Driven stochastic processes with metastable states: Fokker-Planck versus master equations

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Vienna, November 2010

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Acknowledgments

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Financial support by Deutsche Forschungsgemeinschaft and KOSEF-DFG

Introduction

Complex stochastic dynamics typically emerges from a NONLINEAR system under permanent NON-EQUILIBRIUM conditions, such as permanent fluxes of energy or particles through the system. External TIME-DEPENDENT FORCING presents just an example and shall be considered here as the source of non-equilibrium.

RANDOMNESS results from the dynamics of those degrees of freedom of the considered system and its environment that are not explicitly controlled.

TIME-SCALE SEPARATION:
$\underbrace{\text{Fast “microscopic”}}_{\text{noise and friction}}$ versus slow “macroscopic” variables

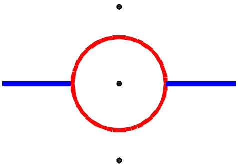
$$\tau_{\text{mic}} \ll \tau,\ \tau_{\text{drive}} \quad \Longrightarrow \text{ Markovian Dynamics,}$$

here: Langevin, Fokker-Planck

Multi- and metastability

In the absence of noise the non-linearity of the equations of motion frequently asymptotically leads to DISTINCT, LOCALLY STABLE STATES. Noise destabilizes these states; at sufficiently WEAK NOISE the system though stays most of the time close to one of these formerly stable states and transitions to other such states occur only rarely.

Hence noise renders the locally stable states of a deterministic system METASTABLE.



Time-scale separation:
deterministic time scale $\tau \ll$ typical residence time

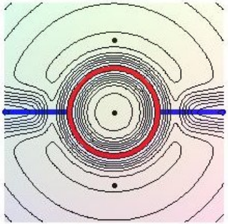
Equilibrium

For EQUILIBRIUM SYSTEMS the transition dynamics between metastable states is well understood and described by master equations:[1]

$$\dot{p}_\alpha(t) = \sum_{\beta\neq\alpha} k_{\alpha,\beta}\, p_\beta(t) - \sum_{\beta\neq\alpha} k_{\beta,\alpha}\, p_\alpha(t)$$

Detailed balance: $\rho(\mathbf{x}) \propto e^{-E(\mathbf{x})/k_B T}$

$$k_{\alpha,\beta} \propto e^{-\Delta E_{\alpha,\beta}/k_B T}$$



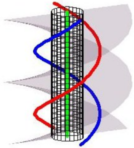
$\Delta E_{\alpha,\beta}$: Activation energy
pre-exponential factor determined by the curvatures of the energy at the initial state and corresponding saddle and the linearized dynamics at the saddle.

[1] P. Hänggi, P. Talkner, M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990); E. Pollak, P. Talkner, Chaos **15**, 026116 (2005)

Driving

PERIODIC driving presents a standard method to test a system. In the presence of metastable states it may lead to stochastic resonance for which the otherwise random transitions between two metastable states synchronize with the external driving signal.

deterministic motion: $\dot{\mathbf{x}}(t) = \mathbf{f}(\mathbf{x}(t), t), \quad \mathbf{f}(\mathbf{x}, t+T) = \mathbf{f}(\mathbf{x}, t)$
$\mathbf{X}(t|\mathbf{y}, s) \to \mathbf{x} \in \mathcal{A}_\alpha(t)$ for $s \to -\infty$, $\alpha = 1 \ldots n$
$\mathcal{A}_\alpha(t + T) = \mathcal{A}_\alpha(t)$: attractors
$\mathcal{D}_\alpha(s) = \{\mathbf{y}|\mathbf{X}(t|\mathbf{y}, s \in \mathcal{A}_\alpha(t)$ for $t \to \infty\}$
$\mathcal{D}_\alpha(s + T) = \mathcal{D}_\alpha(s)$: domain of attraction of $\mathcal{A}_\alpha(t)$



$\mathcal{D}_\alpha(s) \bigcap \mathcal{D}_{\alpha'}(s) = \emptyset$ for $\alpha \neq \alpha'$,
$\bigcup_{\alpha=1}^{m} \mathcal{D}_\alpha(s) = \Sigma$.

RAMPED FORCE: Mechanical probing of chemical bonds by application of a steadily increasing force.

