Kyoto, Yukawa Int Seminar, August 2015

Stochastic thermodynamics and coarse-graining

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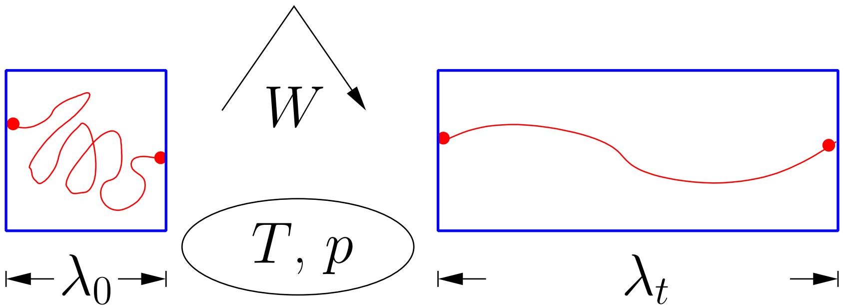
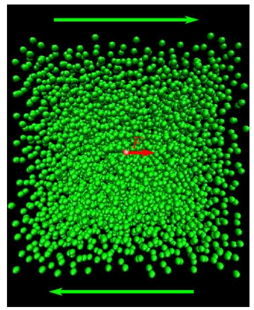
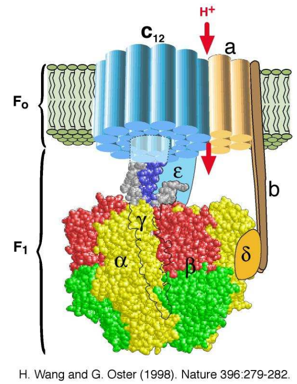
- Stochastic thermodynamics for driven systems emb'd in a heat bath





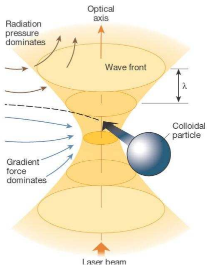


driving: mechanical shear flow (bio)chemical

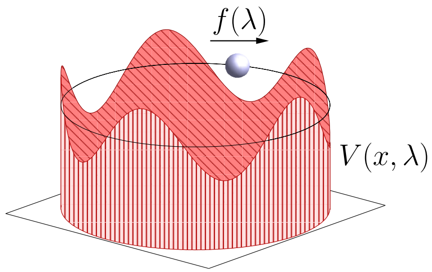
- Energy conservation (1^{st} law) and entropy production (2^{nd} law) are defined along an individual stochastic trajectory

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

- Stochastic th'dynamics for a driven colloidal particle



D.G. Grier A revolution in optical manipulation, Nature **424,** 810 (2003)



– Langevin dynamics

$$\dot{x} = \mu[-V'(x,\lambda) + f(\lambda)] + \zeta$$

with $\langle \zeta_1 \zeta_2 \rangle = 2\mu k_B T \delta_{12}$

– external driving $\lambda(\tau)$

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

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

  – internal energy: $du = dV$

  – dissipated heat: $dq = dw - du = [-\partial_x V(x,\lambda) + f] dx = T ds_{\mathrm{m}}$

- stochastic entropy and second law [U.S., PRL 95, 040602, 2005]

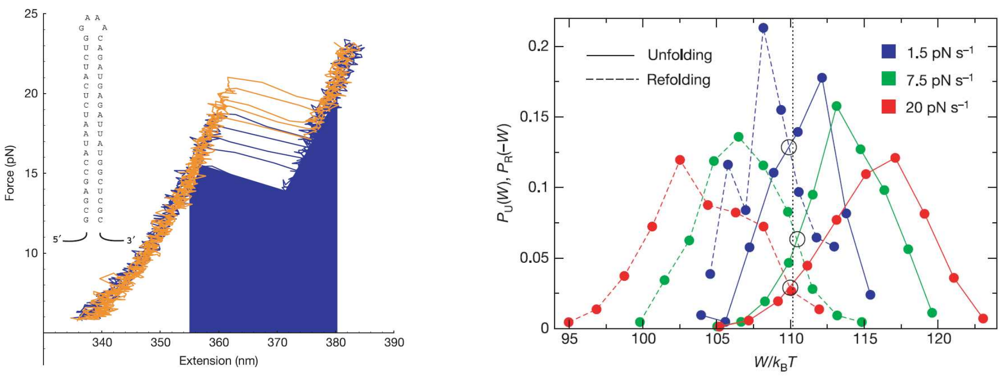
$$\boxed{ds \equiv -d\ [\ln p(x,t)] \quad \Rightarrow \langle \exp[-\Delta(s + s_{\mathrm{m}})] \rangle = 1 \quad \Rightarrow \langle \Delta s_{\mathrm{tot}} \rangle \geq 0}$$

- Exact non-eq work relations
  - Jarzynski relation [Phys. Rev. Lett. 78, 2690 (1997)]

$$\langle \exp[-W] \rangle = \exp[-\Delta F]$$

  - Crooks' relation [Phys. Rev. E 60, 2721 (1999)]

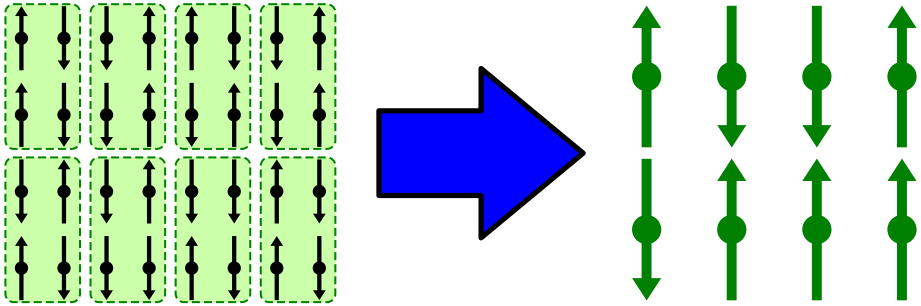
$$p(W)/\tilde{p}(-W) = \exp[(W - \Delta F)/k_B T]$$



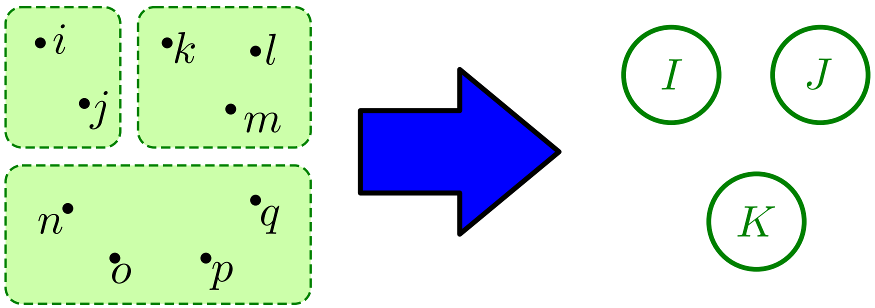
[Collin et al, Nature 437, 231, 2005]

  - identities in stochastic (and Hamiltonian) dynamics for a thermalized initial state

- Coarse-graining
  - in equilibrium
    - spatial coarse-graining



    - clustering states

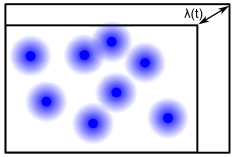


$p_i = \exp[-\beta(E_i - F)]$ $\qquad$ $P_I = \sum_{i \in I} p_i = \exp[-\beta(F_I(\beta) - F)]$

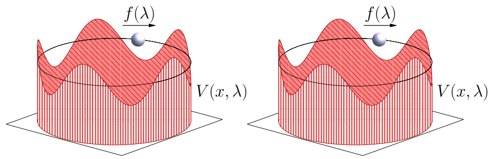
  - in dynamics: Markov property of dynamics is lost

- Coarse graining in stochastic thermodynamics

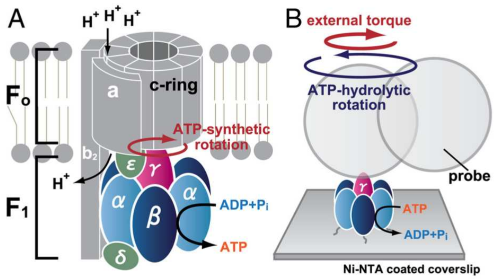
  – fluctuating density field



  – NESS for two driven colloidal particles



  – molecular motors with probe particles



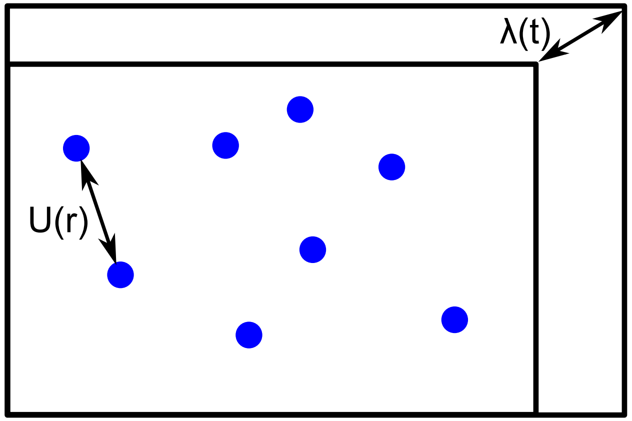
- related work:

