Entropy production far from equilibrium in interacting many-body systems

Sven Dorosz

University of Luxembourg

March, 2011

Far from Equilibrium

- within a non equilibrium steady state (part I)
- relaxation to a non equilibrium state
- driving out of a stationary state (part II)

Table of contents

Stochastic Systems

M_1	$M_{2'}$	M_n	ASEP
$A + A \underset{h}{\overset{\lambda}{\rightleftarrows}} A + 0$	$A + A \overset{\lambda}{\rightarrow} A + 0$ $0 \overset{h}{\rightarrow} A$	$nA \overset{\lambda}{\rightarrow} n0$ $0 \overset{h}{\rightarrow} A$	whiteboard

Stochastic Systems

M_1	$M_{2'}$	M_n	ASEP
$A+A \underset{h}{\overset{\lambda}{\rightleftarrows}} A+0$	$A+A \underset{\varepsilon_\lambda \lambda}{\overset{\lambda}{\rightleftarrows}} A+0$ $0 \underset{\varepsilon_h h}{\overset{h}{\rightleftarrows}} A$	$nA \underset{\varepsilon_\lambda \lambda}{\overset{\lambda}{\rightleftarrows}} n0$ $0 \underset{\varepsilon_h h}{\overset{h}{\rightleftarrows}} A$	

Table: The back-reactions are taking place with rates $\varepsilon_h h$ and $\varepsilon_\lambda \lambda$, with $0 < \varepsilon_h < 1$ and $0 < \varepsilon_\lambda < 1$ for $M_{2'}$ and M_n

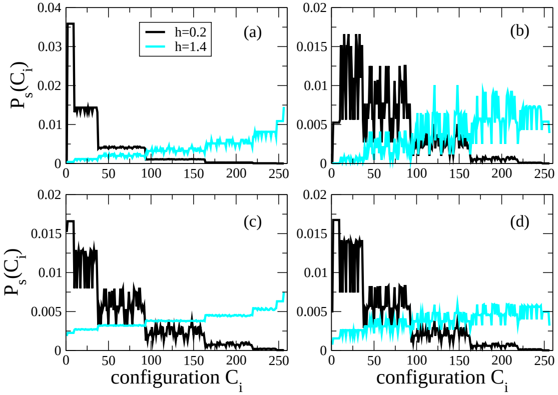
Markov Dynamics and Master Equation

$$\frac{\mathrm{d}P(C_i,t)}{\mathrm{d}t} = \sum_{C_j \neq C_i} [\omega(C_j \to C_i)P(C_j,t) - \omega(C_i \to C_j)P(C_i,t)]$$

$$K_s(C_i,C_j) = \omega(C_j \to C_i)P_s(C_j) - \omega(C_i \to C_j)P_s(C_i)$$

if $K_s(C_i,C_j) = 0 \ \forall i,j$ then detailed balance
if $\exists\ i,j$ s.t. $K_s(C_i,C_j) \neq 0 \quad \Rightarrow$ general stationary state

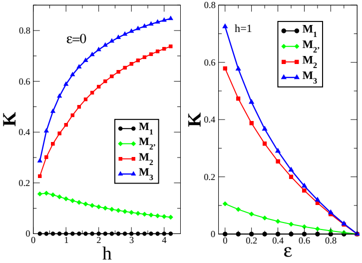
Stationary State Probabilities



SD and M. Pleimling, Phys. Rev. E **80**, 061114 (2009)

Stationary State

$$K = \sum_{i,j} |\omega(C_j \to C_i)P_s(C_j) - \omega(C_i \to C_j)P_s(C_i)|$$



SD and M. Pleimling, Phys. Rev. E **80**, 061114 (2009)

T. Platini, Phys. Rev. E **83**, 011119 (2011)

Stationary State

Steady State Fluctuation Theorem
All parameters are held fixed
and the probabilities are time independent.

