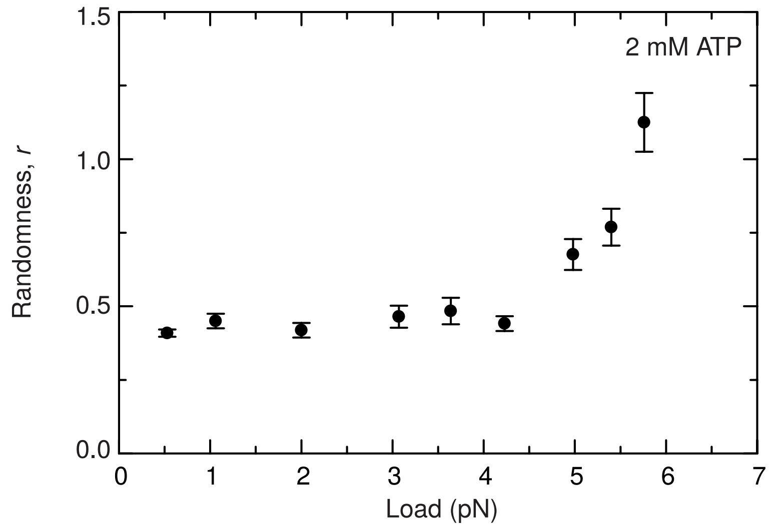
- Thermodynamic inference: Efficiency of a molecular motor



[Visscher et al, Nature, 1999]

- experimental data on
  - velocity v
  - diffusion constant D
  - randomness parameter $r \equiv 2D/v\ell$



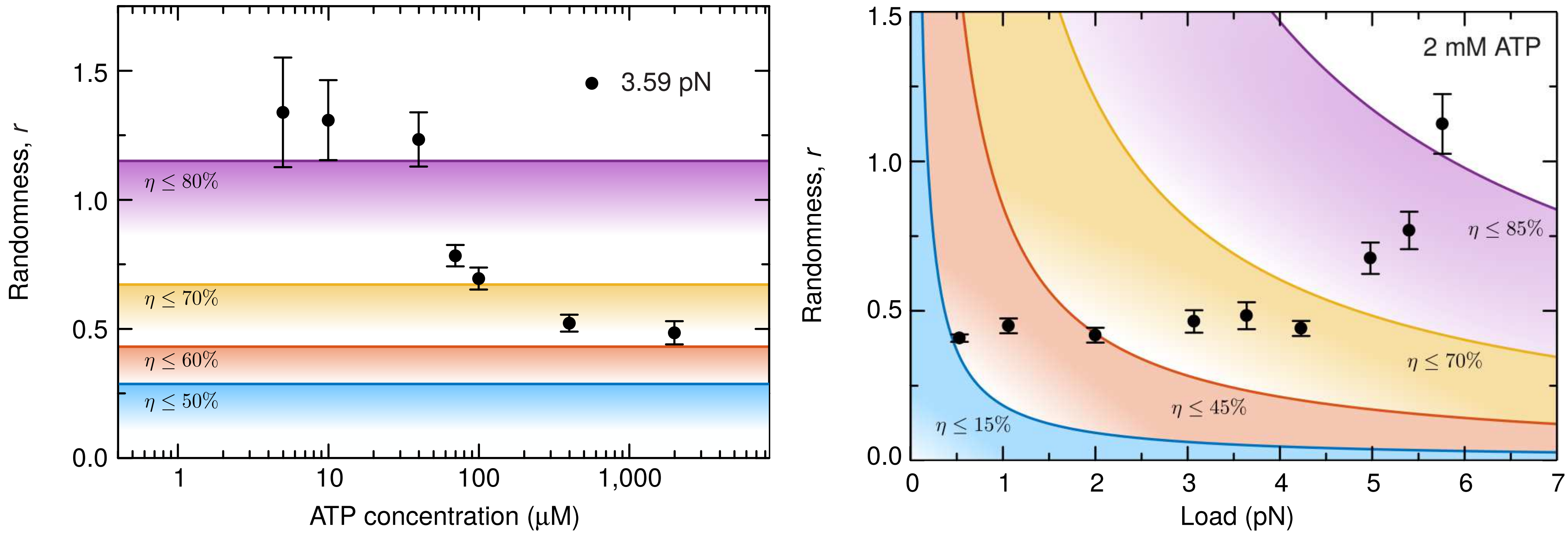


- Uncertainty relation applied to the kinesin data from [Visscher et al, Nature, 1999]