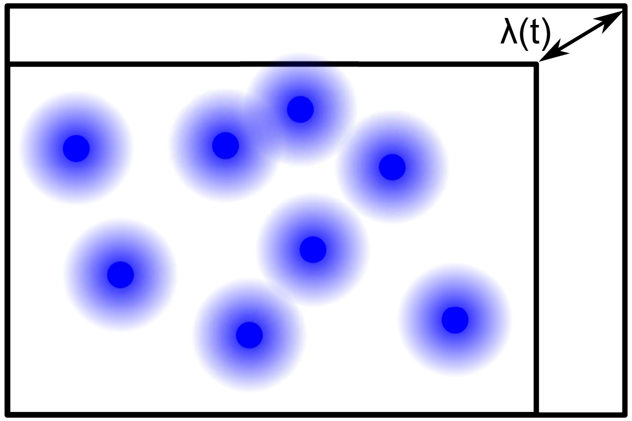
  Rahav and Jarzynski JSM 2007, Kawai et al PRL 2007, Pigolotti and Vulpiani JCP 2008, Esposito PRE 2012.....

- Coarse-graining a fluctuating density field for colloids

  [T. Leonard, B. Lander, U.S., and T. Speck J. Chem. Phys. 139, 204109, 2013]

microscopic $\Rightarrow$ coarse-grained





– $u(r) = \epsilon\,\mathrm{exp}[-\kappa r]/r$

– free energy $\Delta F(T, V/N)$ from Crooks relation

- Microscopic density field
  - overdamped Langevin $\dot{\mathbf{r}}_k = -\sum_l u'(r_{kl})\hat{\mathbf{r}}_{kl} + \zeta_k$
  - microscopic density $\rho_0(\mathbf{r},t) \equiv \sum_k \delta(\mathbf{r} - \mathbf{r}_k(t))$ obeys Dean's (1996) equation

$$\boxed{\partial_t \rho_0(\mathbf{r},t) = \nabla \left[\rho_0 \frac{\delta \mathcal{F}}{\delta \rho_0} + \xi\right]} \qquad \text{with } \langle \xi\xi \rangle \sim 2\rho_0\delta....$$

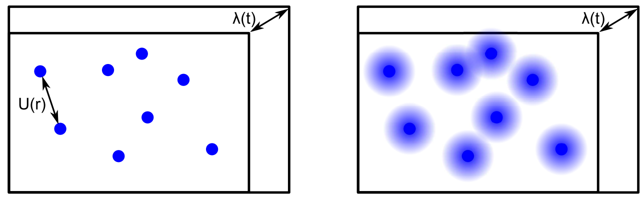
  - with free energy functional

$$\mathcal{F}[\rho] = \mathcal{F}_{IG} + \int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r})u(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}')/2$$

  - Work $W_0 \equiv -\int dt\dot{V}P[\rho_0]$ from fluctuating pressure

$$P[\rho_0(\mathbf{r},t)] = N/V + \int d\mathbf{r}d\mathbf{r}'\rho_0(\mathbf{r},t) \underbrace{f(|\mathbf{r}-\mathbf{r}'|)}_{f(r)\equiv -ru'(r)} \rho_0(\mathbf{r}',t)/4V$$

– coarse-grain density field on scale ℓ



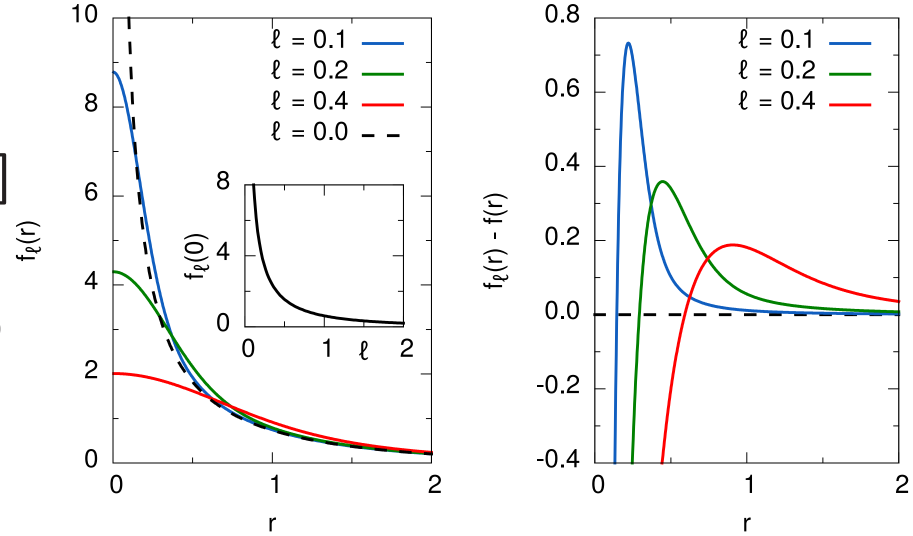
– $\rho_\ell(\mathbf{r}) \equiv \sum_k \exp[-|\mathbf{r}-\mathbf{r}_k|^2/2\ell^2]/2\pi\ell^2$

– fluctuating pressure $\quad P_\ell(t) = \ldots = N/V + \sum_{k<l} f_\ell(|\mathbf{r}_k(t) - \mathbf{r}_l(t)|)/2V$

with effective "two-body" pressure

$$f_\ell(r) \equiv -r u_\ell'(r) - 2\ell^2[u_\ell''(r) + u_\ell'(r)/r]$$

$$u_\ell(r) \equiv \int_0^\infty dq \frac{q}{\sqrt{1+q^2}} \exp[-\ell^2 q^2] J_0(qr)$$



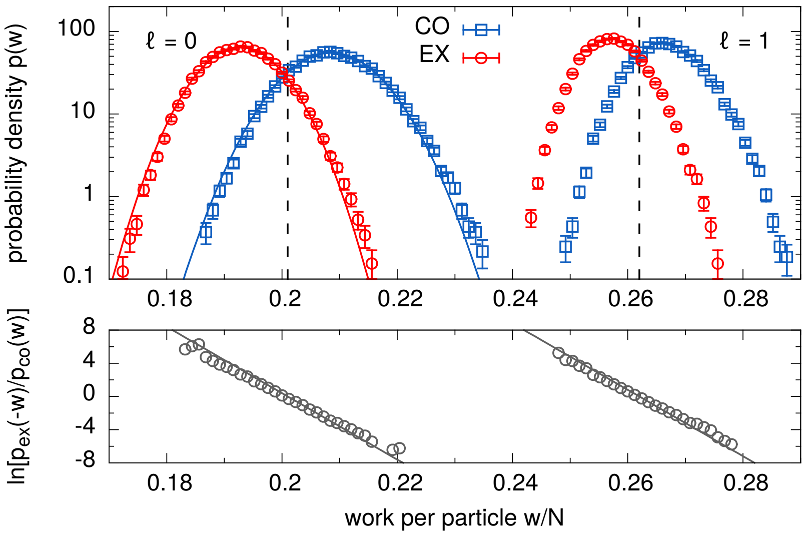
– coarse-grained fluctuating work $\quad W_\ell \equiv -\int dt \dot{V} P_\ell[\rho_\ell]$

