# Stochastic thermodynamics

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thanks to:

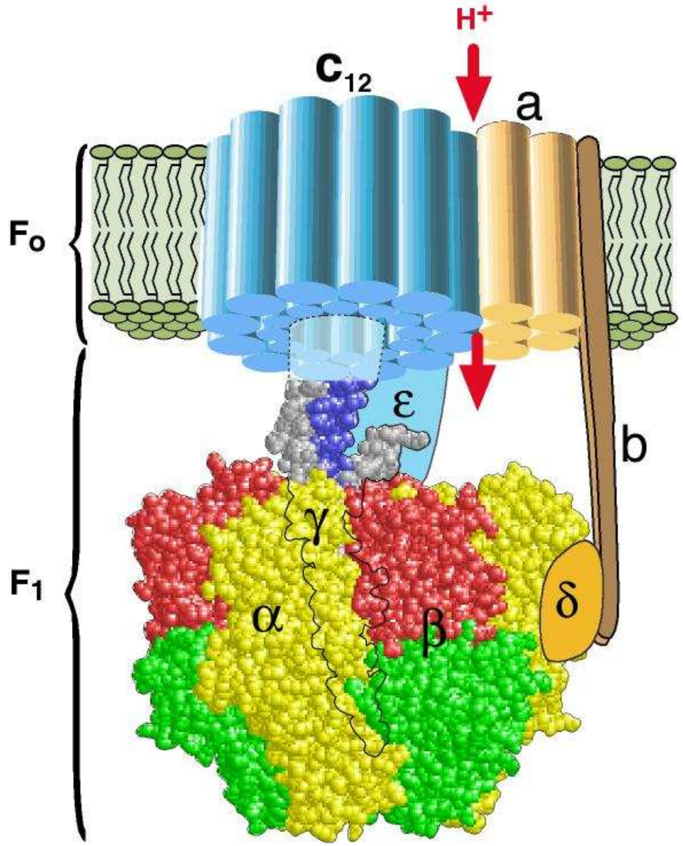
- F. Berger, J. Mehl, T. Schmiedl and Th. Speck (theory)
- V. Blickle and C. Bechinger (expt's on colloidal particles)
- C. Tietz, S. Schuler and J. Wrachtrup (expt's on single atoms)

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

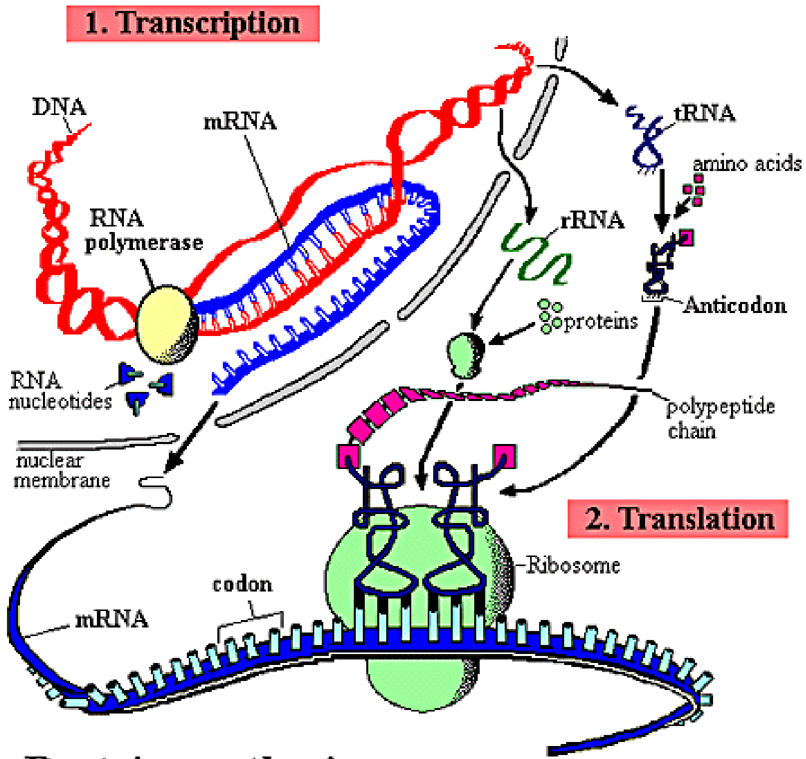
## LECTURE III

- Stochastic dynamics along discrete states
- Fluctuation theorems with examples
- Biochemically driven systems