  [P. Pietzonka, AC Barato, U.S., J Stat Mech, 124004, 2016]

  – efficiency

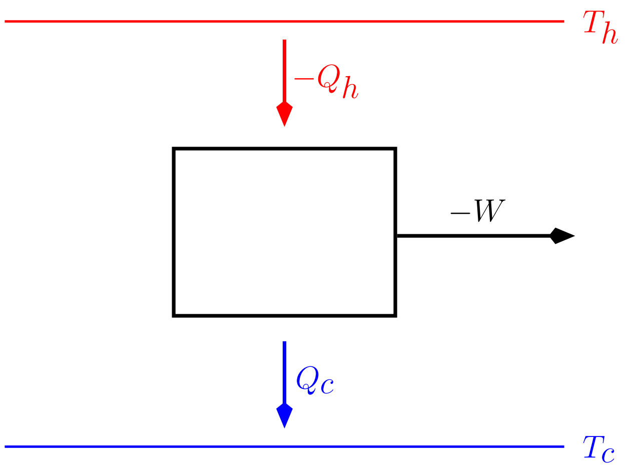
$$\eta \equiv \frac{P^{\text{out}}}{P^{\text{in}}} = \frac{fv}{\text{unknown}} = \frac{fv}{\sigma + fv} \leq \frac{1}{1 + v k_B T/(Df)}$$



  – completely independent of the specific chemo-mechanical cycles and of $\Delta\mu$

- Universal bound on power of steady state heat engines from unc'relation

  [P. Pietzonka and U. Seifert, arxiv 1705.05817, 2017]



  - Carnot efficiency $\eta_c \equiv 1 - T_c/T_h$ but zero power
  - uncertainty relation for work current (=power)

$$\sigma > j_w^2/D_w$$

  - universal bound on power

$$j_w = P \leq \frac{(\eta_C - \eta)D_w}{\eta\ T_c}$$

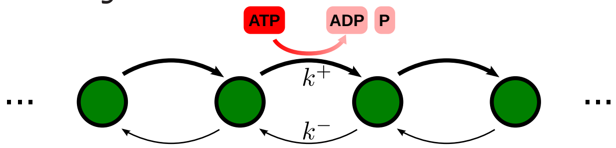
  - settles the debate about "reaching Carnot efficiency at finite power"

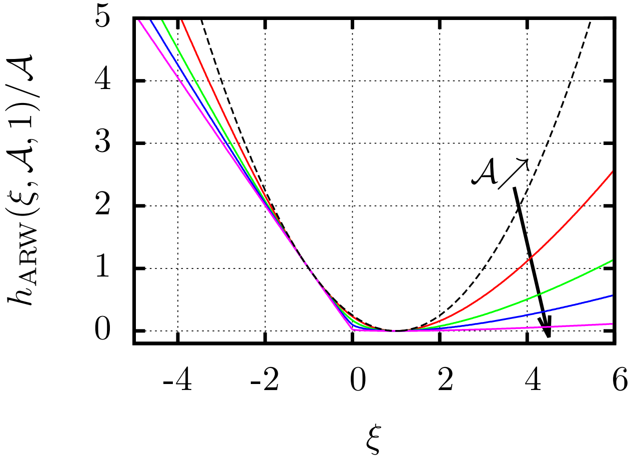
    [cf Shiraishi, Saito, and Tasaki, Phys. Rev. Lett. 117, 190601 (2016)]

- Generalization: bound on the rate function of any current J in any network/Langevin system

[P Pietzonka, AC Barato and US, PRE 93, 052145, 2016, TR Gingrich et al, PRL 2016]

– asymmetric random walk:



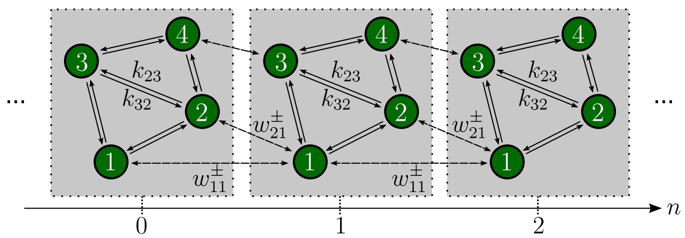


– scaled current:

$$\xi \equiv X(t)/\langle X \rangle = j(t)/j^s$$

– rate function: $p(\xi, t) \sim \mathrm{e}^{-th(\xi)}$

– arbitrary, multicyclic network



– global, universal bound:

$$\boxed{h(\xi) \leq \frac{1}{4}\sigma(\xi - 1)^2}$$

– even extreme fluct's of any current globally constrained by mean entropy production σ