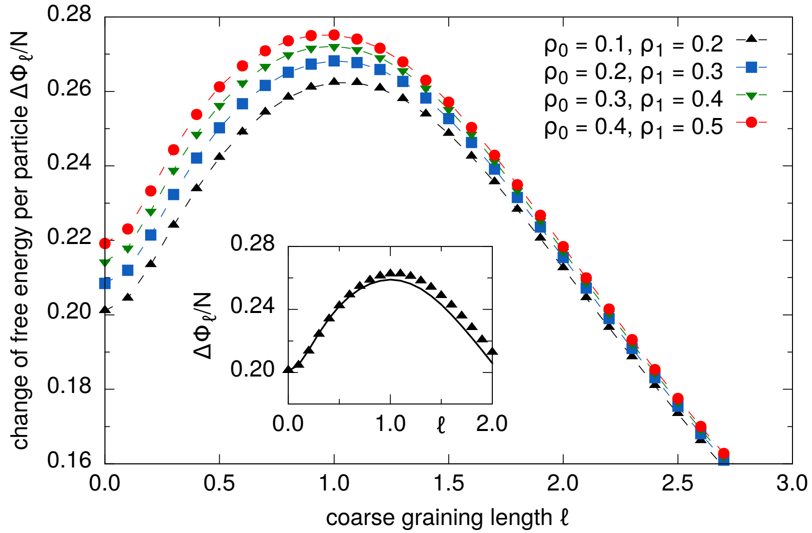
- Free energy from coarse-grained work in Crooks

  – "joint-(W_ℓ, W_0) Crooks" $\boxed{\dfrac{p_{\text{exp}}(-W_\ell,-W_0)}{p_{\text{com}}(+W_\ell,+W_0)} = \exp[-W_0 + \Delta F]}$

  – integrating out exact work W_0

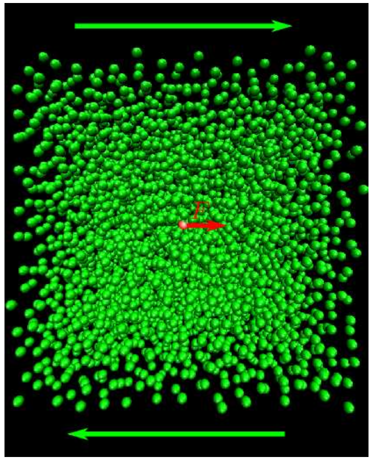
$$\begin{aligned}\ln \frac{p_{\text{exp}}(-W_\ell)}{p_{\text{com}}(+W_\ell)} &= \Delta F + \ln \int dW_0 \; p_{\text{com}}(W_0|W_\ell) \exp[-W_0] \\ &\approx \Delta F + \ln\langle e^{\delta W_\ell}\rangle - W_\ell \equiv \Delta F_\ell - W_\ell\end{aligned}$$

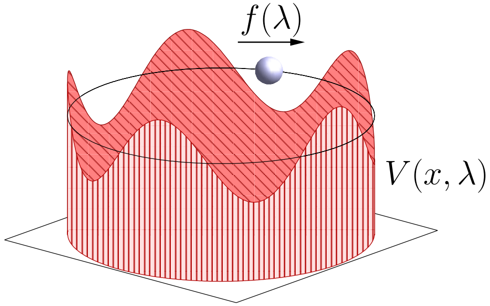


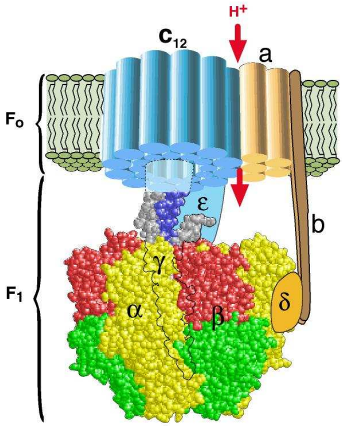


  – slope 1, cg-dependent free energy ΔF_ℓ

- Coarse-graining in NESSs







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

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

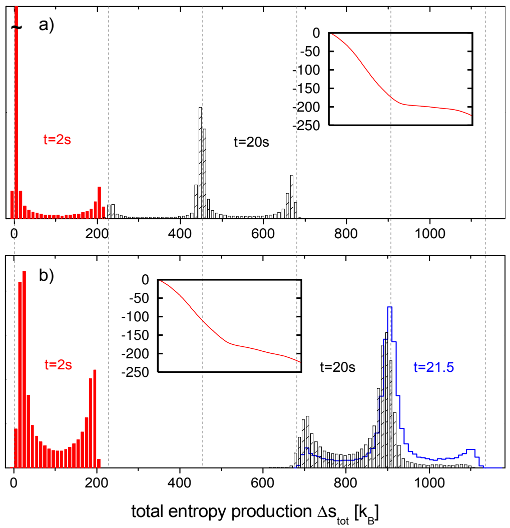
  - long-time limit: Evans et al (1993), Gallavotti & Cohen (1995), Kurchan (1998), Lebowitz & Spohn (1999)

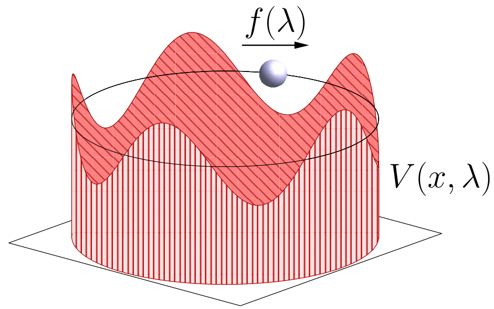
  - finite times: U.S., PRL'05

    $\Delta s_{\text{tot}} \equiv \Delta s_{\text{m}} + \Delta s = \int_0^t d\tau\ \dot{x}(\tau)\nu(x(\tau))$ [with $\nu(x) \equiv \langle \dot{x}|x\rangle = j(x)/p(x)$]

  - experimental data

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





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

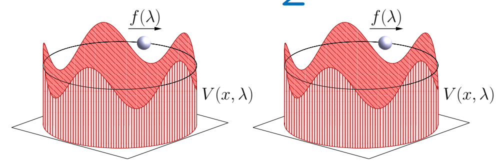
  – suppose x_2 is hidden:

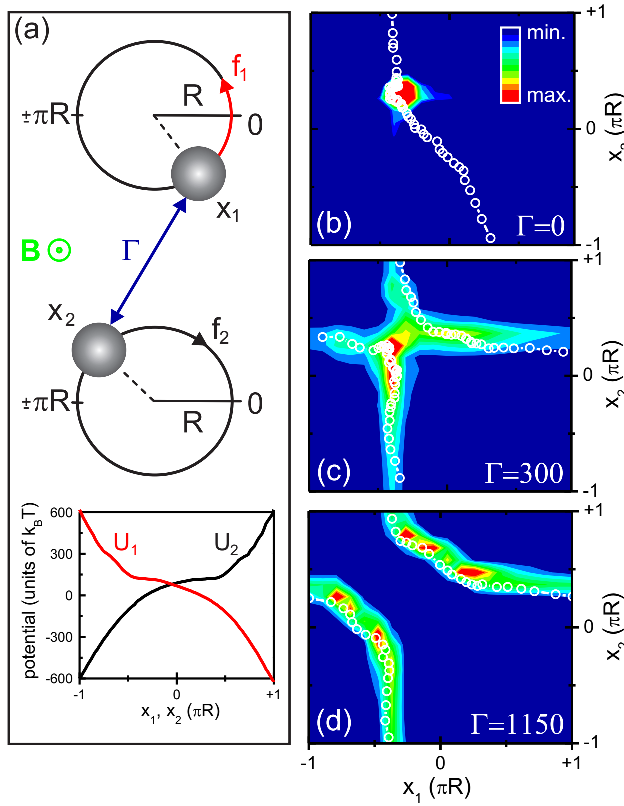
  $$\tilde{\nu}_1(x_1) \equiv \int \nu(x_1, x_2) p(x_2 | x_1) dx_2$$