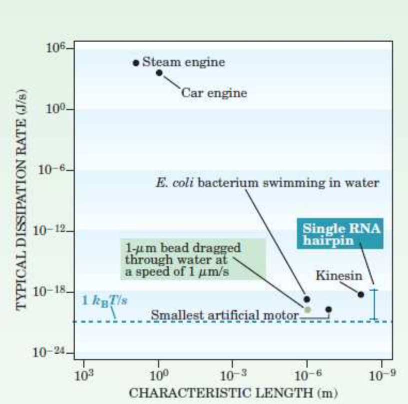
Steady State Fluctuation Theorem

$$
\begin{aligned}
s_{tot} &= \ln \prod_{\{i\}} \frac{\omega(C_i \to C_{i+1})}{\omega(C_{i+1} \to C_i)} + \ln \frac{P_s(C_0)}{P_s(C_\tau)} \\
&= s_m + \Delta s
\end{aligned}
$$

$$
\frac{P(s_{tot})}{P(-s_{tot})} = \exp(s_{tot})
$$

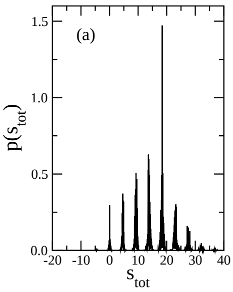
U. Seifert, Europ. Phys. Journal B **64**, 3-4 (2008)

Dissipation and Length Scales



C. Bustamente et al., Physics Today, July 2005

Stationary State



SD and M. Pleimling, accepted for PRE, arXiv:1101.4566

Entropy Change

Investigation of the long time regime.

$$\chi(\sigma) = \lim_{\tau \to \infty} \left[-\frac{1}{\tau} \ln p(s_m, \tau) \right]$$

Numerical Method

$$
\begin{aligned}
L_\mu &= -\left[\sum_j \omega(C_j \longrightarrow C_i) e^{-\mu \ln \frac{\omega(C_j \to C_i)}{\omega(C_i \to C_j)}} - r(C_i)\right] \\
&= -\left[\sum_j \omega(C_j \longrightarrow C_i)^{1-\mu} \omega(C_i \longrightarrow C_j)^{\mu} - r(C_i)\right]
\end{aligned}
$$

J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999)

Numerical Method

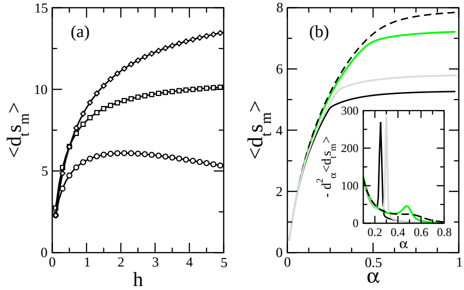
Properties of the LDF

$$\nu(\mu) = \nu(1-\mu)$$

$$\langle \dot{s}_m \rangle = d\nu(\mu)/d\mu|_{\mu=0}$$

J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999)

Mean entropy production rates



SD and M. Pleimling, accepted for PRE, arXiv:1101.4566

Numerical Method

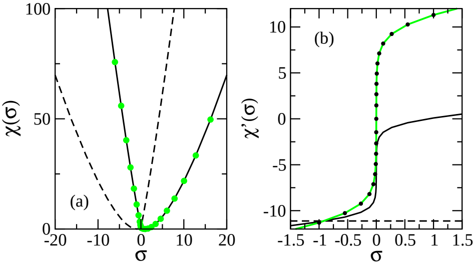
Properties of the LDF

$$\chi(\sigma) = \max_{\mu}\{\nu(\mu) - \langle \dot{s}_m \rangle \sigma \mu\}$$

$$\chi(-\sigma) = \chi(\sigma) + \langle \dot{s}_m \rangle \sigma$$

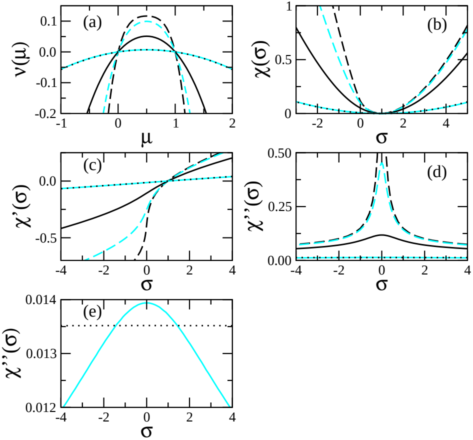
J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999)

