Master equations, coarse graining and entropy production

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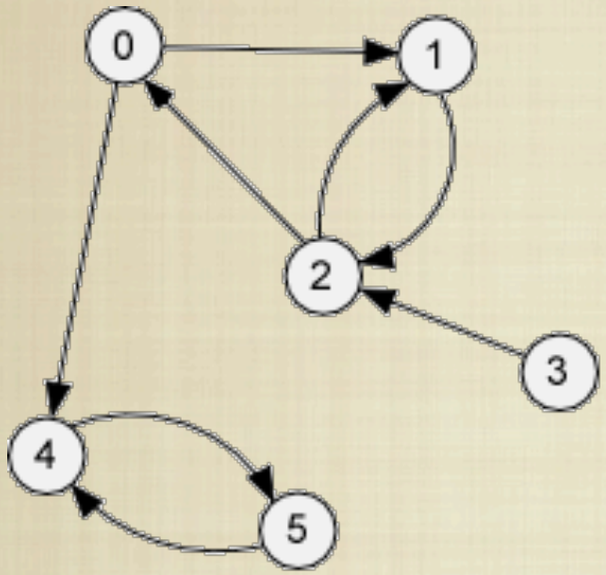
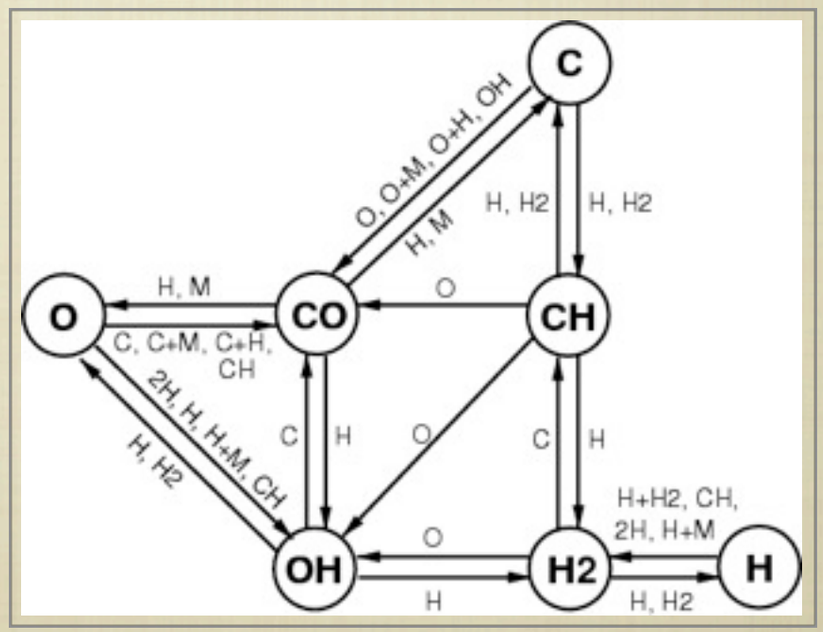
with: A. Puglisi, L . Rondoni, A. Vulpiani

Master Equations

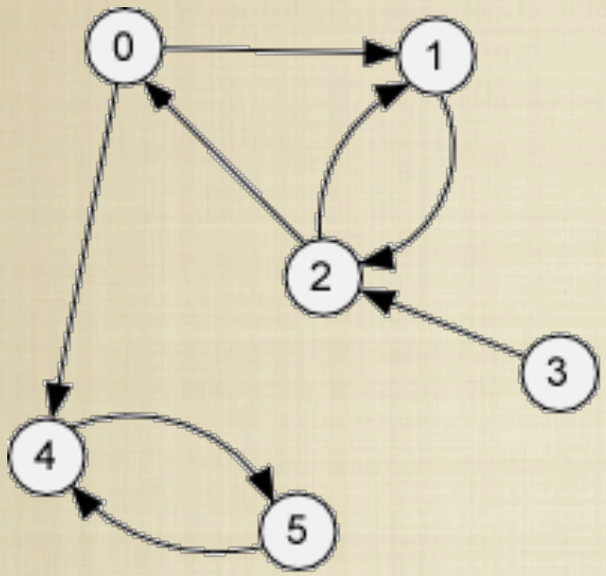


$$\frac{d}{dt}P_n = \sum_M (W_{mn}P_m - W_{nm}P_n)$$

- Discrete state stochastic system
- Relevant in biophysics and chemistry
  (when systems are well mixed but numbers are low)



Master Equations



$$\frac{d}{dt}P_n = \sum_M (W_{mn}P_m - W_{nm}P_n)$$

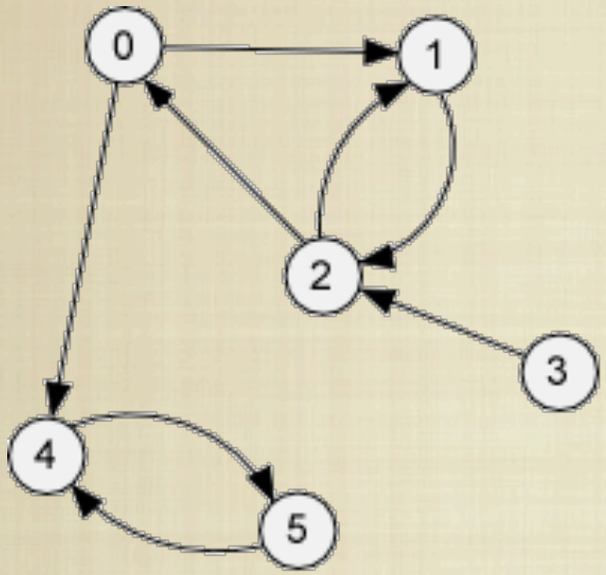
- Efficient to simulate (Gillespie algorithm)

  Generate a trajectory by:

  - drawing the random time of permanence in a given state
  - drawing the next state with the proper probability

- Less efficient when multiple timescales are present

FAST VS SLOW STATES

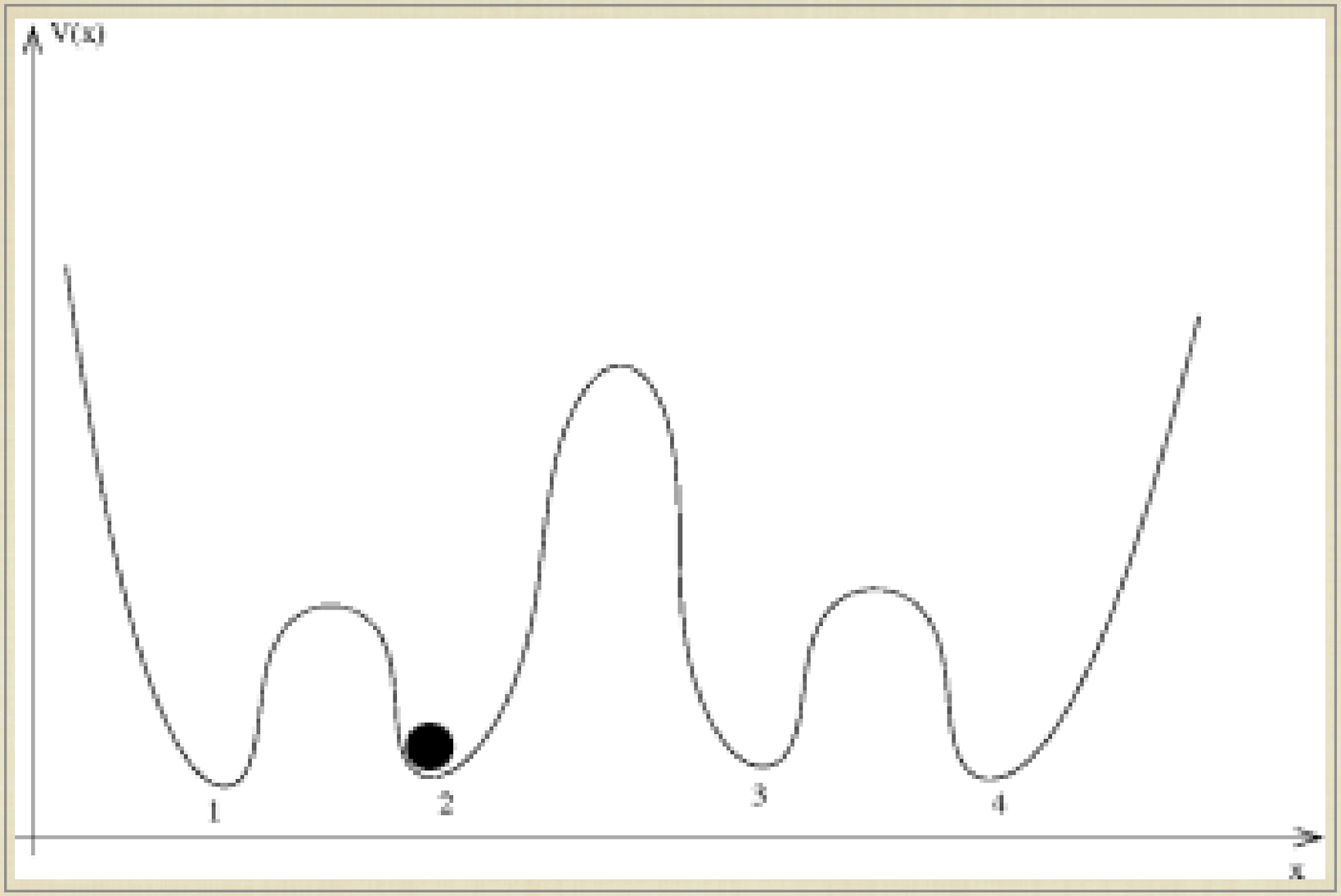


$$\frac{d}{dt}P_n = \sum_M (W_{mn}P_m - W_{nm}P_n)$$

- Markov -> lifetime of states is well defined $\tau_n = \frac{1}{\sum_k W_{nk}}$

- How to eliminate fast states from the description?