  – apparent entropy production

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

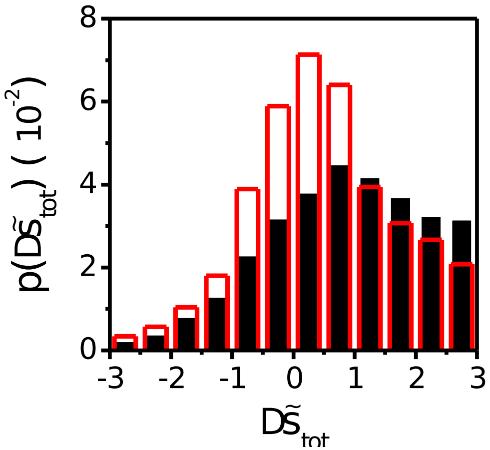
x_1 $\qquad$ x_2

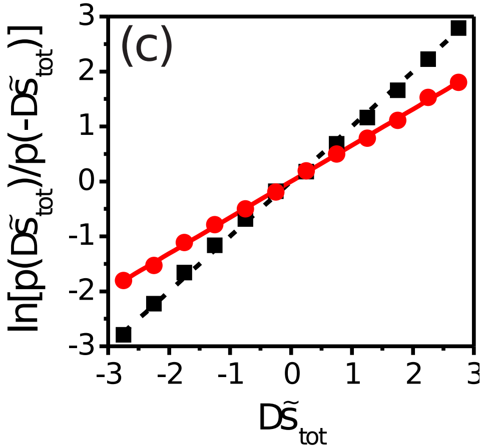


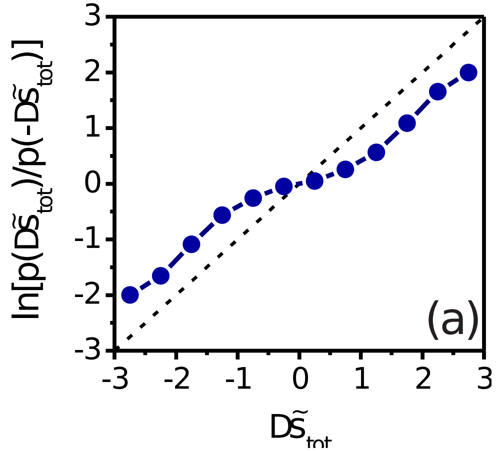


- Experimental data

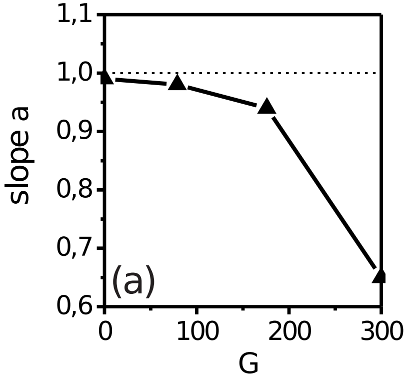
  – with and without coupling [rarely:]

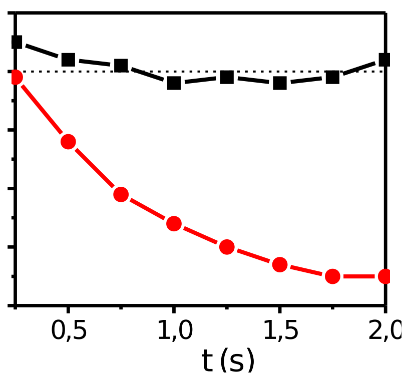




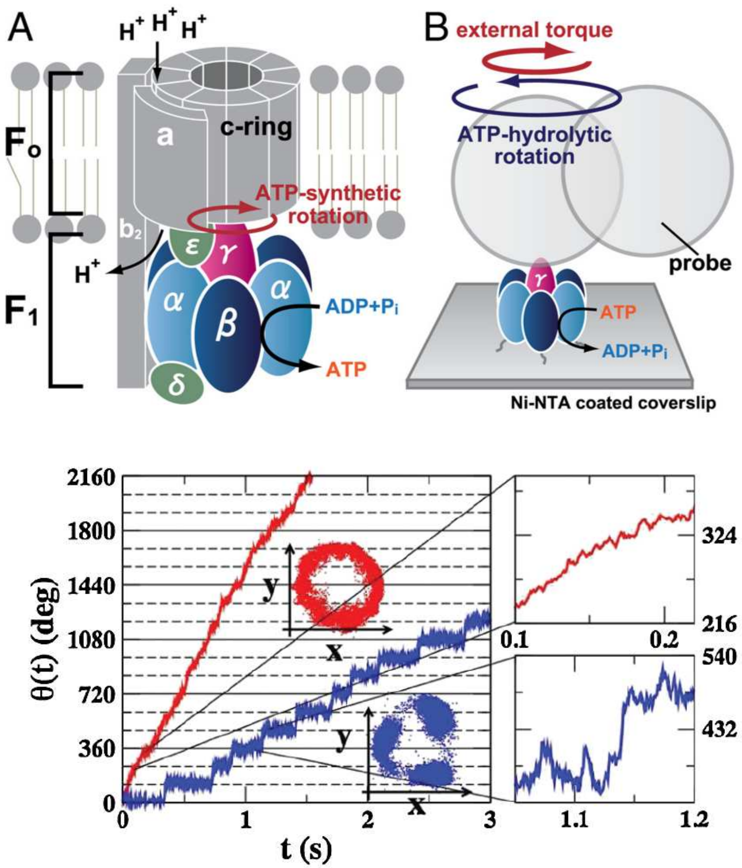


  – FT-slope





- Molecular motor: F1-ATPase



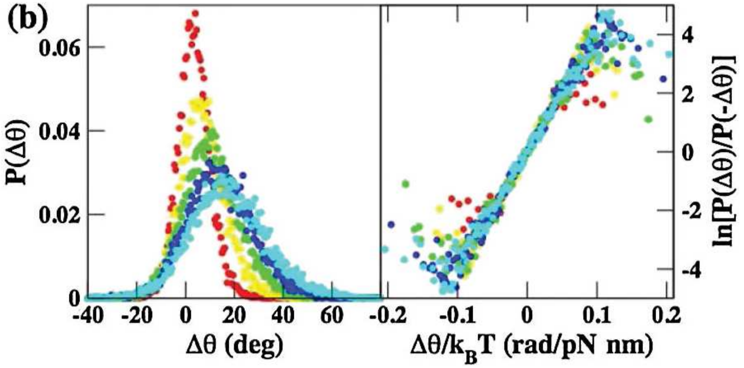
– kinetics vs thermodynamics

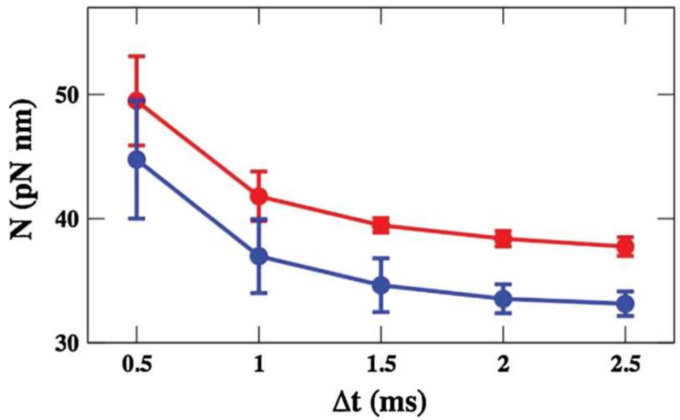
– first law?

– efficiency(ies)?

- F1-ATPase and the fluctuation theorem

  [K. Hayashi, ... H. Noji, PRL 104, 218103 (2010)]





  - $\Gamma\dot{\theta} = N + \zeta \quad \langle\zeta_1\zeta_2\rangle = 2\Gamma k_B T\delta(\tau_1 - \tau_2)$

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

    independent of friction coefficient

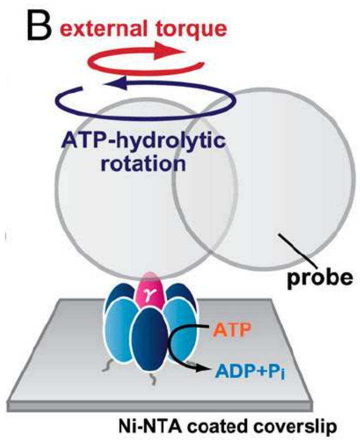
  - cf f'theorem

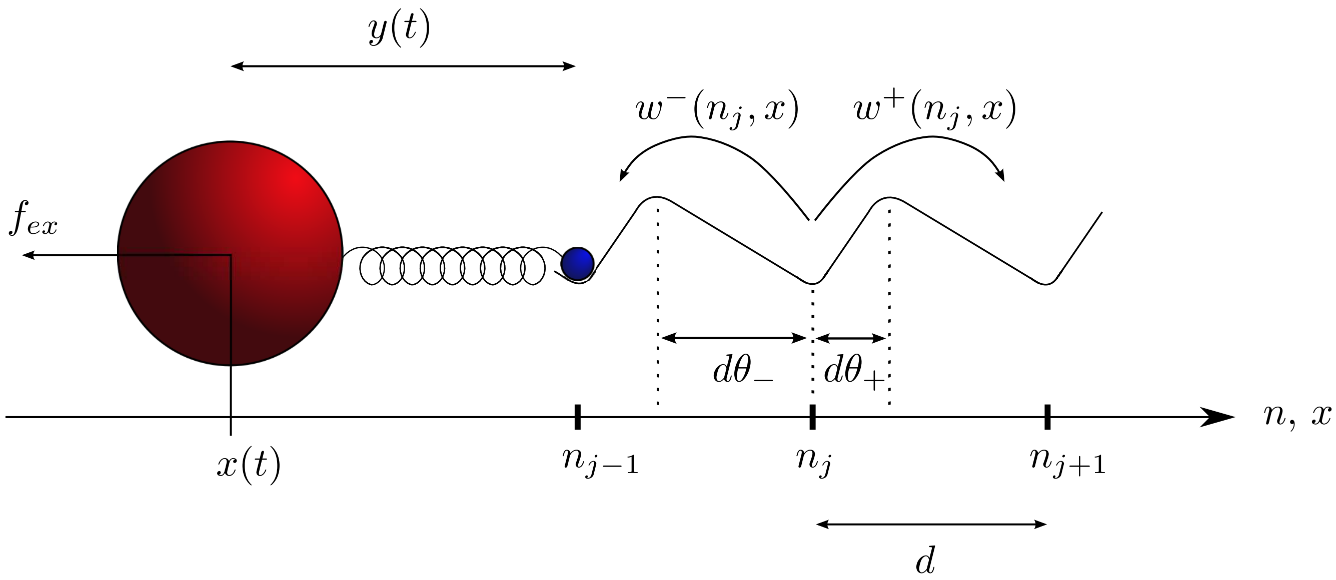
    $\ln[p(\Delta s_{\text{tot}})/p(-\Delta s_{\text{tot}})] = \Delta s_{\text{tot}}/k_B$

time-dependence?