- (Bio)chemically driven systems



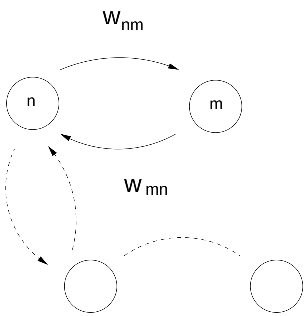

H. Wang and G. Oster (1998). Nature 396:279-282.




Protein synthesis

F1-ATPase

- Master equation dynamics on discrete states




states $\{n\}$ could be

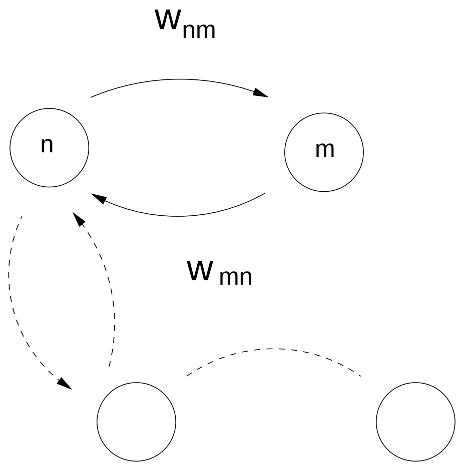
- internal states of a protein
- number of a species
- discrete spatial coordinate
- ....

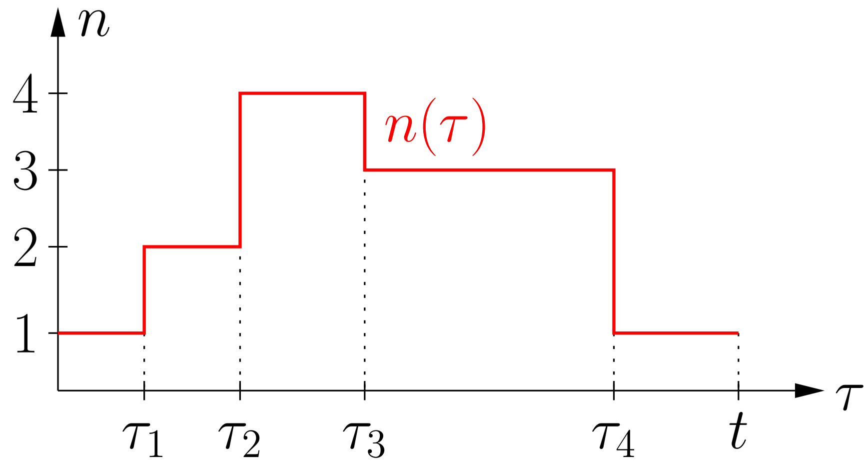
- time-dependent rates given by a "protocol" $\lambda(\tau)$
- $\partial_\tau p_n = \sum_m [w_{mn}(\lambda) p_m - w_{nm}(\lambda) p_n]$
- solution $p_n(\tau)$ depends on initial $p_n(0)$
- unique stationary solution $p_n^s(\lambda)$ for any fixed $\lambda$
  - ∗ detailed balanced

    $p_n^s w_{nm} = p_m^s w_{mn} \rightarrow \frac{w_{nm}}{w_{mn}} = \exp(E_n - E_m)$ 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 $\tau_j$ 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

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

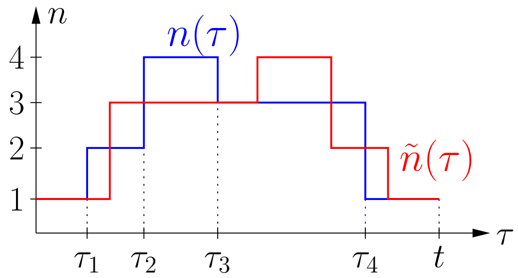
- equation of motion

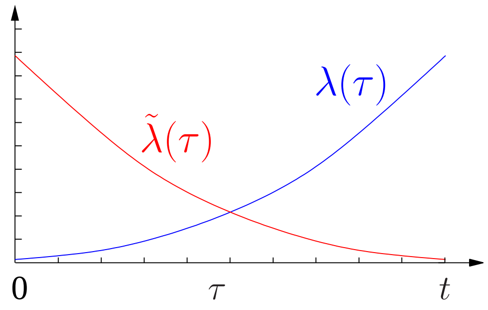
$$\dot{s}(\tau) = -\frac{\partial_\tau p_n(\tau)}{p_n(\tau)}\Big|_{n(\tau)} - \sum_j \delta(\tau-\tau_j) \ln \frac{p_{n_j^+}(\tau_j)}{p_{n_j^-}(\tau_j)}$$

$$= \underbrace{-\frac{\partial_\tau p_n(\tau)}{p_n(\tau)}\Big|_{n(\tau)} - \sum_j \delta(\tau-\tau_j) \ln \frac{p_{n_j^+} w_{n_j^+ n_j^-}}{p_{n_j^-} w_{n_j^- n_j^+}}}_{\equiv \; \dot{s}_{\text{tot}}(\tau)} + \underbrace{\sum_j \delta(\tau-\tau_j) \ln \frac{w_{n_j^+ n_j^-}}{w_{n_j^- n_j^+}}}_{\equiv \; -\dot{s}_{\text{m}}(\tau)}$$