Pictorially:



large state description clumping 1 with 2 and 3 with 4

EXISTING METHODS

- Principal components (reduce the matrix by eliminating large eigenvalues)

- Steady state approximations

- Mixed multiscale methods (consider some degrees of freedoms as continuous)

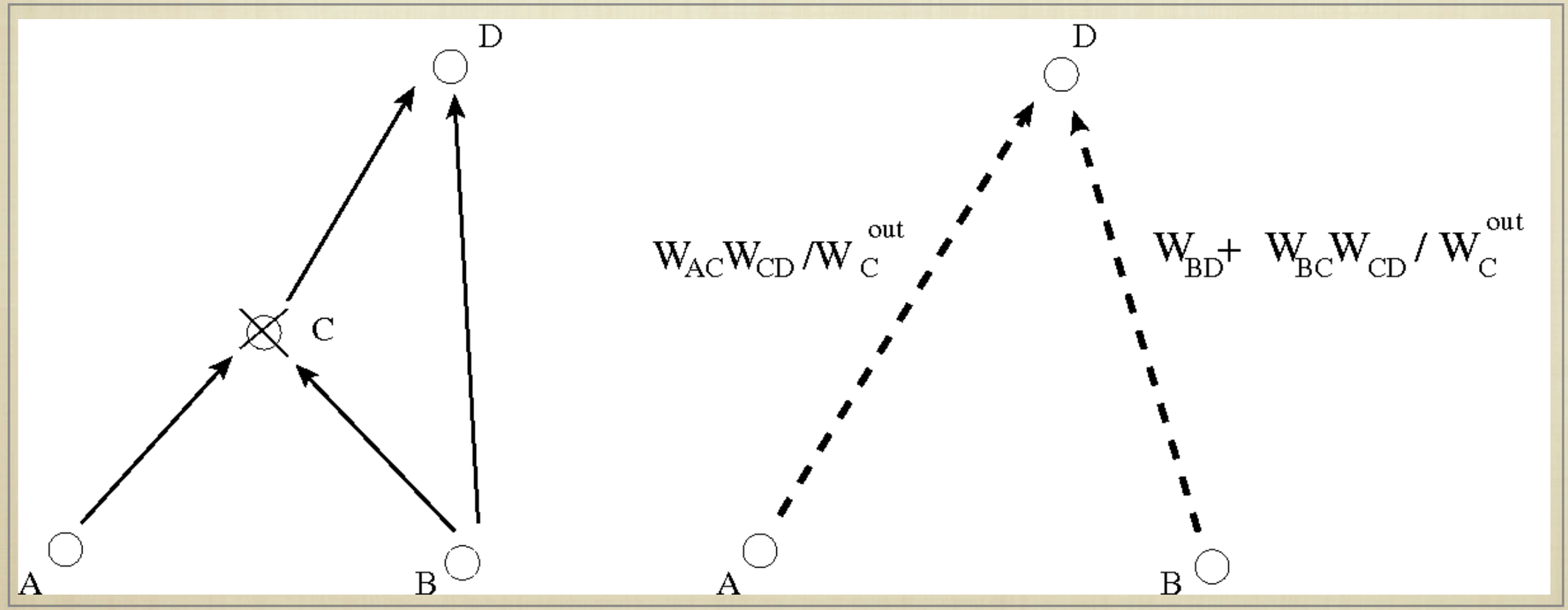
Gfeller and De Los Rios (2007), Rao and Arkin (2003), Haseltine and Rawling (2002)

COARSE GRAINING RECIPE

ANSATZ: TIME SPENT IN FAST STATES = 0

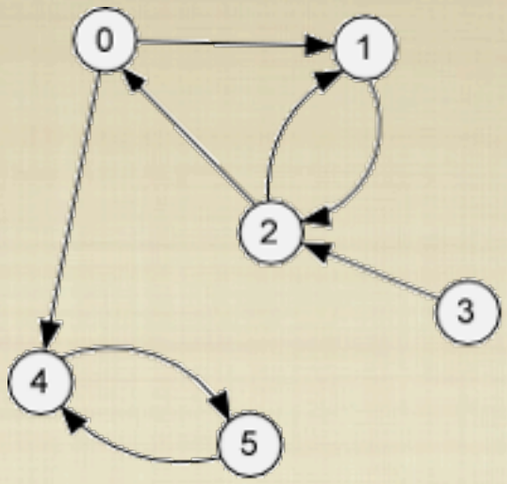
- decimate “fast” states
- renormalize other transitions

$$W^R_{kj} = W_{kj} + W_{kn}\frac{W_{nj}}{W^{out}_n}$$

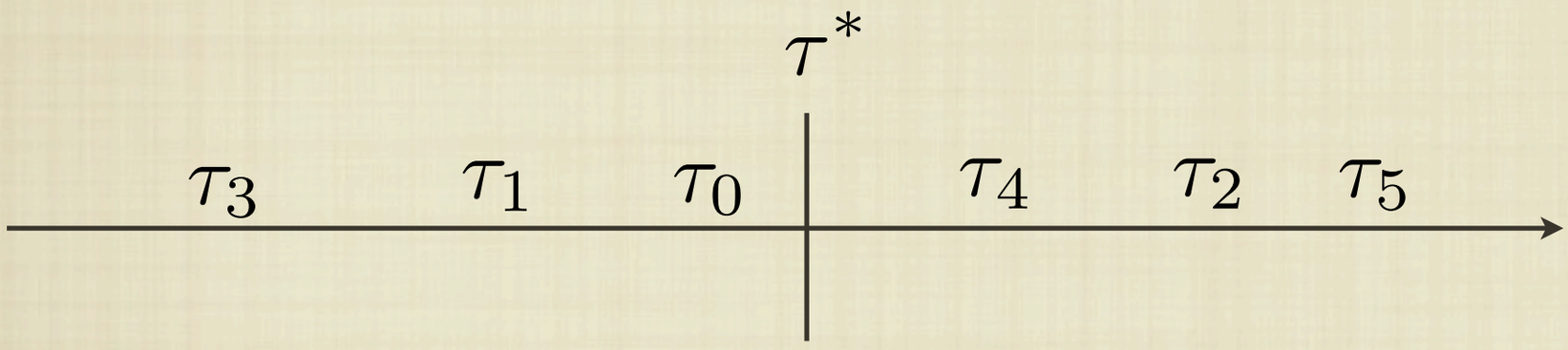


SP AND A. VULPIANI, J. CHEM. PHYS. (2008)