- Thermodynamics of active particles

C. Ganguly and D. Chaudhuri, Stochastic thermodynamics of active Brownian particles, Phys. Rev. E 88, 032102 (2013).

D. Chaudhuri, Active Brownian particles: Entropy production and fluctuation response, Phys. Rev. E 90, 022131 (2014).

U. M. B. Marconi and C. Maggi, Towards a statistical mechanical theory of active fluids, Soft Matter 11, 8768 (2015).

S. Chakraborti, S. Mishra, and P. Pradhan, Additivity, density fluctuations, and nonequilibrium thermodynamics for active Brownian particles, Phys. Rev. E 93, 052606 (2016).

T. Speck, Stochastic thermodynamics for active matter, EPL 114, 30006 (2016).

E. Fodor, C. Nardini, M. E. Cates, J. Tailleur, P. Visco, and F. van Wijland, How far from equilibrium is active matter?, Phys. Rev. Lett. 117, 038103 (2016).

C. Nardini, E. Fodor, E. Tjhung, F. van Wijland, J. Tailleur, and M. E. Cates, Entropy production in field theories without time-reversal symmetry: Quantifying the non-equilibrium character of active matter, Phys. Rev. X 7, 021007 (2017).

D. Mandal, K. Klymko, and M. R. DeWeese, Entropy production and fluctuation theorems for active matter, arXiv:1704.02313 (2017).

P. Gaspard and R. Kapral, Mechanochemical fluctuation theorem and thermodynamics of self- phoretic motors, arXiv:1706.05691 (2017).

U. M. B. Marconi, A. Puglisi, and C. Maggi, Heat, temperature and clausius inequality in a model for active brownian particles, Sci. Rep. 7, 46496 (2017).

A. Puglisi and U. M. B. Marconi, Clausius relation for active particles: what can we learn from fluctuations?, arXiv:1706.03585 (2017).

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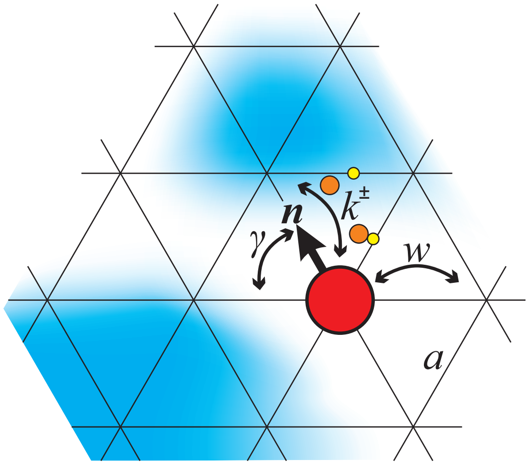
- Entropy production for active particles [P.Pietzonka and U.S., 1707.03772]



  - propulsion along $\mathbf{n}$ by chem' reaction

$$k^+/k^- = \exp \Delta\mu$$

  - for fixed orientation $\mathbf{n}$

    mean velocity $u_{\text{ac}} = (k^+ - k^-)a$

    dispersion $D_{\text{ac}} = (k^+ + k^-)a^2/2$

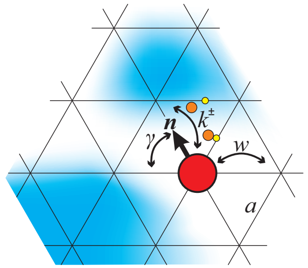
    $k^\pm = D_{\text{ac}}/a^2 \pm u_{\text{ac}}/2a$

  - thermodynamic consistency in $V(\boldsymbol{r}_i)$

$$k^\pm(\boldsymbol{r}_i, \mathbf{n}) = k^\pm \exp[-(V(\boldsymbol{r}_i \pm a\mathbf{n}) - V(\boldsymbol{r}_i))/2]$$

  - local detailed balance condition

$$k^+(\boldsymbol{r}_i, \mathbf{n})/k^-(\boldsymbol{r}_i + a\mathbf{n}, \mathbf{n}) = \exp[V(\boldsymbol{r}_i) - V(\boldsymbol{r}_i + a\mathbf{n}) + \Delta\mu]$$