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

- "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

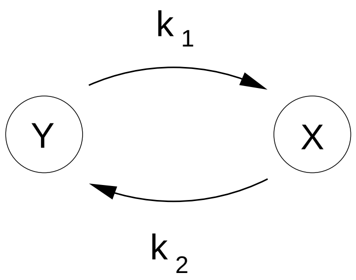
$$
\begin{aligned}
1 &= \sum_{\tilde{n}(\tau),\tilde{n}_0} \tilde{p}[\tilde{n}(\tau)|\tilde{n}_0]\; p_1(\tilde{n}_0) \\
&= \sum_{n(\tau),n_0} p[n(\tau)|n_0]\; p_0(n_0) \frac{\tilde{p}[\tilde{n}(\tau)|\tilde{n}_0]\; p_1(\tilde{n}_0)}{p[n(\tau)|n_0]\; p_0(n_0)} \\
&= \langle \exp[-\Delta s_{\mathrm{m}} + \ln p_1(n_t)/p_0(n_0)] \rangle
\end{aligned}
$$

- choice 1: $p_1(n) = p(n,t) \quad \Rightarrow \quad \boxed{\langle \exp[-\Delta s_{\mathrm{tot}}] \rangle = 1 \quad \Rightarrow \langle \Delta s_{\mathrm{tot}} \rangle \geq 0}$
  - 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 $\boxed{p(-\Delta s_{\mathrm{tot}})/p(\Delta s_{\mathrm{tot}}) = \exp(-\Delta s_{\mathrm{tot}})}$

## Illustration: Birth-death or chemical master equations

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

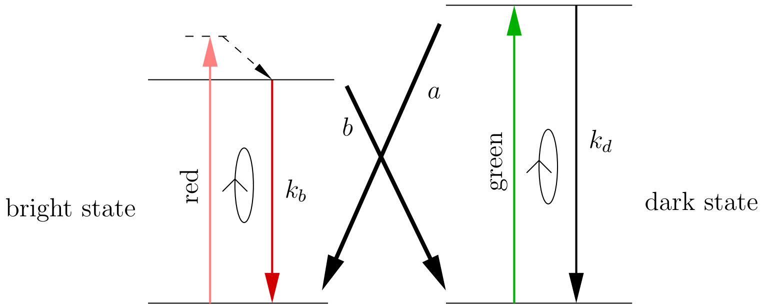
- Simplest case: Isomerization

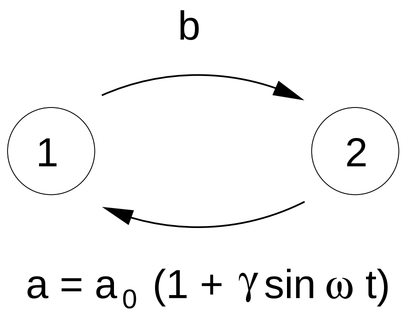



  - $n_X \equiv n = N - n_Y$
  - $q(\tau) \equiv k_1(\tau)/k_2(\tau)$
  - stationary distribution: $p^s(n) = [q/(1+q)]^N \binom{N}{n}$
  - stationary mean $n^s = Nq/(1+q)$
  - $\left\langle \exp\{\int_0^t d\tau \underbrace{[n(\tau) - n^s(\tau)]}_{\text{non-eq lag}} \frac{d}{d\tau} \ln q(\tau)\} \right\rangle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

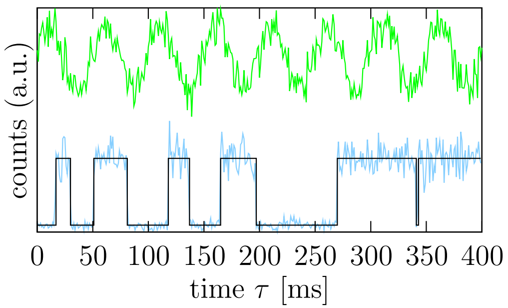
# Periodically driven system: Optically active defect center in diamond

[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]