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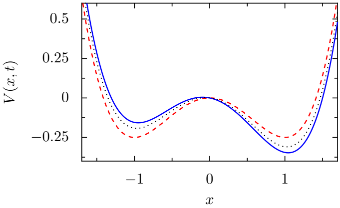
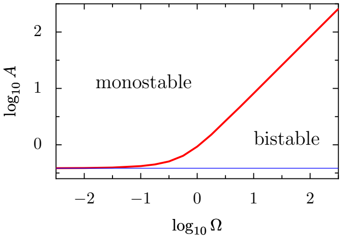
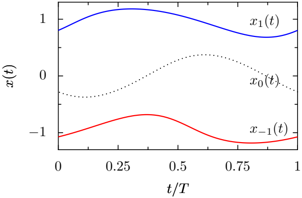
Example

$$\dot{x}(t) = -\partial V(x(t), t)/\partial x + \sqrt{2D}\xi(t)$$

$$V(x,t) = -\frac{1}{2}x^2 + \frac{1}{4}x^4 - Ax\sin\Omega t$$







$A = 0.5$,
$\Omega = 1$

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Langevin and Fokker-Planck equations

Langevin equation : $\dot{x}_i(t) = f_i(\mathbf{x}(t), t) + g_{i,j}(\mathbf{x}(t), t)\xi_j(t)$,

$\xi_i(t)$: Gaussian white noise, $\langle \xi_i(t) \rangle = 0$, $\langle \xi_i(t)\xi_j(s) \rangle = \delta_{i,j}\delta(t-s)$

Equivalent Fokker-Planck equation:

$$\frac{\partial}{\partial t}\rho(\mathbf{x}, t|\mathbf{y}, s) = L_{\mathbf{x}}(t)\rho(\mathbf{x}, t|\mathbf{y}, s), \text{ forward equation}$$

$$-\frac{\partial}{\partial s}\rho(\mathbf{x}, t|\mathbf{y}, s) = L^{+}_{\mathbf{y}}(s)\rho(\mathbf{x}, t|\mathbf{y}, s), \text{ backward equation}$$

$$\rho(\mathbf{x}, t|\mathbf{y}, s),\ t \geq s,\ \rho(\mathbf{x}, s|\mathbf{y}, s) = \delta(t-s) : \text{ cond. prob. dens.}$$

$$L(t) = -\sum_i^d \frac{\partial}{\partial x_i} K_i(\mathbf{x}, t) + \sum_{i,j}^d \frac{\partial^2}{\partial x_i \partial x_j} D_{i,j}(\mathbf{x}, t)\ ,$$

$$L^{+}(s) = \sum_i^d K_i(\mathbf{y}, s)\frac{\partial}{\partial y_i} + \sum_{i,j}^d D_{i,j}(\mathbf{y}, s)\frac{\partial^2}{\partial y_i \partial y_j}\ ,$$

$$K_i(\mathbf{x}, t) = f_i(\mathbf{x}, t) + \text{n.i.t.},$$

$$D_{i,j}(\mathbf{x}, t) = \sum_k g_{i,k}(\mathbf{x}, t) g_{j,k}(\mathbf{x}, t)\ .$$

Periodic driving: Floquet representation of conditional probability

$$\rho(\mathbf{x}, t|\mathbf{y}, s) = \sum_i e^{\mu_i(t-s)}\psi_i(\mathbf{x}, t)\varphi_i(\mathbf{y}, s) \quad \text{conditional probability}$$

$$\frac{\partial}{\partial t}\psi_i(\mathbf{x}, t) = L(t)\psi_i(\mathbf{x}, t) - \mu_i\psi_i(\mathbf{x}, t) \quad \text{forward Floquet eq.,}$$

$$-\frac{\partial}{\partial t}\varphi_i(\mathbf{x}, t) = L^+(t)\varphi_i(\mathbf{x}, t) - \mu_i\varphi_i(\mathbf{x}, t) \quad \text{backward Floquet eq.,}$$

$$\psi_i(\mathbf{x}, t+T) = \psi_i(\mathbf{x}, t) \quad \varphi_i(\mathbf{x}, t+T) = \varphi_i(\mathbf{x}, t) \quad \text{periodicity}$$

$$\int d\mathbf{x}\varphi_j(\mathbf{x}, t)\psi_i(\mathbf{x}, t) = \delta_{i,j} \text{ orthogonality;} \quad \sum_i \psi_i(\mathbf{x}, t)\varphi_i(\mathbf{y}, t) = \delta(\mathbf{x}-\mathbf{y}) \text{ completeness}$$

$\mathrm{Re}\mu_i \leq 0$, $\{\mu_i\}$ constitutes the Floquet spectrum

$\mu_0 = 0$, $\varphi_0(\mathbf{x}, t) = 1$, $\psi_0(\mathbf{x}, t)$ unique asymptotic pdf