- entropy production rate σ_{ac}

$$\sigma_{\text{ac}} = \sum_{i,\mathbf{n}} [p(\boldsymbol{r}_i, \mathbf{n}) k^+(\boldsymbol{r}_i, \mathbf{n}) - p(\boldsymbol{r}_i + a\mathbf{n}, \mathbf{n}) k^-(\boldsymbol{r}_i + a\mathbf{n}, \mathbf{n})] \ln[k^+(\boldsymbol{r}_i, \mathbf{n}) / k^-(\boldsymbol{r}_i + a\mathbf{n}, \mathbf{n})]$$

  - continuum limit $a \to 0$

$$\sigma_{\text{ac}} = \langle (u_{\text{ac}} - D_{\text{ac}} \mathbf{n} \boldsymbol{\nabla} V(\boldsymbol{r}))^2 \rangle / D_{\text{ac}} - D_{\text{ac}} \langle (\mathbf{n} \boldsymbol{\nabla})^2 V(\boldsymbol{r}) \rangle$$

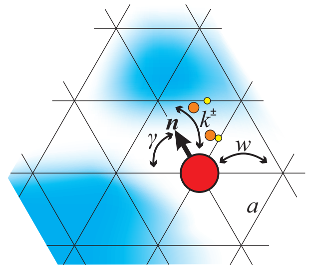
  - non-driven, $\boldsymbol{r}$-independent $\mathbf{n}$-diffusion doesn't contribute

- ordinary thermal translational diffusion

$$\sigma_{\text{tr}} = D_{\text{tr}} \langle [\boldsymbol{\nabla} V(\boldsymbol{r})]^2 - \boldsymbol{\nabla}^2 V(\boldsymbol{r}) \rangle$$

- total entropy production rate

$$\sigma_{\text{tot}} \equiv \sigma_{\text{ac}} + \sigma_{\text{tr}} = u_{\text{ac}}^2 / D_{\text{ac}} - u_{\text{ac}} \langle \mathbf{n} \boldsymbol{\nabla} V(\boldsymbol{r}) \rangle.$$



- corresponding Langevin dynamics

$$\dot{\boldsymbol{r}} = u_{\text{ac}}\mathbf{n} - (D_{\text{tr}} + D_{\text{ac}}\mathbf{n} \otimes \mathbf{n})\boldsymbol{\nabla} V(\boldsymbol{r}) + \zeta_{\text{tr}} + \zeta_{\text{ac}}\mathbf{n}$$

  – ordinary thermal translational noise

$$\langle \zeta_{\text{tr}}(t_2) \otimes \zeta_{\text{tr}}(t_1) \rangle = 2D_{\text{tr}}\mathbf{1}\delta(t_2 - t_1)$$

  – chemical driving leads to an active noise

$$\langle \zeta_{\text{ac}}(t_2)\zeta_{\text{ac}}(t_1) \rangle = 2D_{\text{ac}}\delta(t_2 - t_1)$$

→ active "mobility" $D_{\text{ac}}\mathbf{n} \otimes \mathbf{n}$ [cf Gaspard and Kapral, arxiv]

- Entropy production directly from the Langevin equation and "time-reversal"?

  [Fodor et al PRL 2016, Mandal et al, arxiv, Puglisi et al, arxiv, Speck arxiv]

  – time-reversal: $\boldsymbol{r}(t), \mathbf{n}(t)$ (for $0 \leq t \leq \mathcal{T}$) and $\tilde{\boldsymbol{r}}(t) \equiv \boldsymbol{r}(\mathcal{T}-t), \tilde{\mathbf{n}}(t) \equiv \mathbf{n}(\mathcal{T}-t)$

  – free active motion

$$\dot{\boldsymbol{r}} = u_{\text{ac}}\mathbf{n} + \boldsymbol{\zeta}_{\text{tr}} + \zeta_{\text{ac}}\mathbf{n}$$

  – weight ratio

$$\Sigma \equiv \left\langle \ln \frac{p[\boldsymbol{r}(t)|\mathbf{n}(t)]}{p[\tilde{\boldsymbol{r}}(t)|\tilde{\mathbf{n}}(t)]} \right\rangle / \mathcal{T} = u_{\text{ac}}^2/(D_{\text{tr}} + D_{\text{ac}}) \leq \sigma_{\text{tot}} = u_{\text{ac}}^2/D_{\text{ac}},$$

  – alternative "fails" too:

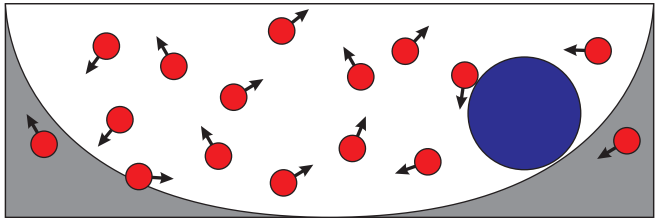
$$\Sigma' \equiv \left\langle \ln \frac{p[\boldsymbol{r}(t)|\mathbf{n}(t)]}{p[\tilde{\boldsymbol{r}}(t)| - \tilde{\mathbf{n}}(t)]} \right\rangle / \mathcal{T} = 0 \quad \text{[with potential} = \ u_{\text{ac}} \langle \mathbf{n} \boldsymbol{\nabla} V(\boldsymbol{r}) \rangle \text{]}$$

  – "sum rules" even with potential

$$\Sigma + \Sigma' = u_{\text{ac}}^2/(D_{\text{tr}} + D_{\text{ac}}) \quad \text{and} \quad \sigma_{\text{tot}} = u_{\text{ac}}^2/D_{\text{ac}} - \Sigma'$$

  – Langevin eq contains implicit coarse-graining over two slow processes

- Interacting active and passive particles



[experiments: Sood-group, Nature physics 2016; Volpe-group, arxiv 2016]

– M passive colloidal particles ($j = N+1, \ldots, N+M$)

  in a non-equilibrium bath of N active ones ($j = 1, ..., N$)

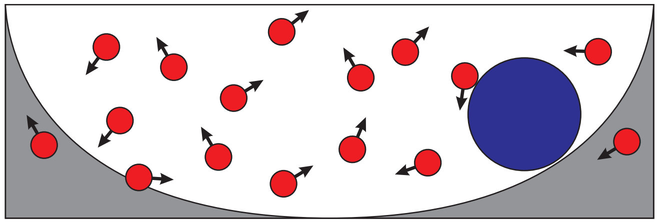
$$\sigma_{\text{tot}} = \sum_{j=1}^{N} \left\{ \langle (u_{\text{ac}} - D_{\text{ac}} \mathbf{n}^j \boldsymbol{\nabla}^j V(\{\boldsymbol{r}^j\})^2 \rangle / D_{\text{ac}} - D_{\text{ac}} \langle (\mathbf{n} \boldsymbol{\nabla}^j)^2 V(\{\boldsymbol{r}^j\}) \rangle \right\} + \sum_{j=1}^{M+N} \left\{ \langle D_{\text{tr}}^j (\boldsymbol{\nabla}^j V(\{\boldsymbol{r}^j\})^2 \rangle - D_{\text{tr}}^j \langle (\boldsymbol{\nabla}^j)^2 V(\{\boldsymbol{r}^j\}) \rangle \right\}$$

$$= N u_{\text{ac}}^2 / D_{\text{ac}} - u_{\text{ac}} \sum_{j=1}^{N} \left\langle \mathbf{n}^j \boldsymbol{\nabla}^j V(\{\boldsymbol{r}^j\}) \right\rangle$$

– one active in a harmonic potential of strength k with hard-core repulsions

$$\sigma_{\text{tot}} = \rho N u_{\text{ac}}^2 / D_{\text{ac}} + D_{\text{tr}} k (k \langle \boldsymbol{r}^2 \rangle - 3)$$

  ρ available phase space volume



- Generalizations
  - rod-like particles $\mathbf{D}_{\text{tr}} = D_{\text{tr}}^{||}\mathbf{n} \otimes \mathbf{n} + D_{\text{tr}}^{\perp}(\mathbf{1} - \mathbf{n} \otimes \mathbf{n})$
  - different reaction channels indexed by ρ, each with a different u_{ac}^{ρ} and D_{ac}^{ρ}
  - add further internal degrees of freedom: active Ornstein-Uhlenbeck particles

- Extreme fluctuations of active Brownian motion

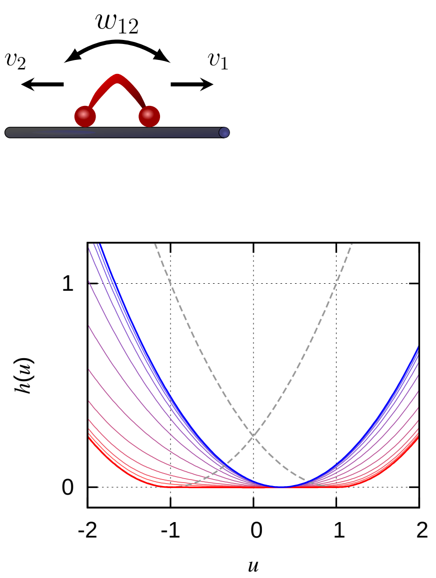
  [P. Pietzonka, K. Kleinbeck, U.S., New. J. Phys. 18, 052001, 2016]