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

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





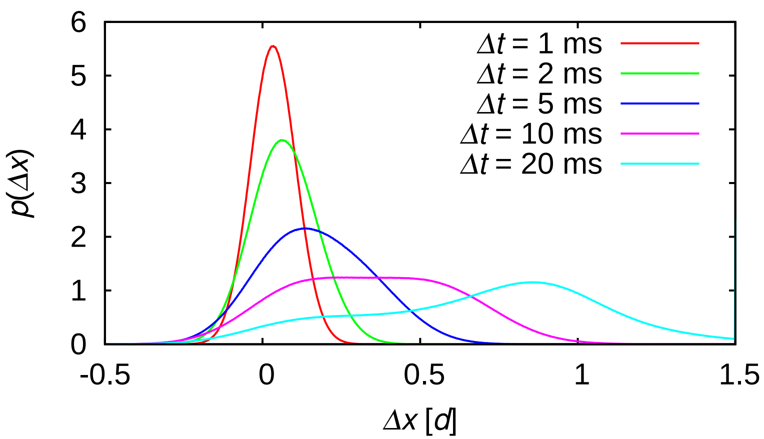
– probe particle

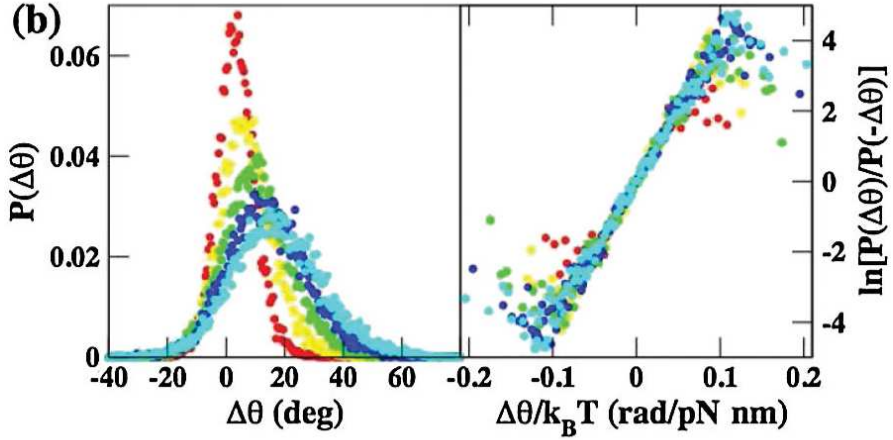
  * $\dot{x} = \mu(-\partial_y V(y) + f^{\text{ex}}) + \zeta$ with $y(\tau) \equiv n(\tau) - x(\tau)$

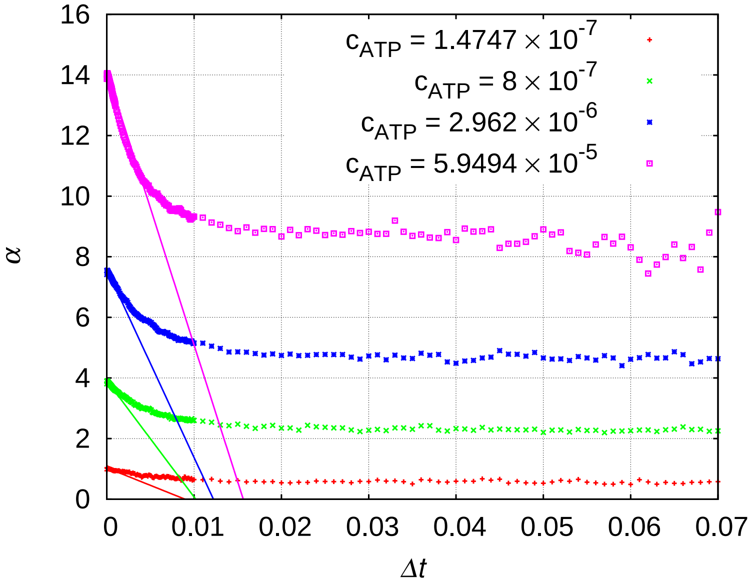
– motor

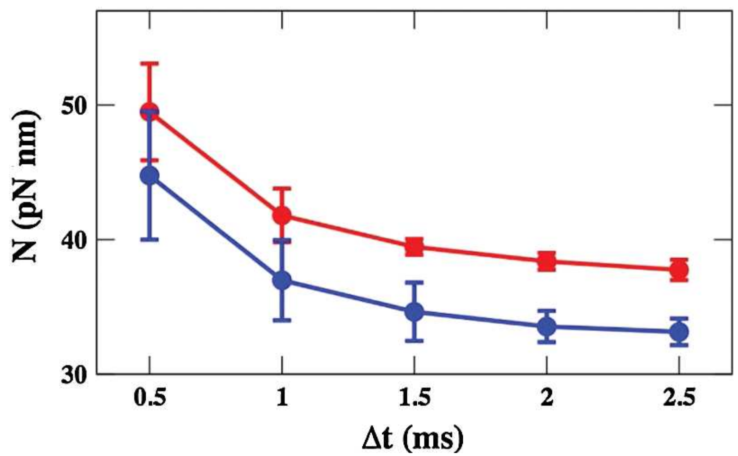
  * $w^+/w^- = \exp[\Delta\mu - V(n+d, x) - V(n, x)]$
  * local detailed balance condition

- FT-slope from simulations vs experiment





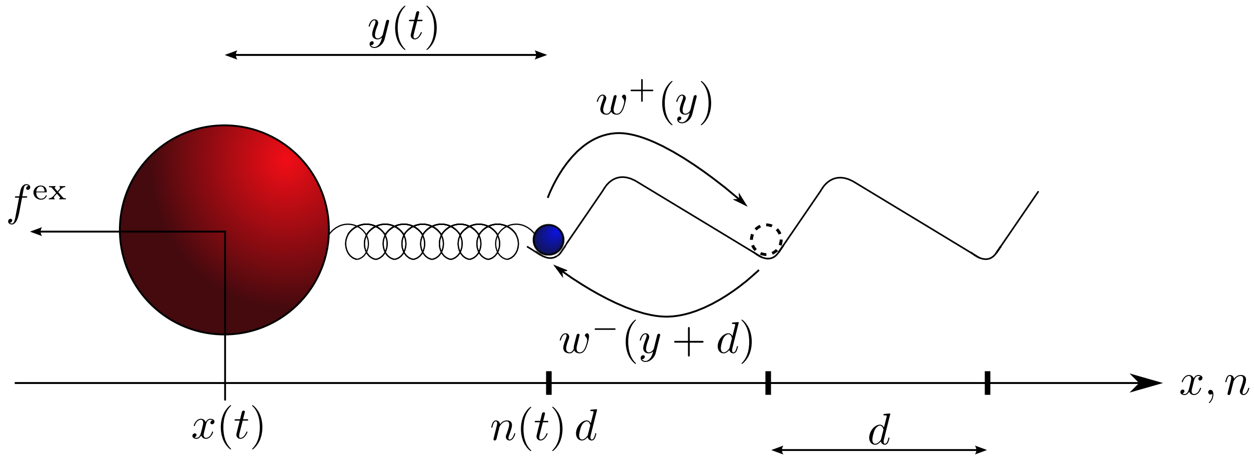




$\Delta t \to 0$ limit yields average force/torque

- Fine-structured large deviations

  [P. Pietzonka, E. Zimmermann and U.S., EPL **107** 20002, 2014]