Deterministic limit

$$L^+_{\text{det}} = \sum_i f_i(\mathbf{x},t)\frac{\partial}{\partial x_i}, \quad \text{characteristics}: \; \dot{\mathbf{x}} = \mathbf{f}(\mathbf{x},t)$$

$$-\frac{\partial}{\partial t}\varphi_{\text{det}}(\mathbf{x},t) = L^+(t)\varphi_{\text{det}}(\mathbf{x},t) \quad \text{has } n \text{ independent solutions}:$$

$$\varphi_{\text{det},\alpha}(\mathbf{x},t) = \begin{cases} 1 & \text{for } \mathbf{x} \in \mathcal{D}_\alpha(t) \\ 0 & \text{else} \end{cases}$$

Hence, $\mu_0 = 0$ is n-fold degenerate in the deterministic limit. Weak noise lifts this degeneracy and the spectrum contains a group of n Floquet-exponents $\mu_i \; 0 = 1, \ldots n$ which have a much smaller absolute value than the rest: $|\mu_i| \ll |\mu_j|$ for $i < n$, $j \geq n$.

$$\rho(\mathbf{x},t|\mathbf{y},s) = \sum_{i=0}^{n-1} e^{\mu_i(t-s)}\psi_i(\mathbf{x},t)\varphi_i(\mathbf{y},s) \qquad \text{for } t-s \gg \tau$$

τ: deterministic relaxation time

Alternative representation of the large time conditional probability[2]

THREE STEPS to go from $\mathbf{y}$ at s to $\mathbf{x}$ at t for $t - s \gg \tau$:

Step 1: Go in time $\tau_1 \approx \tau$ from $\mathbf{y}$ at s nearby to the next attractor $\mathcal{A}_\beta(s + \tau_1)$; probability given by the localizing function $\chi_\beta(\mathbf{y}, s)$.

Step 2: A transitions from the metastable state β at time $s + \tau_1 \approx s$ to α at time t occurs with the transition probability $p(\alpha, t|\beta, s)$.

Step 3: To each metastable state α at time t a continuous state is allocated with state specific pdf $\rho(\mathbf{x}, t|\alpha)$.

Steps 1, 2 and 3 are INDEPENDENT from each other

$$\rho(\mathbf{x}, t|\mathbf{y}, s) = \sum_{\alpha,\beta} \rho(\mathbf{x}, t|\alpha) p(\alpha, t|\beta, s) \chi_\beta(\mathbf{y}, s)$$

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[2] C. Kim, P.Talkner, E.K. Lee, P. Hänggi, Chem. Phys. **370**,277 (2010)

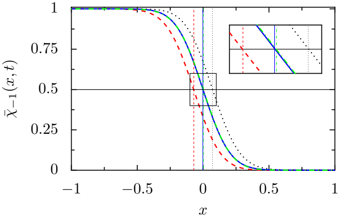
Properties of localizing functions and state-specific pdfs

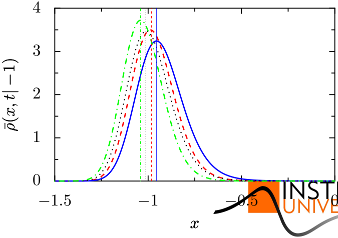
$$\chi_\alpha(\mathbf{x}, t) \approx \begin{cases} 1 & \text{for } \mathbf{x} \in \mathcal{D}_\alpha(t) \\ 0 & \text{else} \end{cases} \qquad \begin{array}{l} \text{interpolates smoothly} \\ \text{in a region near } \partial\mathcal{D}_\alpha(t) \end{array}$$

$$\sum_\alpha \chi_\alpha(\mathbf{x}, t) = 1$$

$\rho(\mathbf{x}, t|\alpha)$ concentrated near $\mathcal{A}_\alpha(t)$, vanishes elswhere.