COMMUTATIVITY

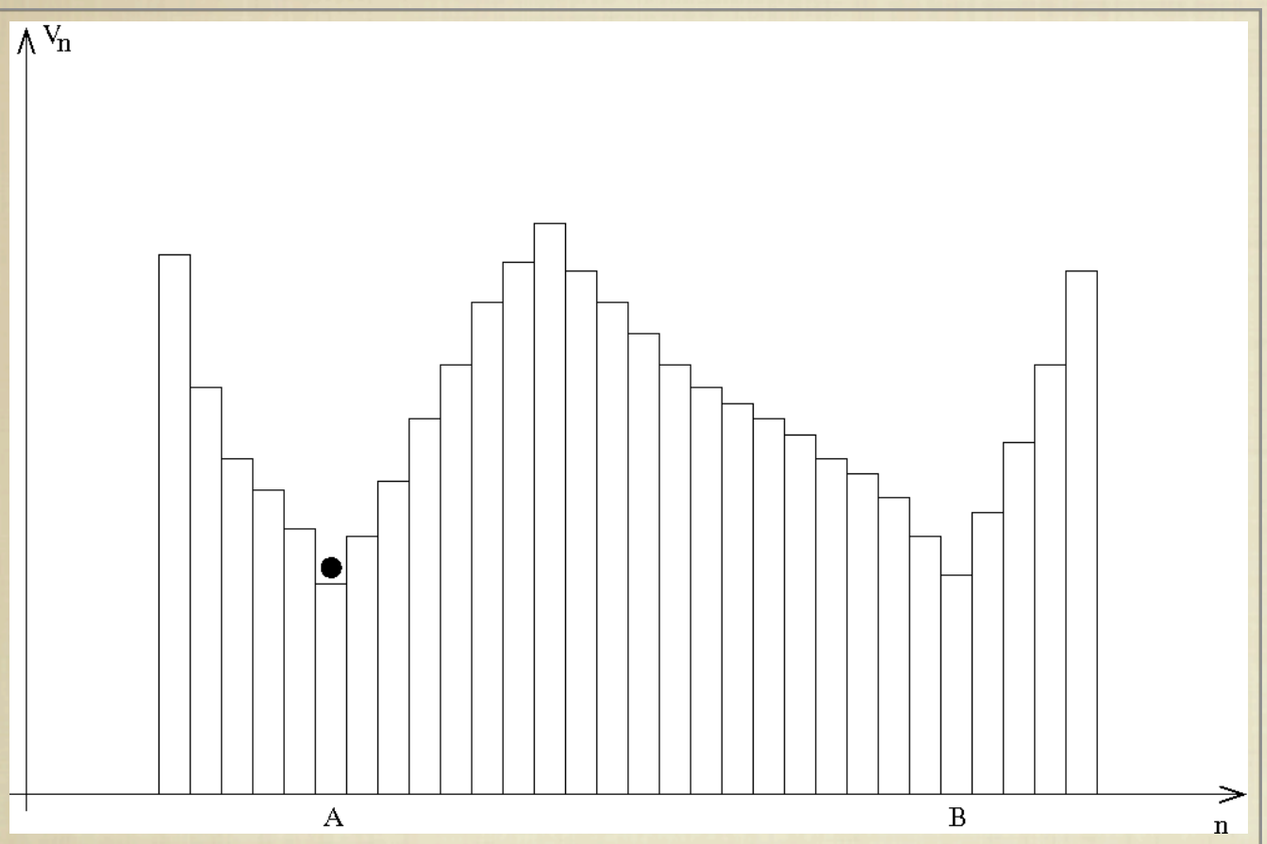


$$\tau_n = \frac{1}{\sum_k W_{nk}}$$ CHANGE DURING SEQUENCIAL DECIMATION



IF FAST STATES ARE DEFINED UNAMBIGUOSLY,
THE DECIMATION PROCEDURE IS COMMUTATIVE

EXAMPLE: ESCAPE RATE



$$W_{j\to j\pm1} = \exp\left[\frac{\beta}{2}(V_j - V_{j\pm1})\right]$$

$$W^R_{A\to B} = \frac{W_{A\to A+1}W_{A+1\to A+2}\cdots W_{A+N\to B}}{W^{out,R}_{A+1}W^{out,R}_{A+2}\cdots W^{out,R}_{A+N}}$$

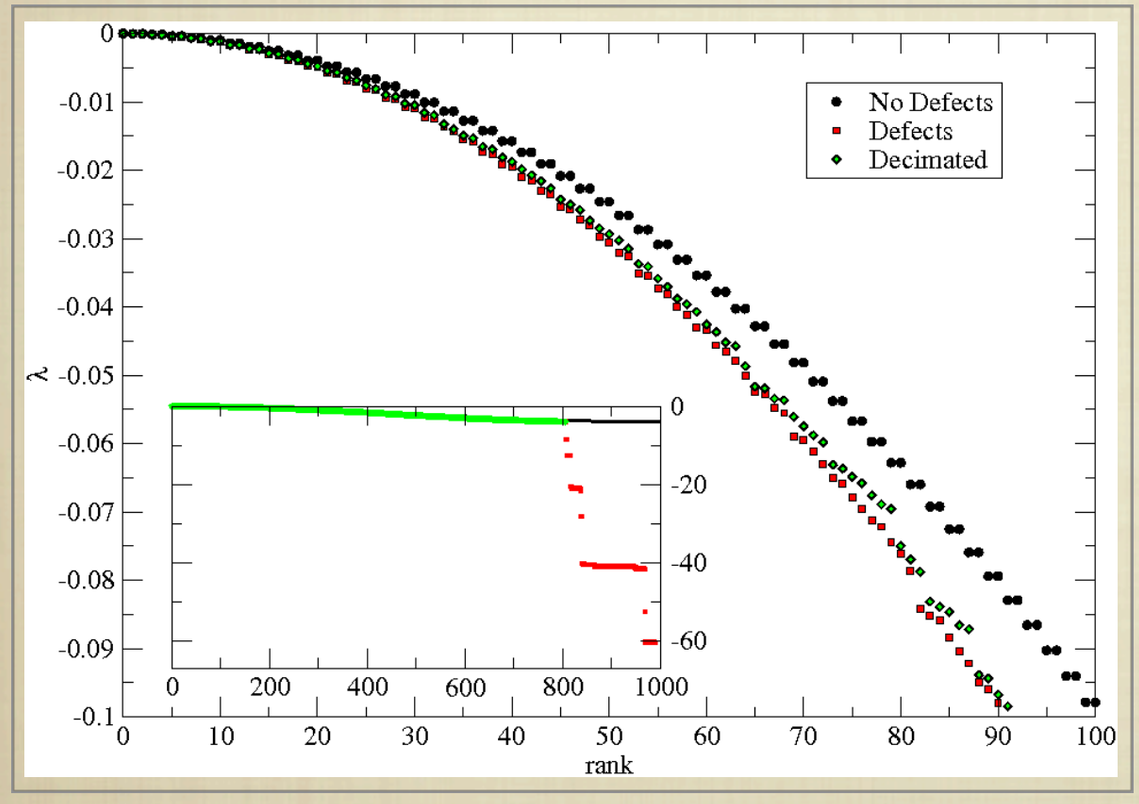
RESULT: $$W^R_{A\to B} = \frac{1}{\sum_{j=0}^{N}\exp[\frac{\beta}{2}(V_{A+j}+V_{A+j+1})]} \sim \frac{1}{\sum_{j=0}^{N}\exp(\beta V_{A+j})}$$