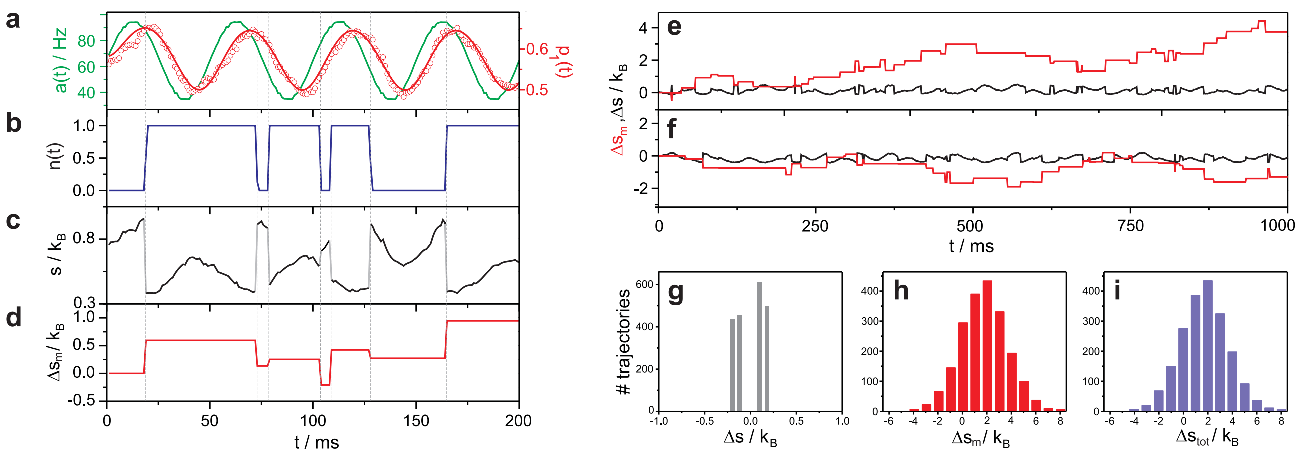




- Trajectories



- Entropy production along a single trajectory

Figure 1




- Int FT

Det FT

Figure 2

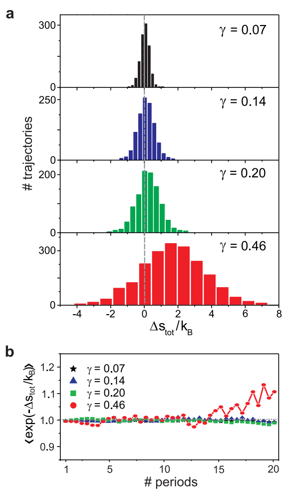
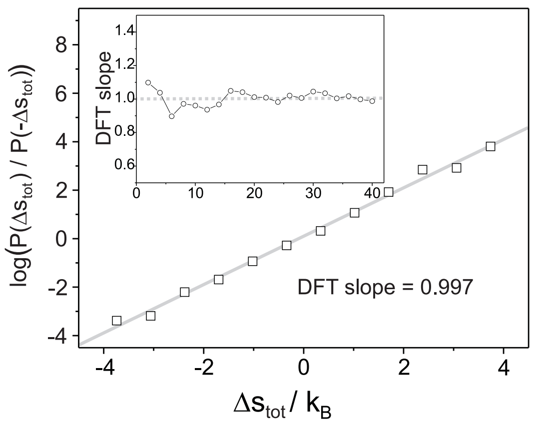


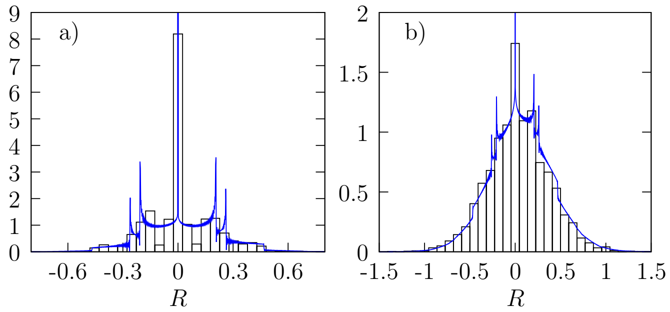

Figure 3



- Generalized JR:

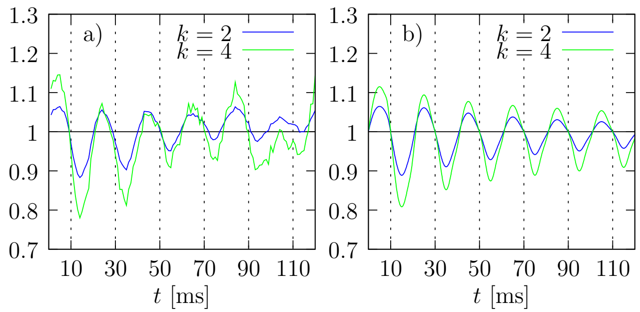
  $\langle \exp[-R] \rangle = 1$ for $R[n(\tau)] \equiv -\int_o^t d\tau \dot{\lambda} \partial_\lambda \ln p^s_{n(\tau)}(\lambda) \quad (= W - \Delta F)$

  probability distribution $p(R)$



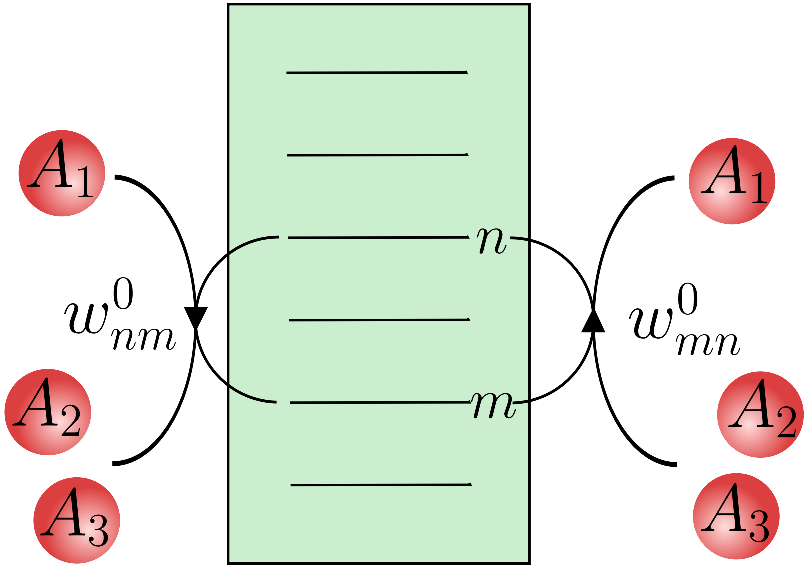

- Detailed theorem for symmetric protocols $\lambda(\tau) = \lambda(t-\tau)$:

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



- Stochastic th'dynamics of a driven enzym with internal states

  [T.Schmiedl, T.Speck and U.S., J. Stat. Phys. **128**, 77 (2007)]

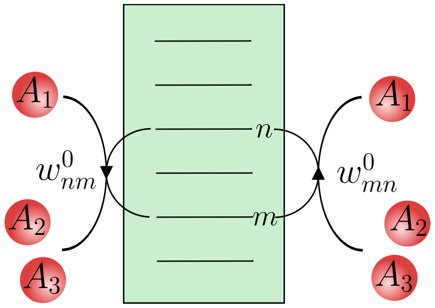



$$A_1 + n \underset{w_{mn}}{\overset{w_{nm}}{\rightleftharpoons}} m + A_2 + A_3$$

  - Green enzym
    * internal states with energy $E_n$
  - Red species
    * fixed (non-equilibrium) chemical potential

$$\mu = \mu^0_\alpha + \ln\left\{[A_\alpha]/c^0\right\} = E_\alpha + \ln\{[A_\alpha]\omega_\alpha\}$$

- Mass action law kinetics




$$A_1 + n \underset{w_{mn}}{\overset{w_{nm}}{\rightleftharpoons}} m + A_2 + A_3$$

– $\frac{w_{nm}}{w_{mn}} = \frac{w^0_{nm}}{w^0_{mn}}[A_1]/[A_2][A_3]$

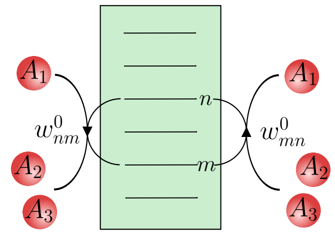
– in hypothetical eq.: $\frac{w^{\text{eq}}_{nm}}{w^{\text{eq}}_{mn}} = \frac{w^0_{nm}}{w^0_{mn}}\{[A_1]/[A_2][A_3]\}^{\text{eq}} = \frac{p^{\text{eq}}_m}{p^{\text{eq}}_n} = \exp(-\Delta G)$

with $\Delta G \equiv -[E_n - E_m + \{\mu_1 - \mu_2 - \mu_3\}^{\text{eq}}]$

and $\mu^{\text{eq}}_\alpha \equiv E_\alpha + \ln\{[A_\alpha]^{\text{eq}}\omega_\alpha\}$