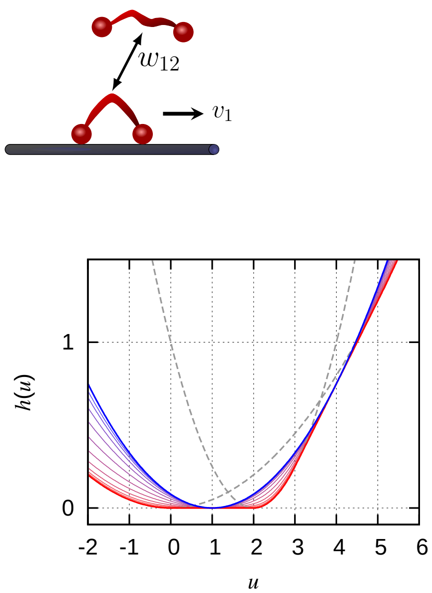
  – different internal states $i \longleftrightarrow j$ at a rate w_{ij}

  – active force depends on state i

$$\dot{x} = \mu_i f_i + \zeta_i \quad \text{with} \quad \langle \zeta_i(t)\zeta_i(t')\rangle = 2D_i\delta(t-t') \quad \text{and} \quad D_i = k_B T \mu_i$$

  – ldf: $p(x,t) \sim \exp[-t h(x/t)]$

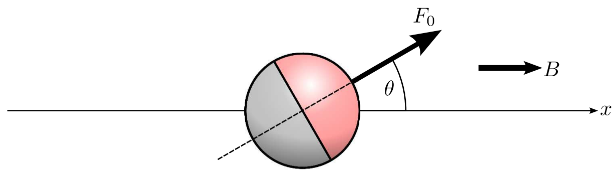




- fast switching between internal states: $h(u) \to (u-1)^2/4D_{\text{eff}}$ with $D_{\text{eff}} = \sum_i p_i^s D_i$

- slow switching: $h(u) \to$ convex envelope of two parabolas

- Extreme fluctuations of active Brownian motion II: Janus particles



– different internal states $\longrightarrow$ rotational diffusion

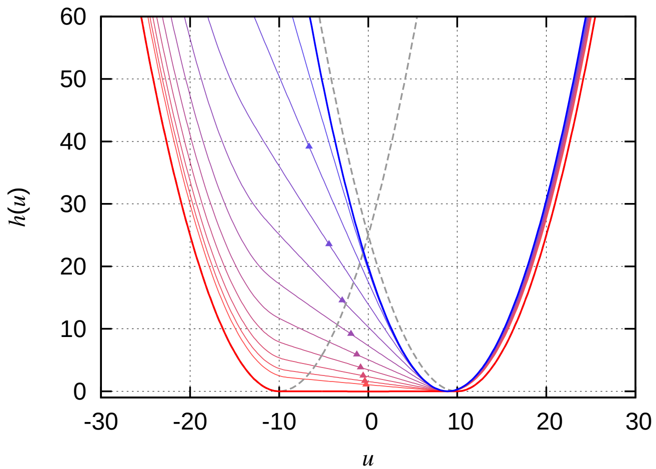
– active force depends on state i

$$\dot{x} = \mu F_0 \cos\theta + \zeta$$

$$- \quad \dot{\theta} = -\mu_r B \sin\theta + \zeta_r$$

with $\langle \zeta_r(t)\zeta_r(t')\rangle = 2D_r\delta(t-t')$

– ldf: $p(x,t) \sim \exp[-th(x/t)]$



– rot'diffusion: slow vs. fast

- New symmetry: $\boxed{h(u - D_rB/F_0) = h(-u - D_rB/F_0) - (D_rB/F_0D)\ u}$ $\neq$ GC-symmetry!

- Stochastic thermodynamics established as

  . universal, thermodynamically consistent, quantitative framework

- fluctuation theorem for ent'prod as a mathematical identity
  - ....but only if all slow variables are monitored!

- thermodynamic uncertainty relation provides a universal constraint on
  - ... the dispersion of any current in terms of the overall ent'prod rate
  - ... efficiency of any molecular motor (-complex)
  - ... power of any (steady state) heat engine

- thermodynamic inference
  - reveals hidden properties of biochemical/-physical/-molecular systems

- ("correct") entropy production of active particles
  - ....requires a (more) microscopic description