EXAMPLE/2: RW WITH DEFECTS

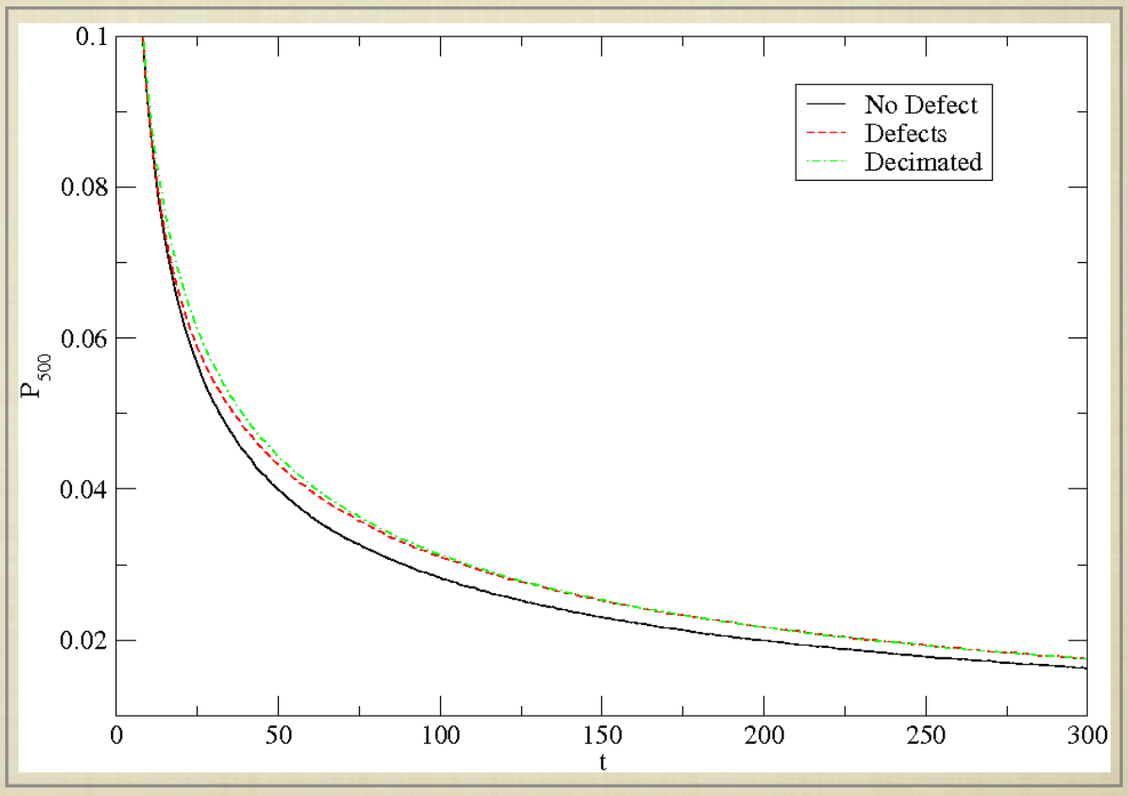
- $N = 10^3$ STATES ON A LINEAR CHAIN

- RATES: $W_{n,n-1} = W_{n,n+1} = 1$ OR

$W_{n,n-1} = W_{n,n+1} = 20$ WITH PROB. P QUENCHED



EIGENVALUES



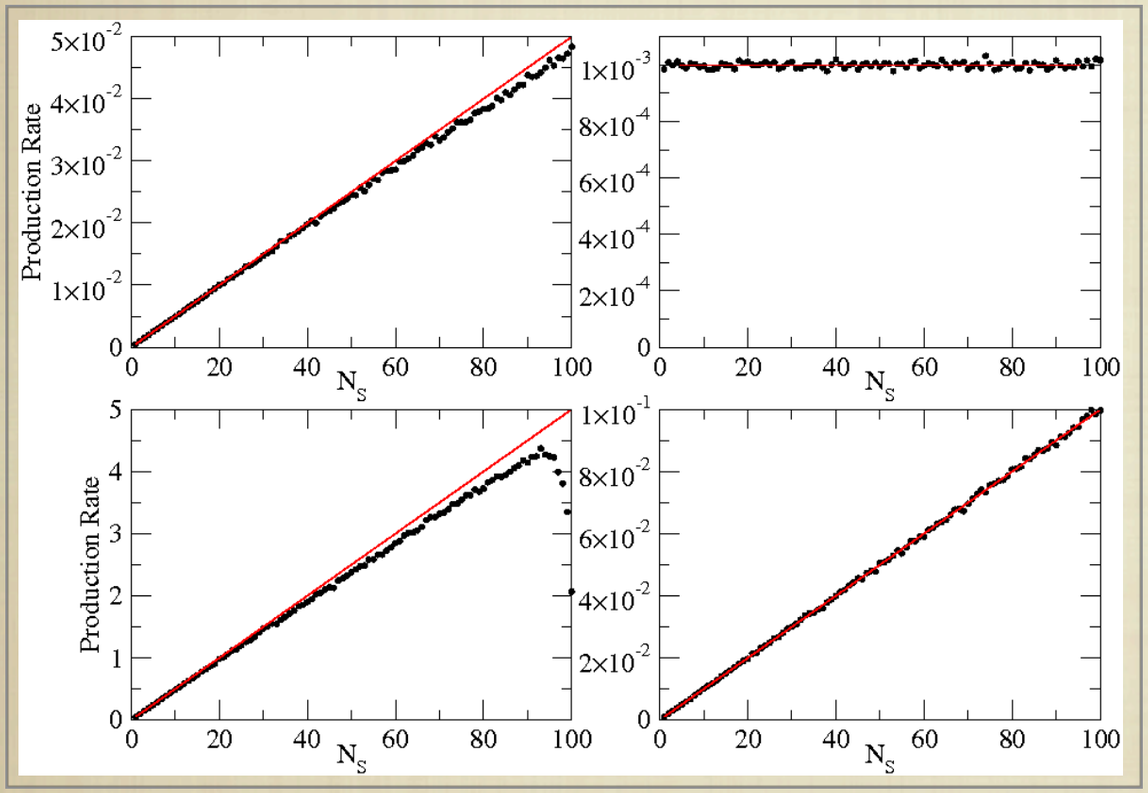
DECAY OF CORRELATION FUNCTIONS

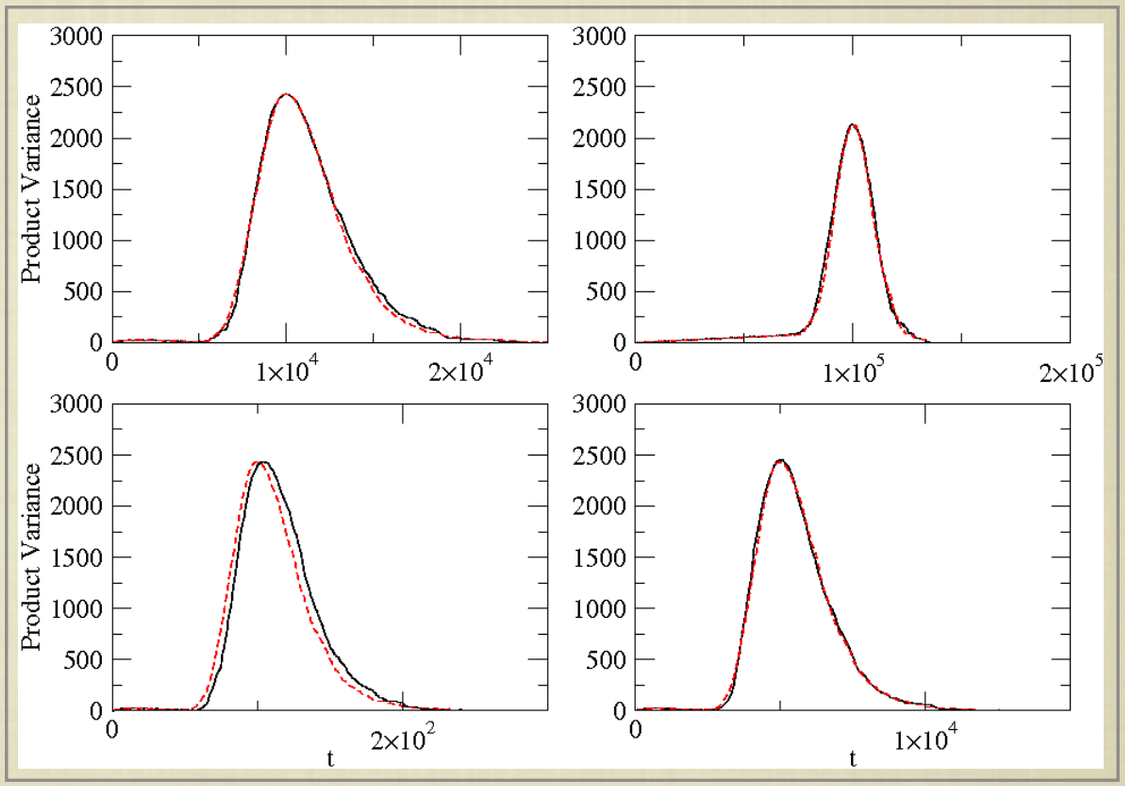
EXAMPLE/3: ENZYMATIC REACTION

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P$$

- SIMPLE MODEL OF ENZYMATIC REACTION

QUASI-EQUILIBRIUM: MICHAELIS-MENTEN $v = \dfrac{k_1 k_2 E_T S}{k_{-1} + k_2 + k_1 S}$





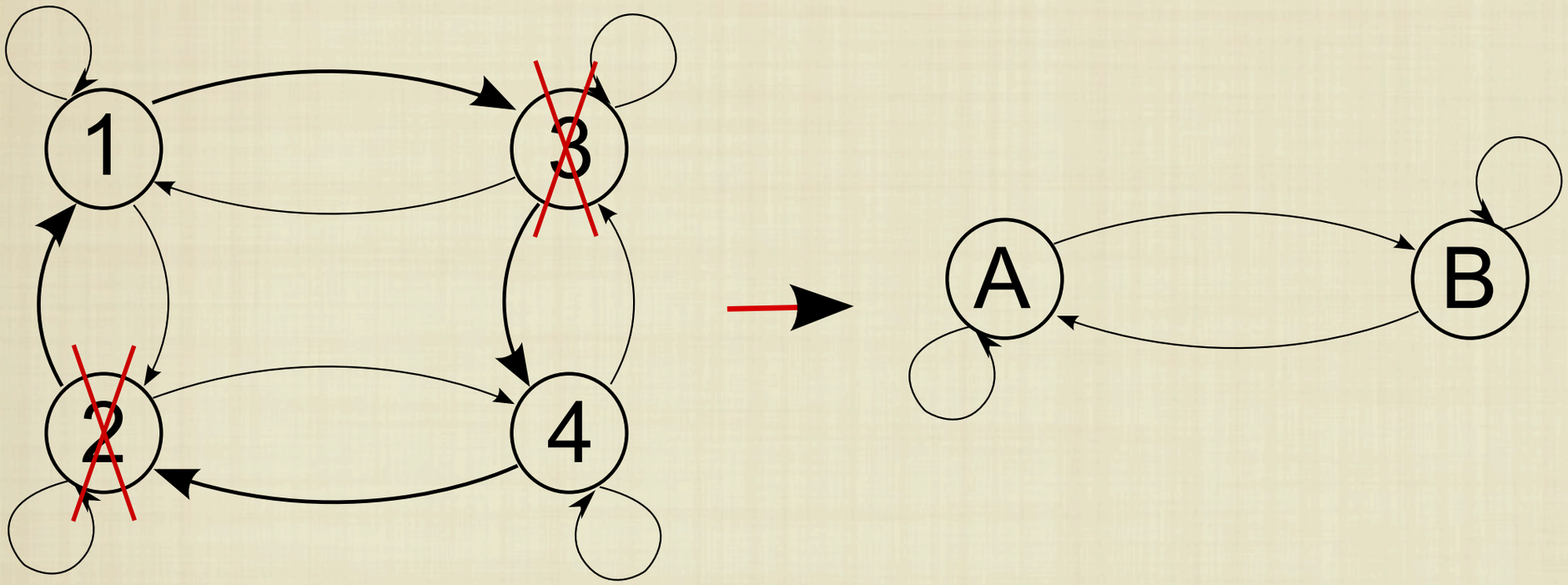
100 SUBSTRATE MOLECULES

ENZYMES: (TOP) 1 (BOTTOM) 100

(LEFT) $k_1 \ll k_{-1}, k_2$ (RIGHT) $k_1 \gg k_{-1}, k_2$

Question:

what is the effect of coarse graining on (fluctuation of) entropy production?