– Ratio of intrinsic rates: $\frac{w^0_{nm}}{w^0_{mn}} = \frac{\omega_1}{\omega_2\omega_3}\exp[E_n - E_m + (E_1 - E_2 - E_3)]$
relation between the bare rates and the energy is indep't of $[A_\alpha]$

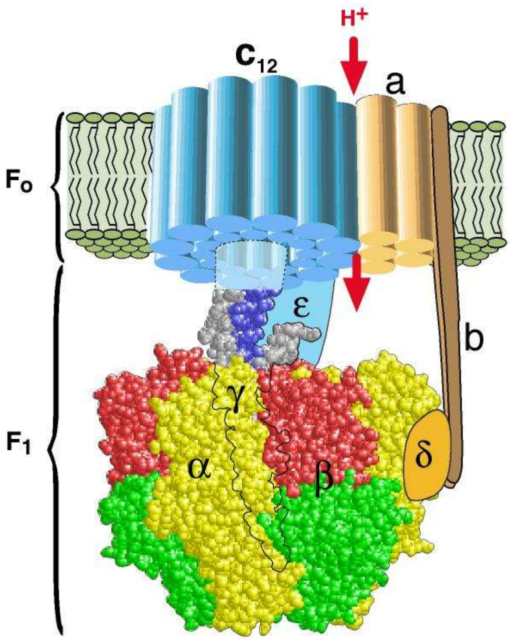
- First law along stochastic trajectory




$w = \Delta E + q$ for a single step

- chemical work: $w^{nm}_{\text{chem}} \equiv \mu_1 - \mu_2 - \mu_3$
- internal energy: $\Delta E^{nm} \equiv E_m - E_n$
- dissipated heat: $q^{nm} \equiv w^{nm}_{\text{chem}} - \Delta E^{nm} = \ln \frac{[A_1]}{[A_2][A_3]} \frac{w^0_{nm}}{w^0_{mn}}$
- previous abstract definition: $\Delta s^{nm}_m \equiv \ln w_{nm}/w_{mn} = q^{nm}$
- abstract approach consistent with usual phys chem
- can be summed over full reaction history

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

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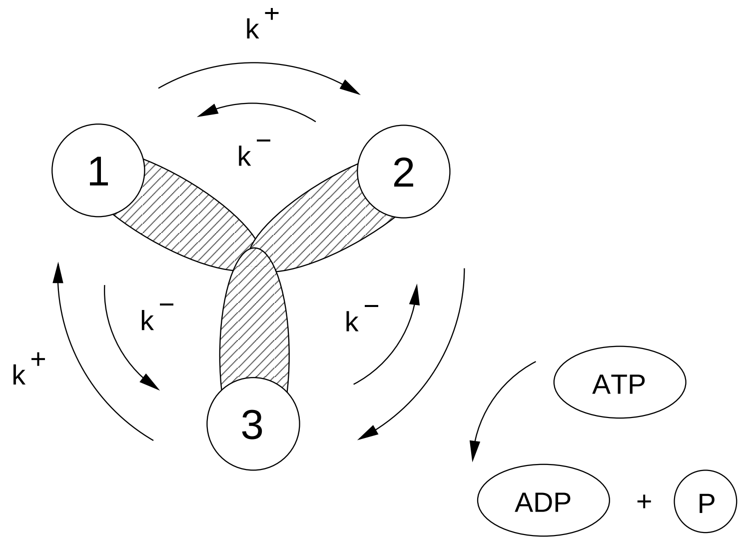
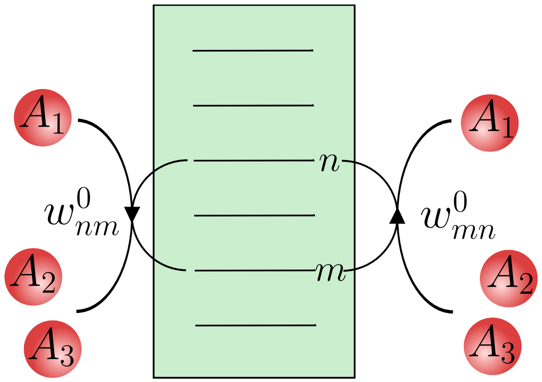