  - dynamics $\partial_t p(n,y,t) = (L_1 + L_2)p(n,y,t)$

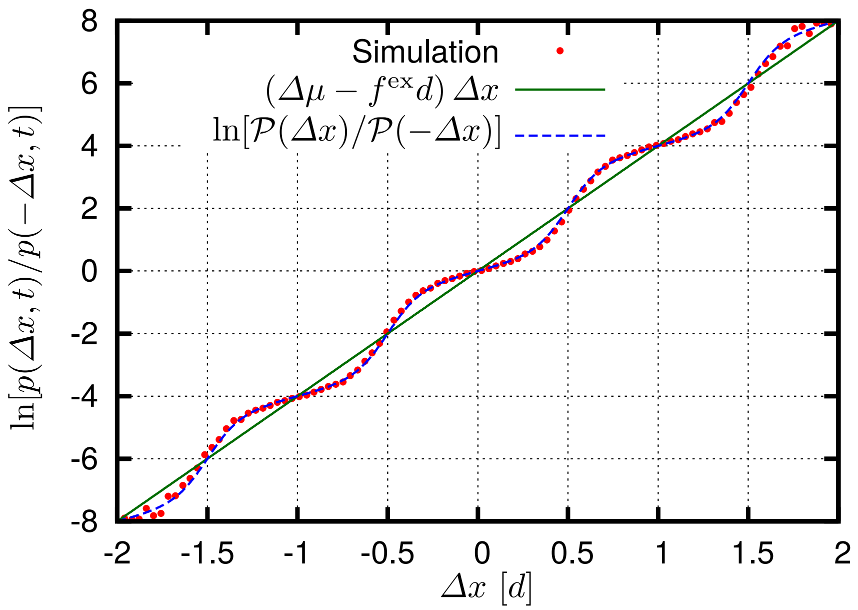
  - generating function $g(\lambda,y,t) \equiv \sum_{n=-\infty}^{\infty} \mathrm{e}^{\lambda n} p(n,y,t) \approx e^{\alpha_0(\lambda)t} Q(\lambda,y,y_0)$

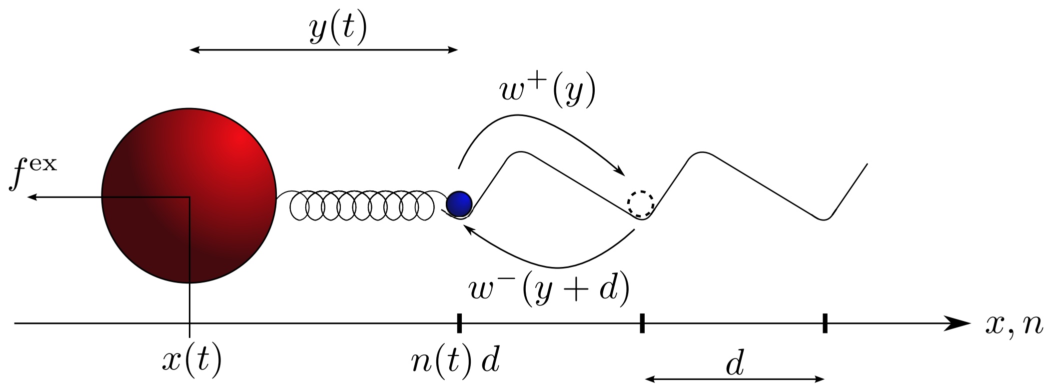
  - large deviation form with amplitude

$$p(n,y,t|y_0) \approx \mathrm{e}^{-th(n/t)} Q(\lambda(n/t),y,y_0)$$

  - rate function $h(u) \equiv u\lambda(u) - \alpha_0(\lambda(u))$

- Fine-structured fluctuation theorem





- for $t \to \infty$: discrete symmetry: $\mathcal{P}(\Delta x + m) = \mathrm{e}^{-\lambda_0 m}\mathcal{P}(\Delta x)$

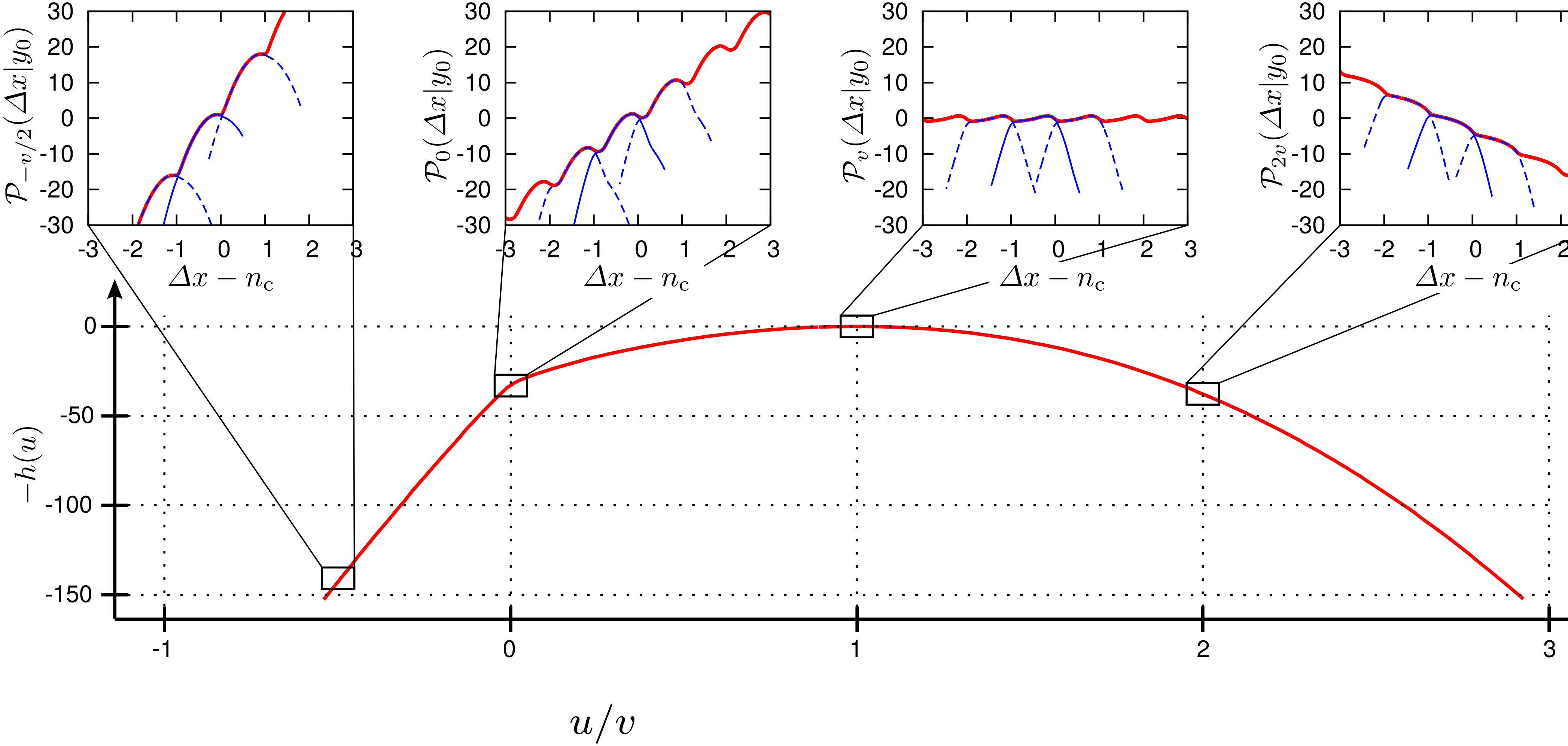
- $\ln \frac{\mathcal{P}(\Delta x)}{\mathcal{P}(-\Delta x)} = -2\lambda_0 \Delta x + \psi(\Delta x)$ with $\lambda_0 = -(\Delta\mu - f^{\mathrm{ex}} d)/2.$

  and periodic antisymmetric $\psi(\Delta x)$

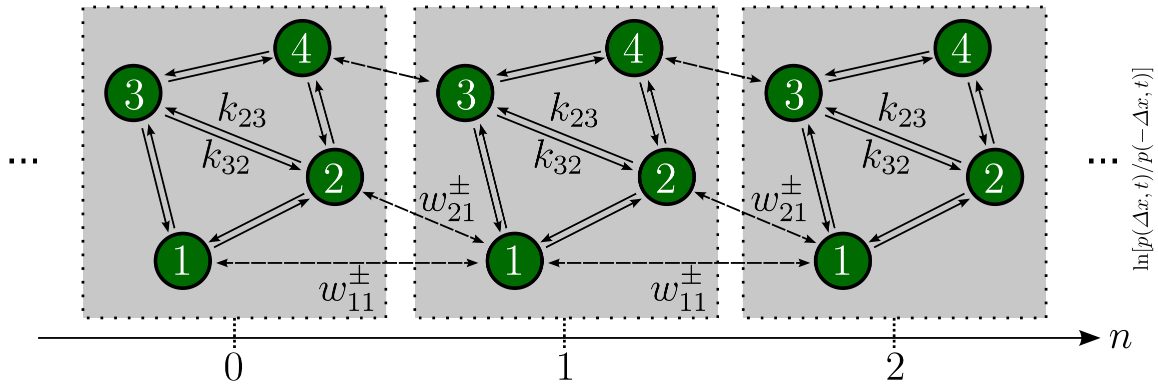
- slope at 0 not given by entropy production