NON-EQUILIBRIUM

DETAILED BALANCE

A. Puglisi, SP, L. Rondoni, A. Vulpiani, JSTAT (2010)

ENTROPY PRODUCTION

LEBOWITZ-SPOHN FUNCTIONAL

$$\mathcal{W}_t = \frac{1}{t} \ln \frac{W_{\omega_0 \to \omega_1} W_{\omega_1 \to \omega_2} \dots W_{\omega_{m-1} \to \omega_m}}{W_{\omega_1 \to \omega_0} W_{\omega_2 \to \omega_1} \dots W_{\omega_m \to \omega_{m-1}}}$$

IF DETAILED BALANCE HOLDS $\langle \mathcal{W}_t \rangle = 0$

THE CRAMER FUNCTION $C(\mathcal{W}_t) = -\lim_{t \to \infty} \frac{1}{t} \log[f(\mathcal{W}_t)]$

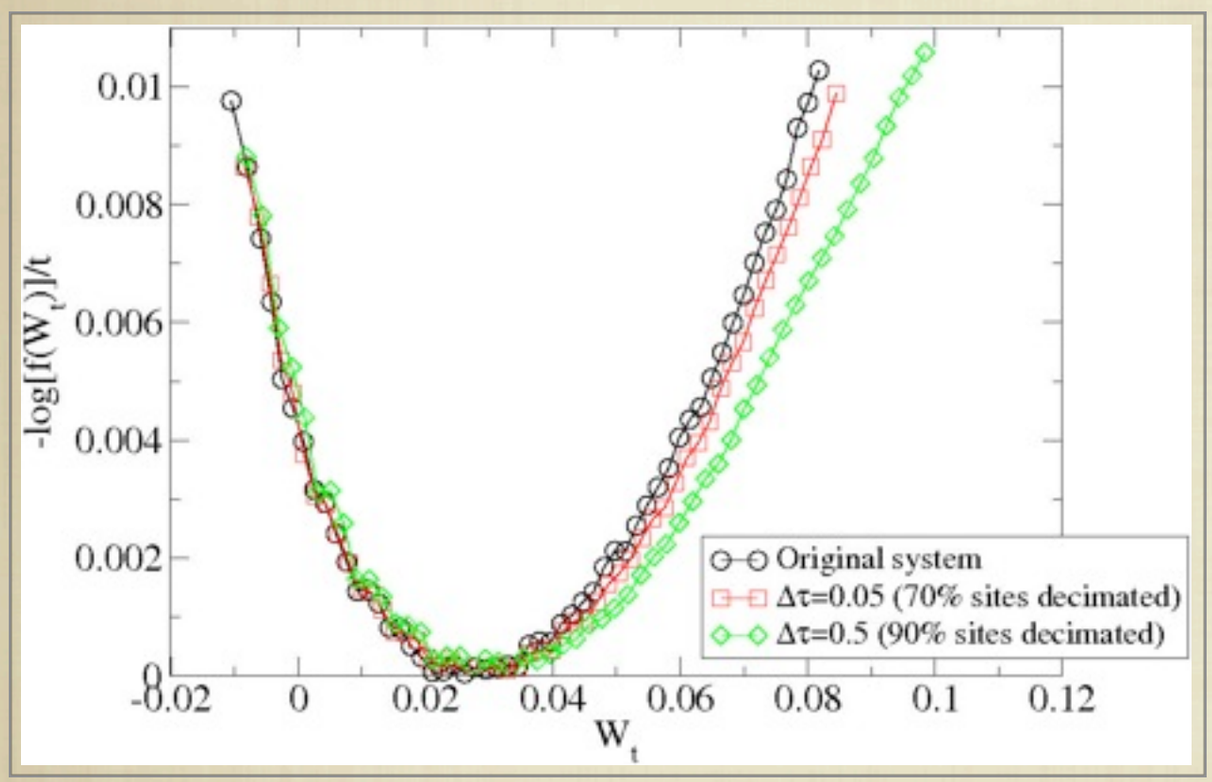
ALWAYS SATISFIES $C(\mathcal{W}_t) - C(-\mathcal{W}_t) = -\mathcal{W}_t$

(STEADY STATE FLUCTUATION RELATION)

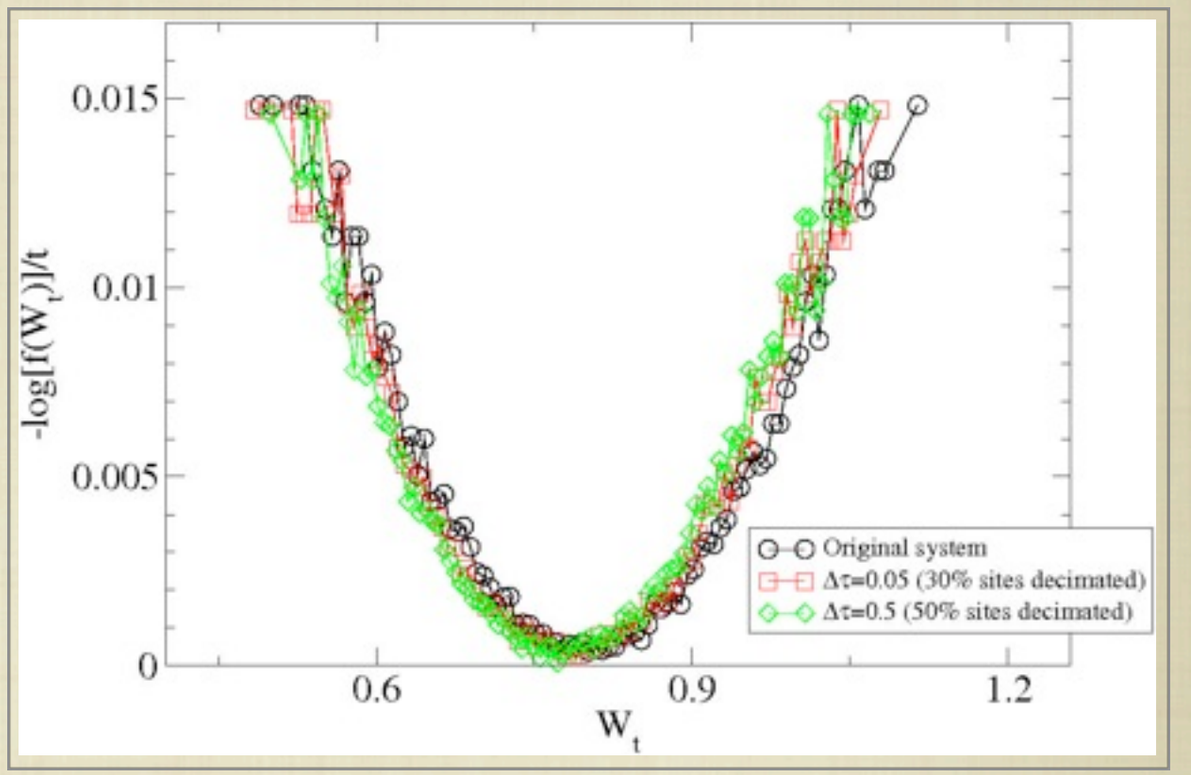
J. LEBOWITZ AND H. SPOHN, J. STAT. PHYS. (1999)

FIRST TESTS

(ASYMMETRIC) RANDOM WALK WITH DEFECTS



1D



2D

COARSE GRAINING DOES NOT ALTER THE CRAMER FUNCTION

(TENTATIVE) THEORY

$$\mathcal{W}_t = \frac{1}{t} \ln \frac{W_{\omega_0 \to \omega_1} W_{\omega_1 \to \omega_2} \dots W_{\omega_{m-1} \to \omega_m}}{W_{\omega_1 \to \omega_0} W_{\omega_2 \to \omega_1} \dots W_{\omega_m \to \omega_{m-1}}}$$