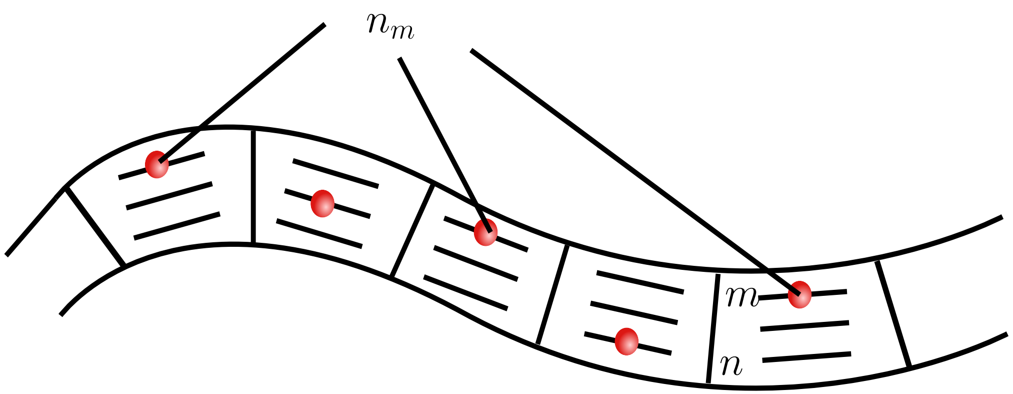

– $\partial_\tau p_1 = -(k^+ + k^-)p_1 + k^+ p_2 + k^- p_3$ & cyc

– $\Delta s_{\text{tot}} = n \ln(k^+/k^-) = n[\mu_{ATP} - \mu_{ADP} - \mu_P]/T$

– $\boxed{p(-n)/p(n) = \exp[-n \ln(k^+/k^-)]}$

- Degeneracy

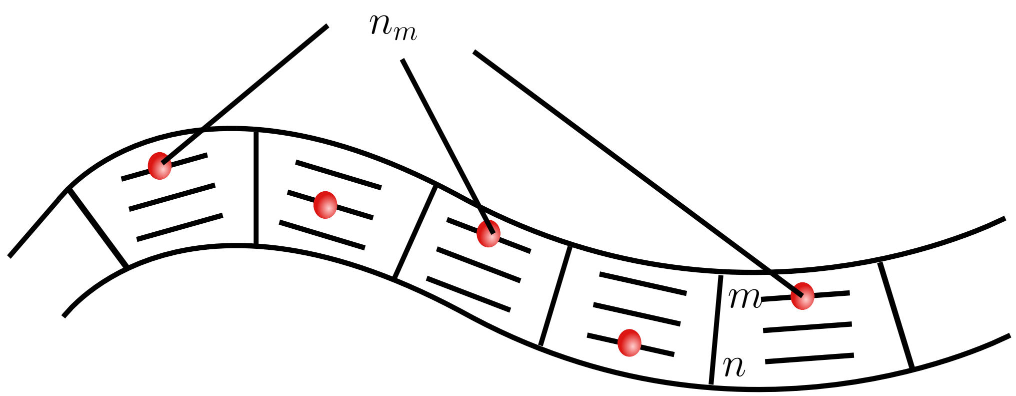



$N$ of those OR N-domain protein/...

  - $\mathbf{n}(\tau) = (n_1(\tau), n_2(\tau), ..., n_M(\tau))$
  - for $n_n \to n_n - 1, \quad n_m \to n_m + 1$ $\qquad \frac{W_{nm}}{W_{mn}} = \frac{w_{nm} n_n}{wmn(n_m+1)}$
  - heat released $\Delta s^{nm}_m = \ln \frac{w_{nm}}{w_{mn}}$ as before
  - but: $\Delta s^{nm}_m = \ln \frac{W_{nm}}{W_{mn}} = \ln \frac{w_{nm}}{w_{mn}} + \ln\left[n_n/(n_m + 1)\right]$
  - an apparent inconsistency?

- Degeneracy cont'd

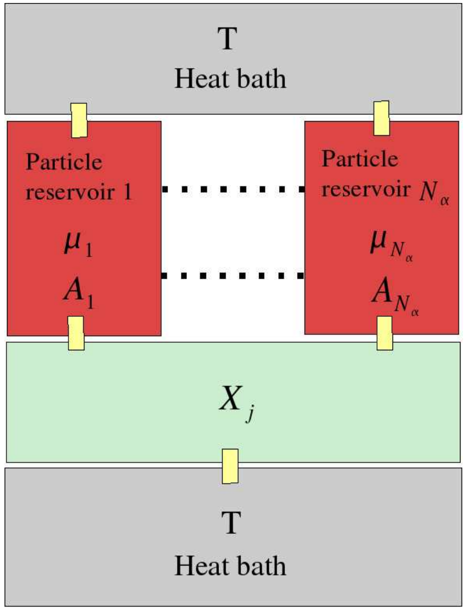



- for $n_n \to n_n - 1, \quad n_m \to n_m + 1$ $\qquad \frac{W_{nm}}{W_{mn}} = \frac{w_{nm} n_n}{wmn(n_m+1)}$
- heat released $\Delta s_m^{nm} = \ln \frac{w_{nm}}{w_{mn}}$ as before
- but: $\Delta s_m^{nm} = \ln \frac{W_{nm}}{W_{mn}} = \ln \frac{w_{nm}}{w_{mn}} + \ln\left[n_n/(n_m + 1)\right]$