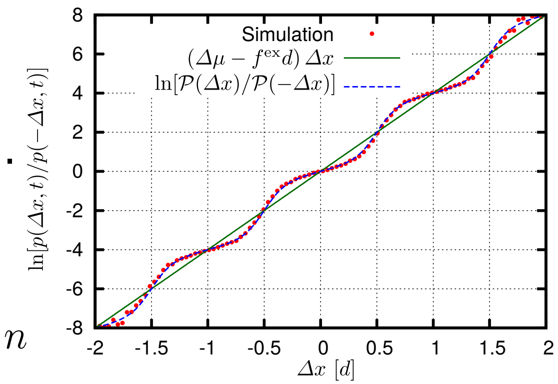
- "finite-difference slope" determines ent' production

- Fine structure at any "base point" $n_c = ut$



- Generalizations
  - fine structure holds for any model with spatial periodicity and hidden degrees of freedom

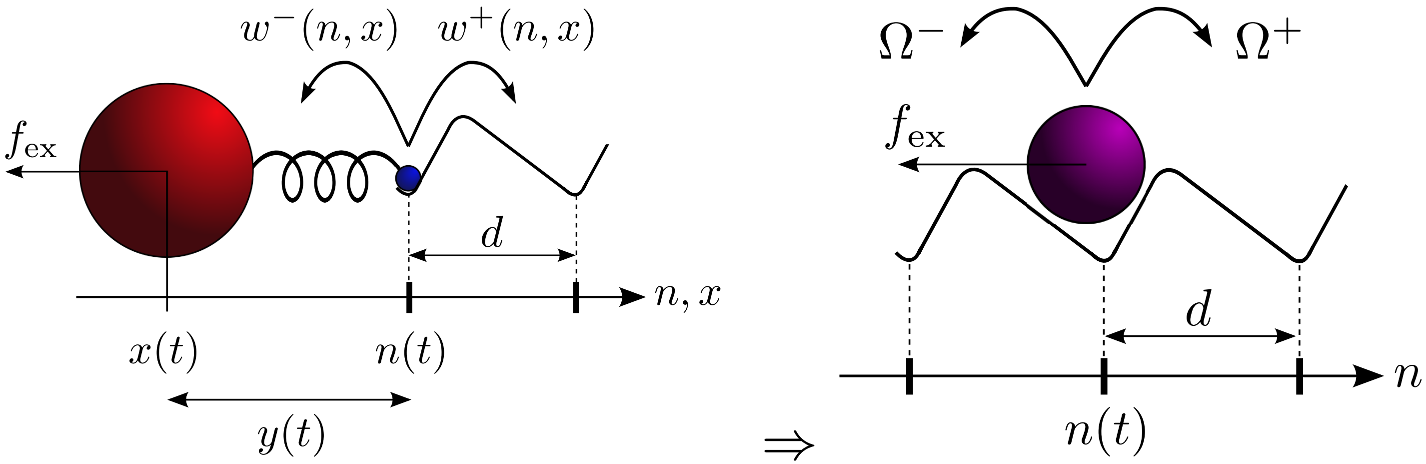




- Dynamically and thermod'y consistent coarse-graining of molecular motor models

  [E. Zimmermann and U.S., Phys Rev E 91, 022709, 2015]

  – one-state motor



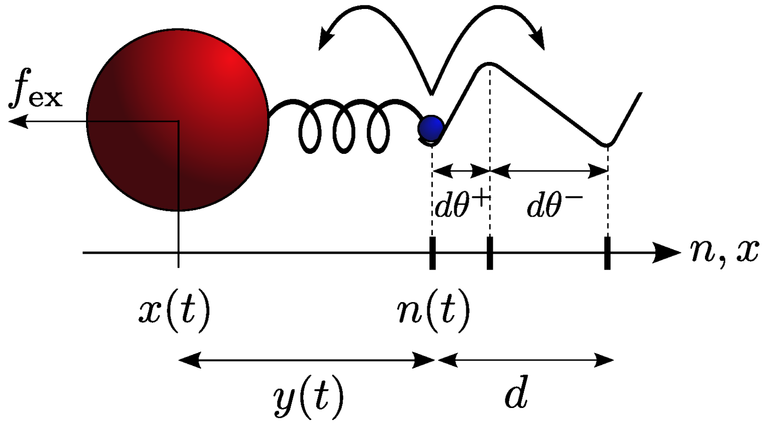
  – conditions: $v = d(\Omega^+ - \Omega^-)$ $\quad \frac{\Omega^+}{\Omega^-} = \exp[\Delta\mu - f_{\rm ex} d]$

  – coarse-grained rates

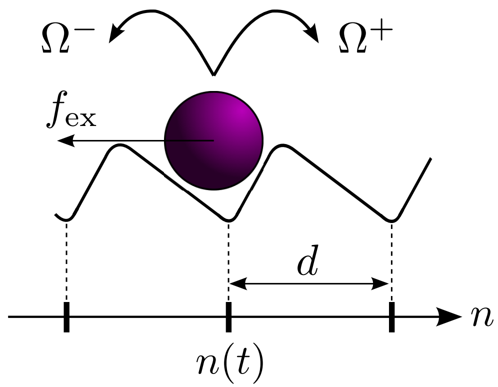
$$\Omega^+ = \frac{v \exp[\Delta\mu - f_{\rm ex} d]/d}{\exp[\Delta\mu - f_{\rm ex} d] - 1} \qquad \Omega^- = \frac{v/d}{\exp[\Delta\mu - f_{\rm ex} d] - 1}$$

- Coarse-graining versus traditional model

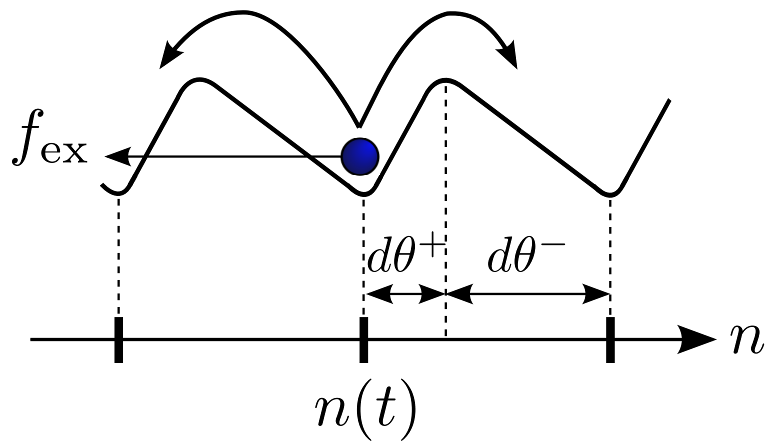
$$w^-(y) = k^- e^{\Delta V^-(y,\theta^-)} \quad w^+(y) = k^+ e^{-\Delta V^+(y,\theta^+)}$$



$\Downarrow$



$$\hat{w}^-(f_{\mathrm{ex}}) = k^- e^{f_{\mathrm{ex}} d\theta^-} \quad \hat{w}^+(f_{\mathrm{ex}}) = k^+ e^{-f_{\mathrm{ex}} d\theta^+}$$