APPROXIMATED BY $Q_t = \sum_\alpha A(\vec{C}_\alpha) G_\alpha(t)$

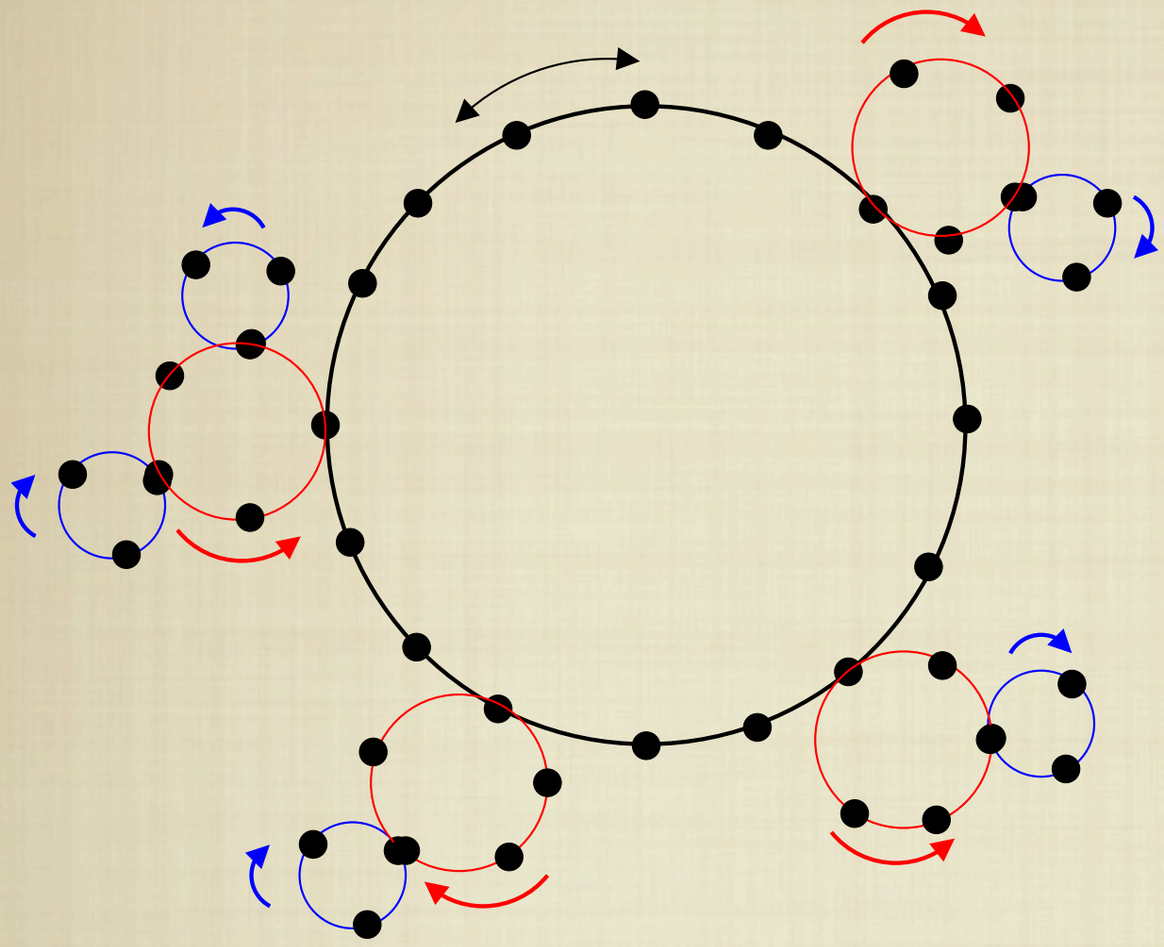
NETWORK DECOMPOSED INTO LOOPS INDEXED BY α

WHERE G ARE THE LOOP CURRENTS AND A ARE THE AFFINITIES

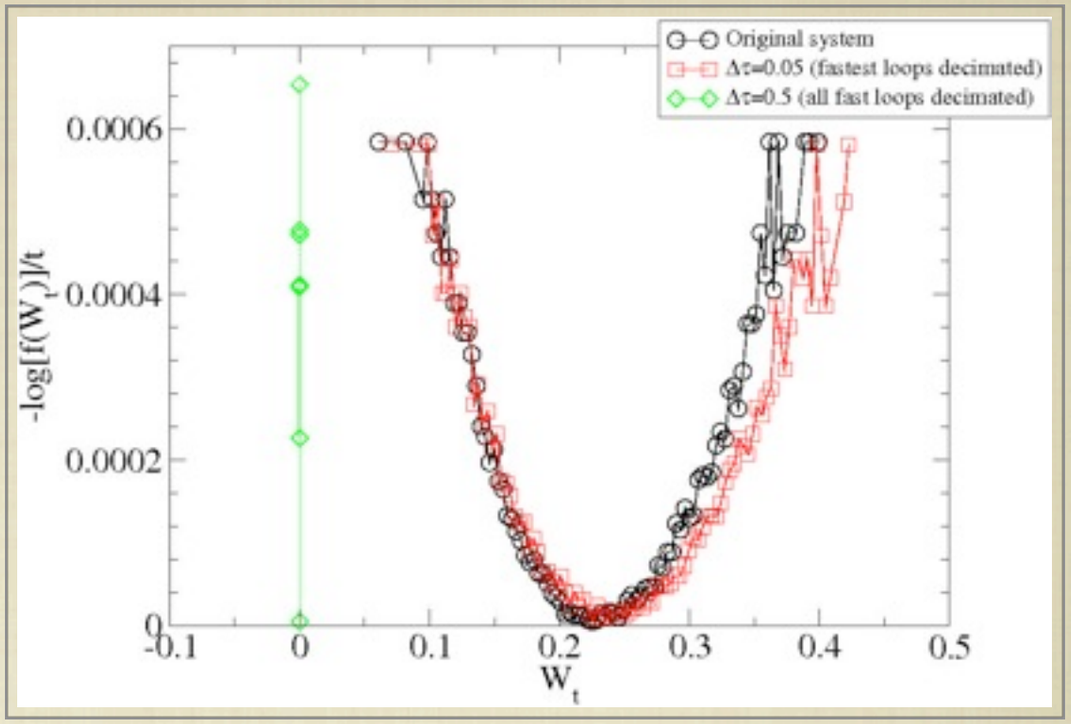
$$A = \log \left(\prod_j \frac{W_{n_j, n_{j+1}}}{W_{n_{j+1}, n_j}} \right)$$

COARSE GRAINING DOES NOT ALTER THE AFFINITIES AND (USUALLY) DOES NOT CHANGE MUCH THE CURRENTS - SIGNIFICANT CHANGE ONLY IF LOOPS CARRYING CURRENT ARE DESTROYED