- solution
  - $s^{\mathbf{n}} = s_0^{\mathbf{n}} + \ln g^{\mathbf{n}}$
  - $\Delta s_m^{\mathbf{nn}'} \equiv \Delta s_{m0}^{\mathbf{nn}'} - \ln(g^{\mathbf{n}}/g^{\mathbf{n}'})$
  - FT's for $\Delta s_{\text{tot}}$ remain valid

- Stochastic th'dynamics of general (bio)chemical reaction networks

  [ T. Schmiedl and U.S., J. Chem. Phys. 126, 044101, 2007]

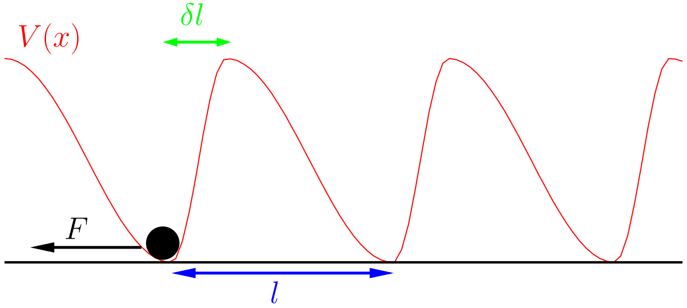



$$r_\alpha^\rho A_\alpha + p_j^\rho X_j \rightleftharpoons s_\alpha^\rho A_\alpha + q_j^\rho X_j$$

  – two sorts of species:
    * chemiostated $A_\alpha$ (like ATP, ADP, ...)
    * number-tracked $X_j$ with $n_j(\tau)$
  – energy and entropy along a trajectory $\{n_j(\tau)\}$

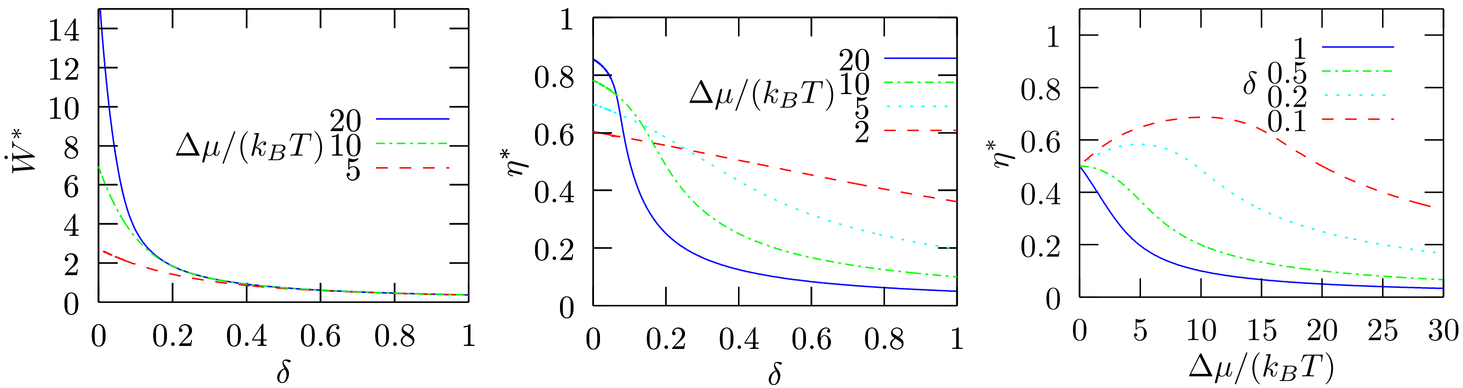
- Efficiency of molecular motors at maximum power

[T. Schmiedl and U.S., EPL 83: 30005, 2008]




$$w^+ = [ATP]k^+ \exp[-\delta l\ F]$$

$$w^- = [ADP][P]k^- \exp[(1-\delta)l\ F]$$




- "Power stroke" ($\delta \simeq 0$) highest efficiency at max power
- $\eta^*$ can increase beyond lin response regime ($\eta^* = 1/2$)

- **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 (conc. done, pract. open)
    * stochastic field theories (like KPZ-eq)
    * quantum systems (JR done, DFT open)
    * ...