Rate functions



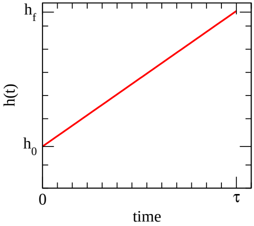
SD and M. Pleimling, accepted for PRE, arXiv:1101.4566

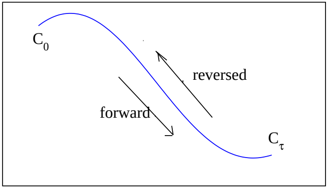
Rate functions



SD and M. Pleimling, accepted for PRE, arXiv:1101.4566

transient processes
the system is driven out of its steady state
by a time dependent reaction rate





The Jarzynski relation

System S described by a Hamiltonian $H(\lambda)$

$$h(t) = \{h_0, h_1, ..., h_{M-1}, h_M\}$$

definition of work $W = \sum_{i=0}^{M-1} H(C_i, h_{i+1}) - H(C_i, h_i)$

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \quad \forall\ h(t)$$

The average is taken over all trajectories in configuration space.

C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997)

The Crooks Relation

Comparing a process and its time reversed process:

$$P_F(W) \quad = \quad P_R(-W)e^{\beta(W-\Delta F)}$$

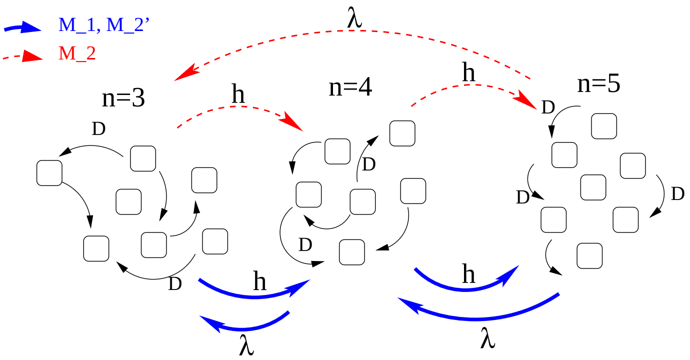
D.E.Crooks, J.Stat. Phys. **90**, 1481 (1998)
discrete case expressed as stationary probabilities

$$\phi = \sum_{i=0}^{M-1} \ln\left[\frac{P_s(C_i, h_i)}{P_s(C_i, h_{i+1})}\right]$$

Three Reaction Diffusion Systems

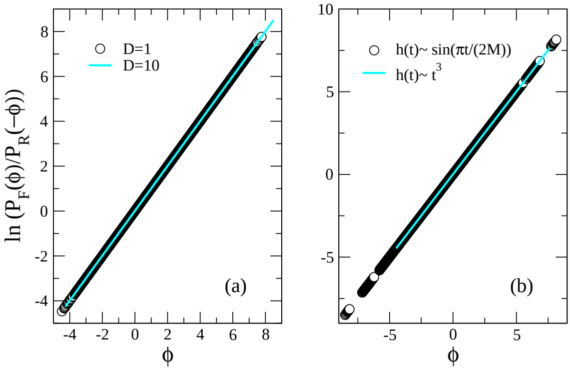
M_1	$M_{2'}$	M_2
$A + A \xrightarrow{\lambda} 0 + A$ $0 + A \xrightarrow{h} A + A$	$A + A \xrightarrow{\lambda} 0 + A$ $0 \xrightarrow{h} A$	$A + A \xrightarrow{\lambda} 0 + 0$ $0 \xrightarrow{h} A$