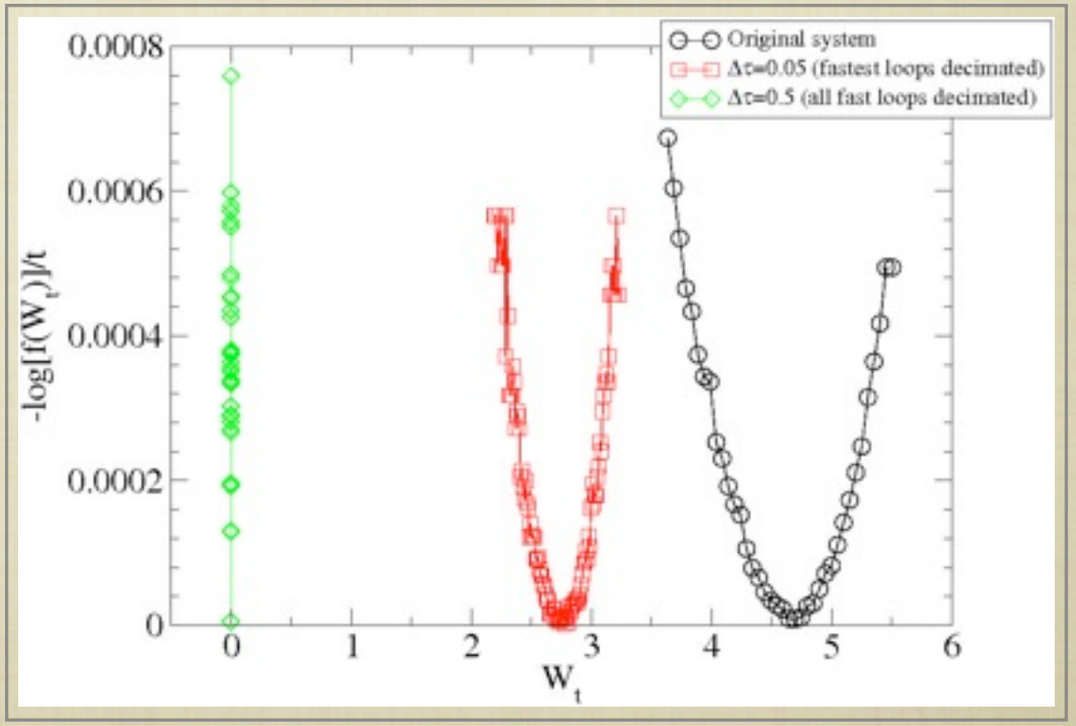
HIERARCHICAL LOOPS



MODEL SYSTEM, TUNABLE AVERAGE CURRENT AND TYPICAL RATES OF EACH LEVEL OF LOOPS

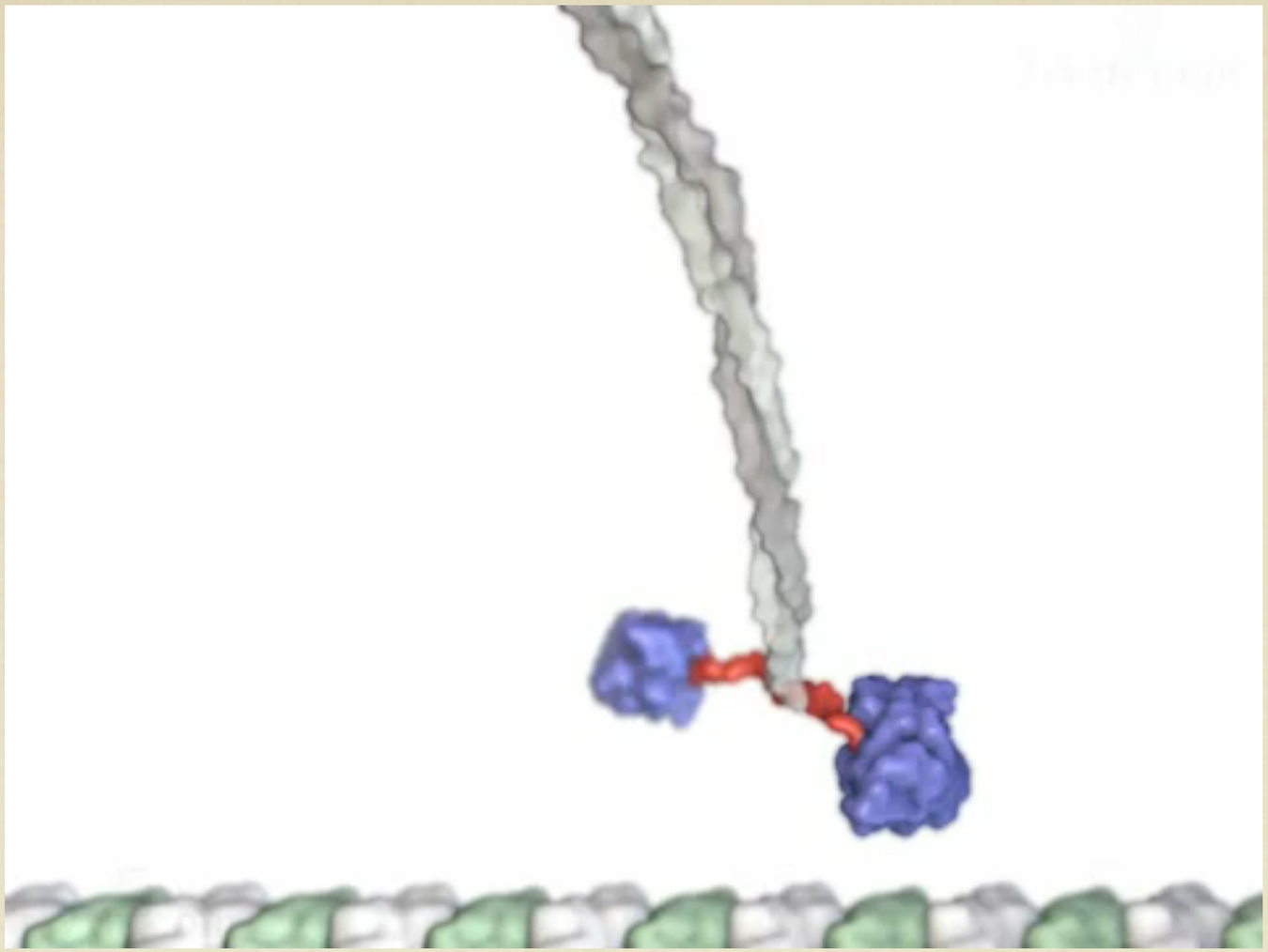


NO CURRENT ON 3RD LEVEL



CURRENT ON 3RD LEVEL

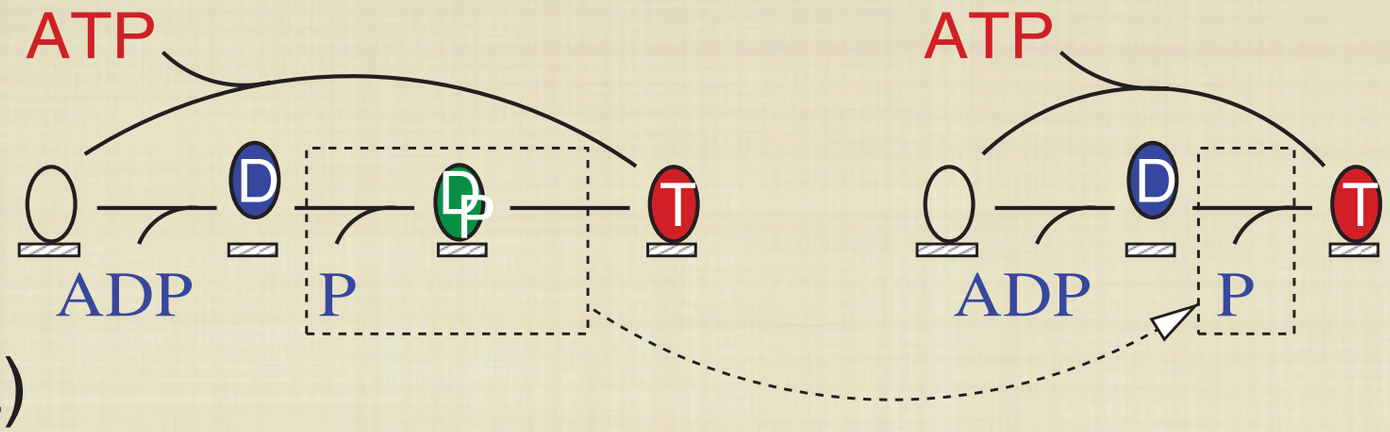
EXAMPLE/2 KINESIN



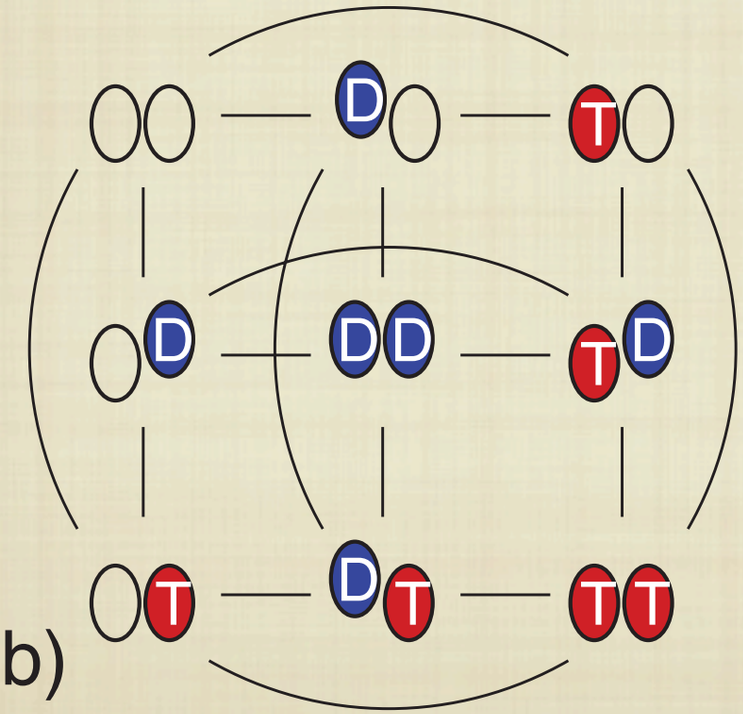
PARADIGMATIC MOTOR PROTEIN
WALKS ON MICROTUBULES BY ALTERNATING THE TWO (IDENTICAL) HEADS

R.D.V.A. YILDIZ ET AL. SCIENCE (2004)

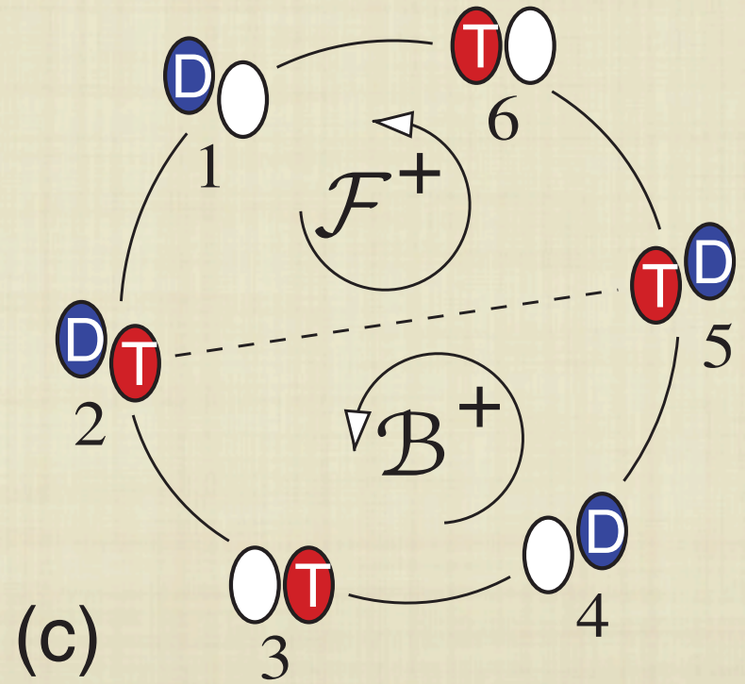
KINESIN NETWORK



(a)