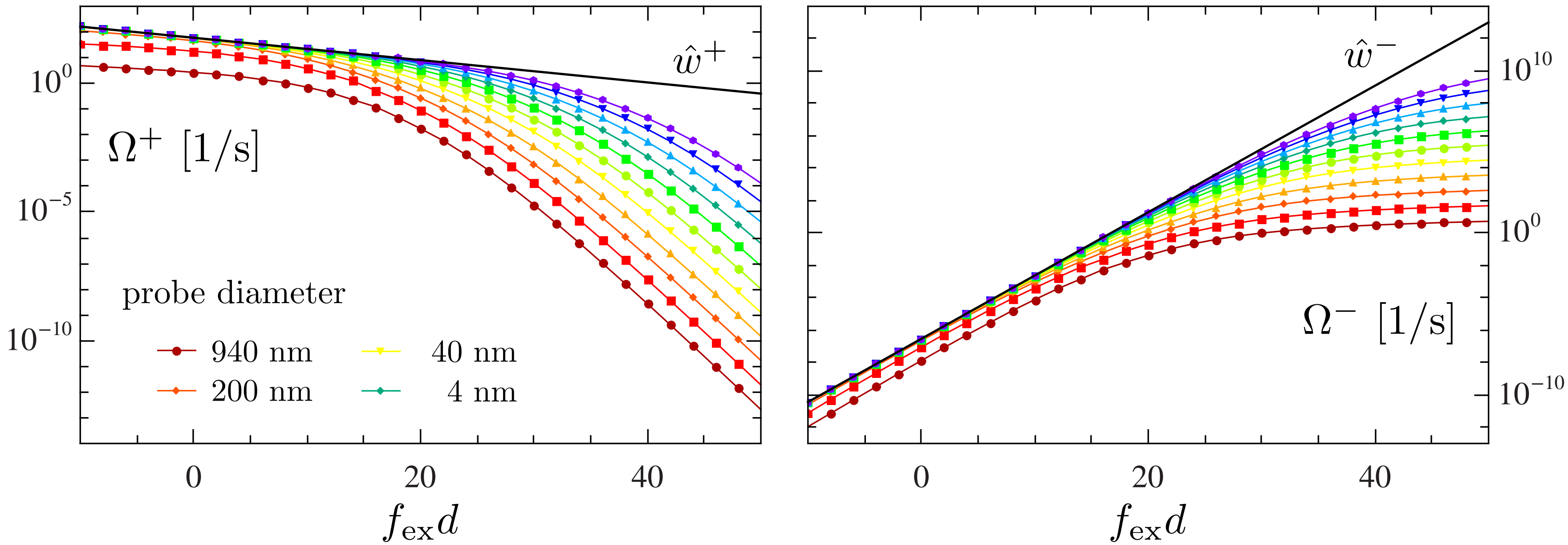


– probe particle omitted

– external force assumed to act directly on the motor

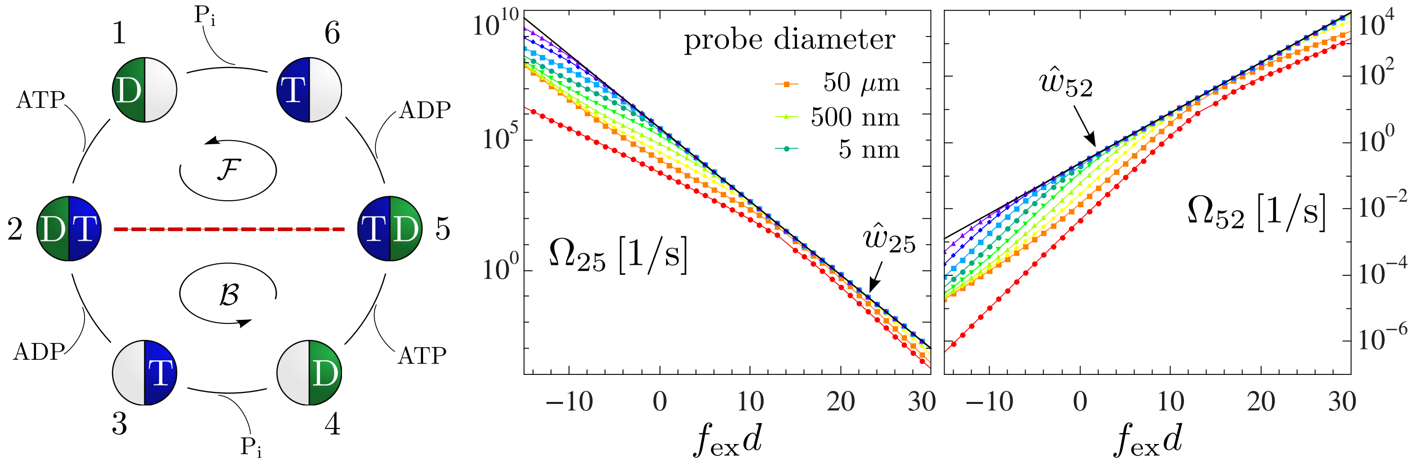
– exponential dependence of the rates on the external force

- Example: F_1-ATPase

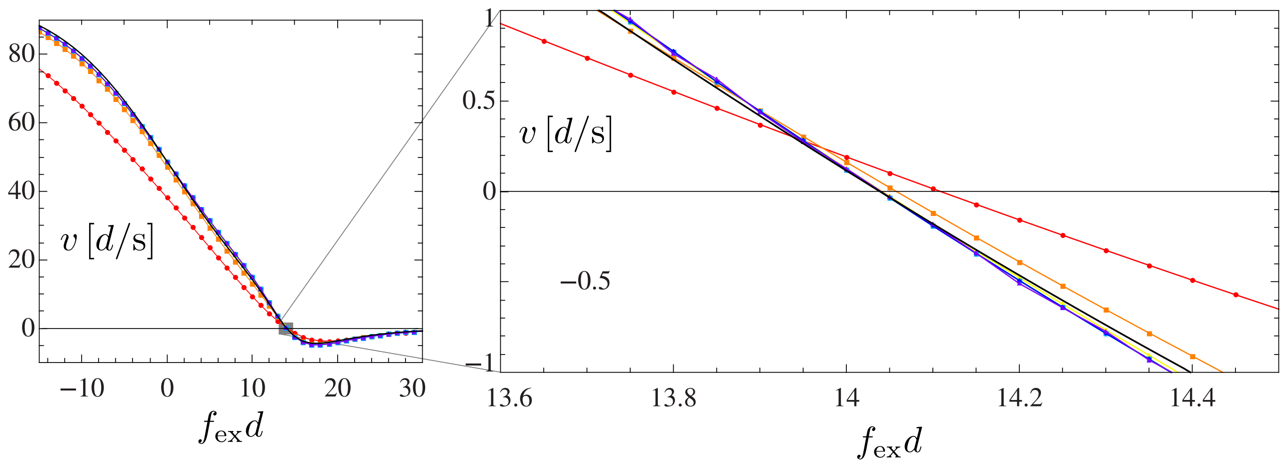


  - $\Omega^\pm$ approach $\hat{w}^\pm$ with decreasing probe size
  - non-exponential dependence of $\Omega^\pm$ on external force

- Coarse-graining multi-state models (Example: Kinesin)

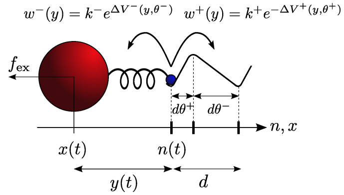


[S. Liepelt et al, PRL 98 (2007)]



– stall force depends on probe size

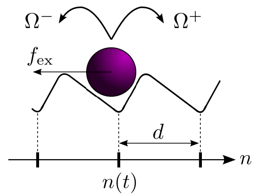
- Invariance of entropy production under coarse-graining



  – detailed model with explicit dynamics of the probe particle:

$$\dot{S}_{\text{tot}} = \underbrace{\sum_i \int \frac{\gamma j_i^{x2}}{p_i(y)} \mathrm{d}y}_{\text{probe}} + \underbrace{\sum_{i,j} \int p_i(y) w_{ij}(y) \ln \frac{p_i(y) w_{ij}(y)}{p_j(y+d_{ij}) w_{ji}(y+d_{ij})} \mathrm{d}y}_{\text{motor}}$$

$$= \sum_{i<j} \Delta\mu_{ij} j_{ij} - f_{\text{ex}} v$$



  – coarse-grained model:

$$\dot{S}_{\text{tot}} = \sum_{i,j} P_i \Omega_{ij} \ln \frac{P_i \Omega_{ij}}{P_j \Omega_{ji}} = \sum_{i<j} \Delta\mu_{ij} j_{ij} - f_{\text{ex}} v$$

  – entropy production is conserved

- Conclusions
  - Coarse-graining, in general, compromises the exact ST-relations
  - colloidal suspension:
    - * pseudo Crooks relation for coarse-grained work
    - * extension/relation to DFT?
  - colloids and molecular motors in a NESS
    - * FT-slope time-dependent for small t
    - * long-time asymptotics: fine structure with modulated slope
    - * th'dynamically and dyn'y consistent coarse-graining possible