Configuration space



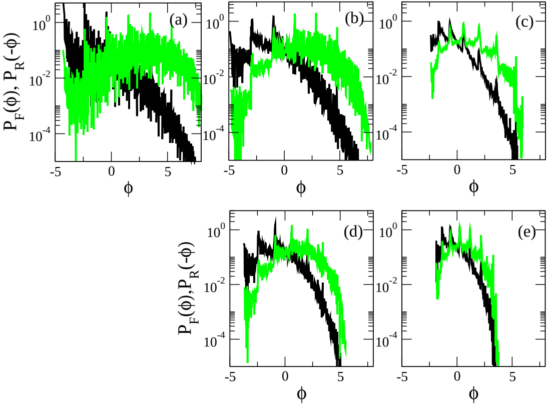
SD and M. Pleimling, Phys. Rev. E **80**, 061114 (2009)

Exact Fluctuation Relation for ϕ



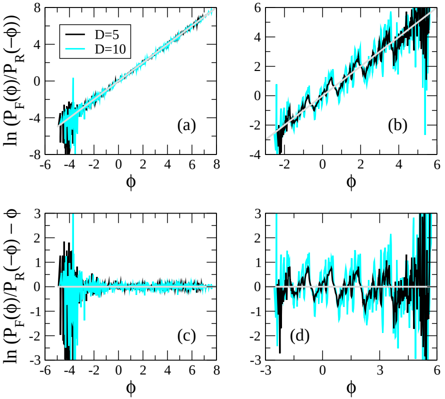
SD and M. Pleimling, Phys. Rev. E **80**, 061114 (2009)

Distributions for the Observable ϕ



SD and M. Pleimling, Phys. Rev. E **80**, 061114 (2009)

General Fluctuation Ratios for ϕ



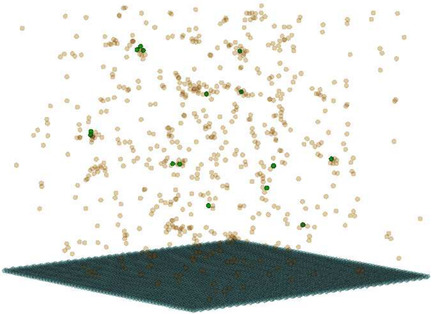
SD and M. Pleimling, Phys. Rev. E **80**, 061114 (2009)

Conclusion

- Detailed characterization of non equilibrium steady states (NESS) for reaction diffusion systems
- Discussion of stationary probabilities
- and $|K|$ as a distance from equilibrium
- Characterization of entropy production in NESS
- Analysis of transient behavior through Fluctuation Relations

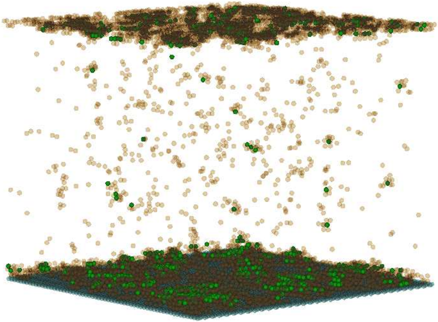
Heterogeneous Nucleation near Structured Wall

Hard Spheres at t=1



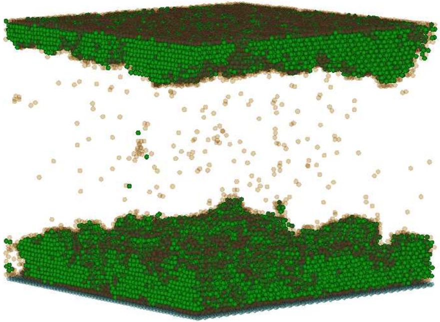
Heterogeneous Nucleation near Structured Wall

Hard Spheres at t=10



Heterogeneous Nucleation near Structured Wall

Hard Spheres at t=100



Heterogeneous Nucleation

Hard Ellipsoids