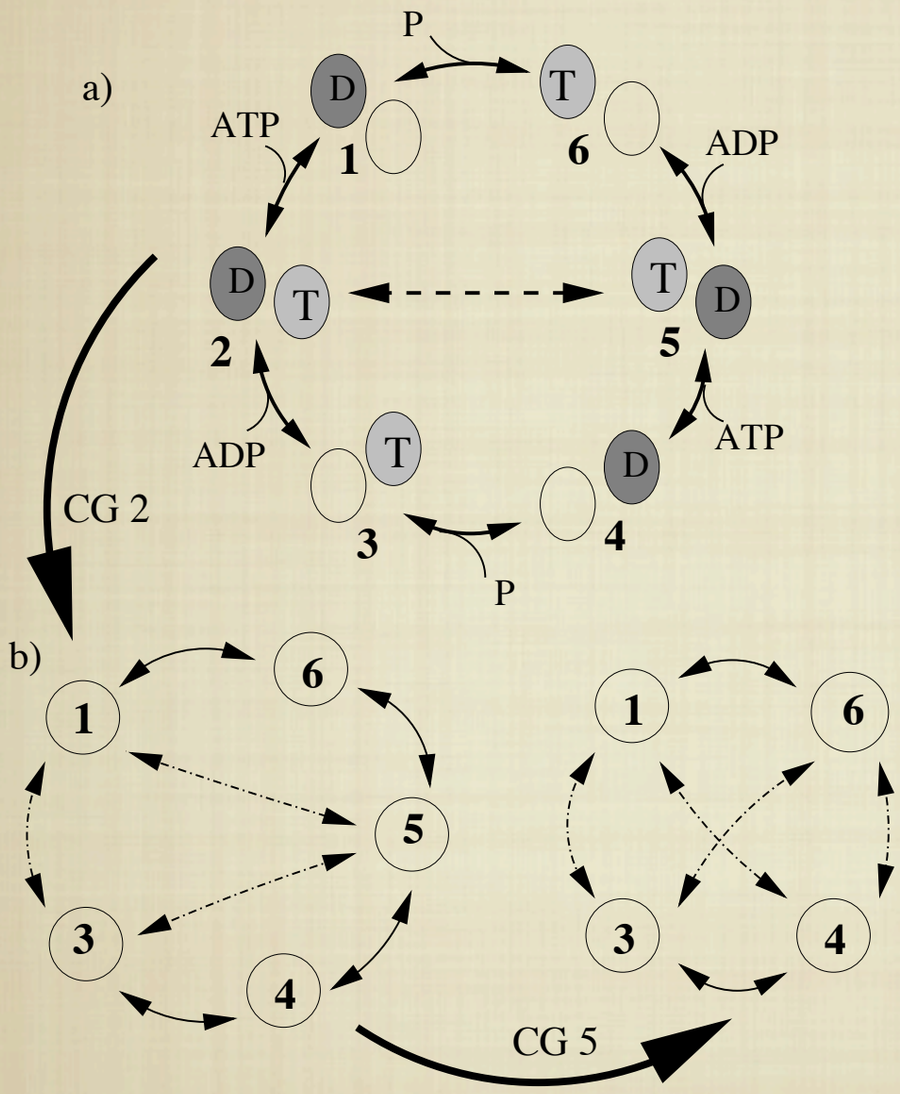
(b)



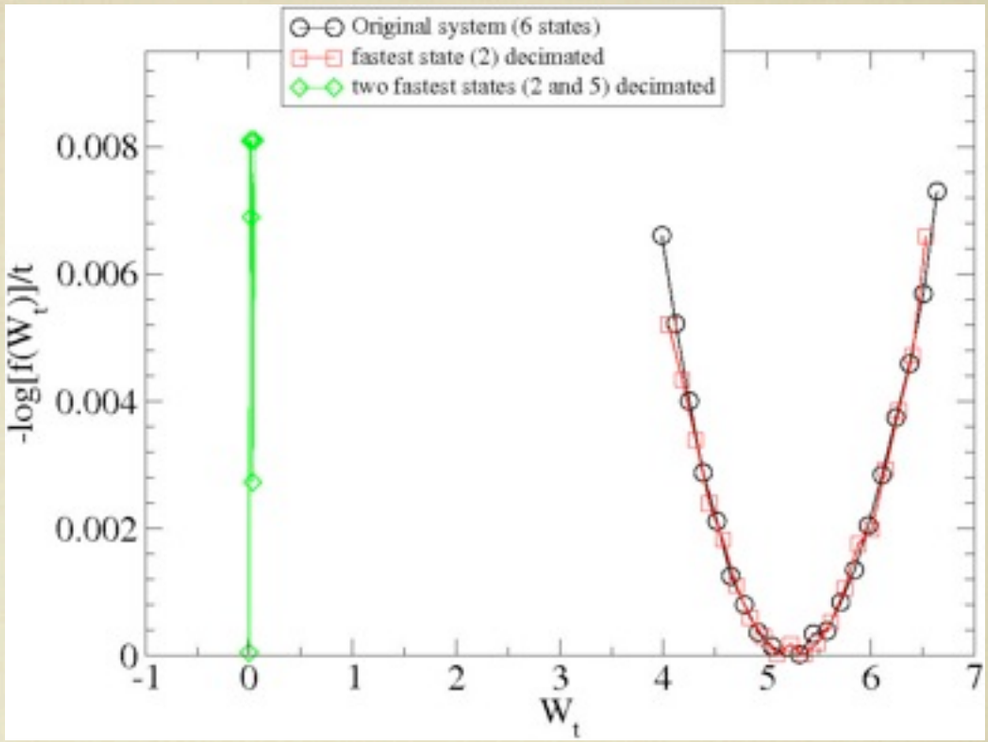
(c)

S. LIEPELT AND R. LIPOWSKY, PRL (2007)

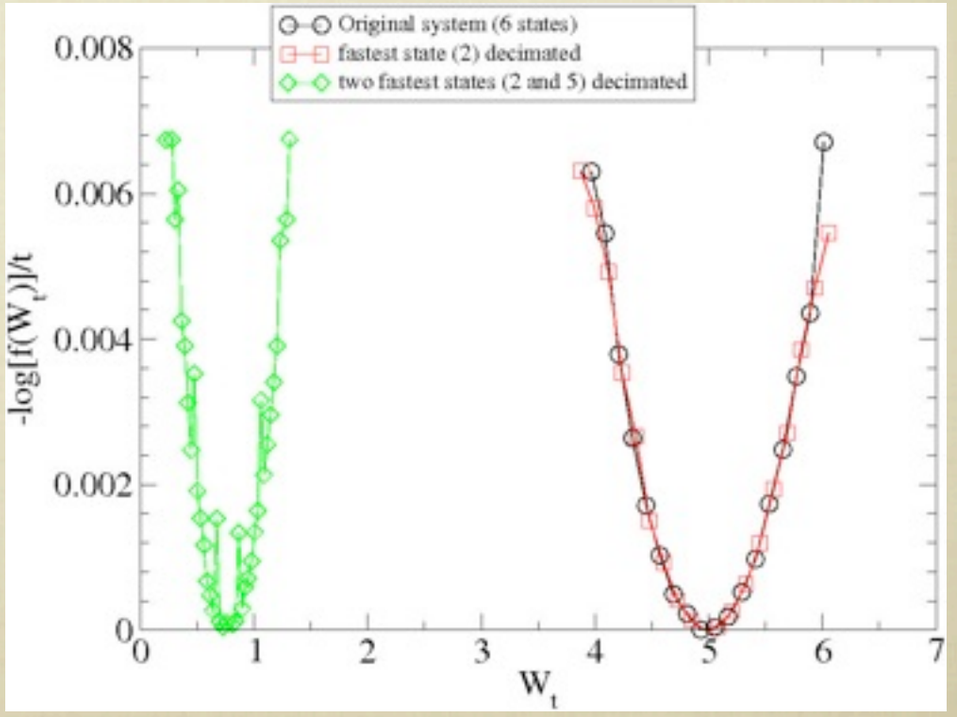
KINESIN NETWORK / 2



NO LOAD



LOAD



CONCLUSIONS

- SIMPLE COARSE GRAINING RECIPE APPLIABLE IN DIFFERENT CONTEXTS

- ENTROPY PRODUCTION IS WEAKLY DEPENDENT ON COARSE GRAINING, IF CURRENT-CARRYING LOOPS ARE NOT DESTROYED

- QUESTION: HOW MACROSCOPIC IS THE ENTROPY PRODUCTION? CASES IN WHICH THE SCALE OF THE RELEVANT LOOPS IS NOT OBVIOUS.