$$\int_\Sigma d\mathbf{x}\, \rho(\mathbf{x}, t|\alpha) = 1\,,$$





$A = 0.1,\ \Omega = 1,\ D = 0.025$

$$p_\alpha(t) = \int_\Sigma d\mathbf{x}\, \chi_\alpha(\mathbf{x},t)\rho(\mathbf{x},t)$$

$$\rho_p(\mathbf{x},t) = \sum_\alpha \rho(\mathbf{x},t|\alpha)p_\alpha(t)$$

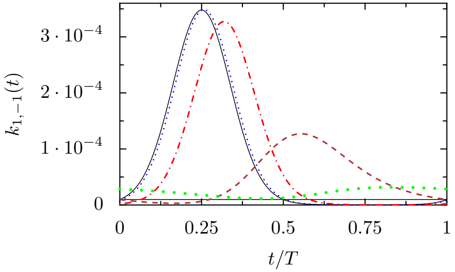
$$\Longrightarrow \quad \int_\Sigma d\mathbf{x}\, \chi_\alpha(\mathbf{x},t)\rho(\mathbf{x},t|\beta) = \delta_{\alpha,\beta}$$

$$\rho(\mathbf{x},t) = \int_\Sigma d\mathbf{y}\rho(\mathbf{x},t|\mathbf{y},s)\rho(\mathbf{y},s) \quad \Longrightarrow \quad p_\alpha(t) = \sum_{\alpha,\beta} p(\alpha,t|\beta,s)p_\beta(s)$$

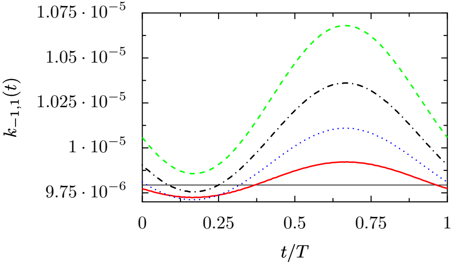
$$\dot{p}_\alpha(t) = \sum_{\beta\neq\alpha} k_{\alpha,\beta}(t)p_\beta(t) - \sum_{\beta\neq\alpha} k_{\beta,\alpha}(t)p_\alpha(t) \quad \text{master equation}$$

$$k_{\alpha,\beta}(t) = \int_\Sigma d\mathbf{x}\, \frac{\partial\chi_\alpha(\mathbf{x},t)}{\partial t}\rho(\mathbf{x},t|\beta) + \int_\Sigma d\mathbf{x}\, \chi_\alpha(\mathbf{x},t)L(t)\rho(\mathbf{x},t|\beta)$$

example



A=0.1, D= 0.025
$\Omega = 0,\ 10^{-3},\ 10^{-2},$
$0.1,\ 0.5,\ 1,\ \infty$



$\Omega = 10,\ D = 0.025$
$A = 0,\ 0.1,\ 0.2$
$0.3,\ 0.4$

Equations for $\chi_\alpha(\mathbf{y}, s)$ and $\rho(\mathbf{x}, t|\alpha)$

$$\chi_\alpha(\mathbf{x}, t) = \sum_{i=0}^{n-1} D_{\alpha,i}(t)\varphi_i(\mathbf{x}, t)$$

$$\rho(\mathbf{x}, t|\alpha) = \sum_{i=0}^{n-1} C_{i,\alpha}(t)\psi_i(\mathbf{x}, t)$$

$$-\frac{\partial}{\partial t}\chi_\alpha(\mathbf{x}, t) = L^{+}(t)\chi_\alpha(\mathbf{x}, t) - \sum_{\beta\neq\alpha} k_{\alpha,\beta}(t)\chi_\beta(\mathbf{x}, t) + \sum_{\beta\neq\alpha} k_{\beta,\alpha}(t)\chi_\alpha(\mathbf{x}, t)$$

$$\frac{\partial}{\partial t}\rho(\mathbf{x}, t|\alpha) = L(t)\rho(\mathbf{x}, t|\beta) \underbrace{- \sum_{\beta\neq\alpha} k_{\beta,\alpha}(t)\rho(\mathbf{x}, t|\beta)}_{\text{sink-}} \underbrace{+ \sum_{\beta\neq\alpha} k_{\beta,\alpha}(t)\rho(\mathbf{x}, t|\alpha)}_{\text{source-term}}$$

Absorbing boundary approximation

Sink-terms $-\sum_{\beta\neq\alpha} k_{\beta,\alpha}(t)\rho(\mathbf{x},t|\beta)$: LARGE if $\mathbf{x}$ near one of $\mathcal{A}_\beta(t)$
$\Longrightarrow$ replace sink by absorbing boundary at $\partial\mathcal{B}_\beta(t)$;
$\mathcal{B}_\beta(t)$: neighborhood of $\mathcal{A}_\beta(t)$

$$\frac{\partial}{\partial t}\rho(\mathbf{x},t|\alpha) = L(t)\rho(\mathbf{x},t|\alpha)+k_\alpha(t)\rho(\mathbf{x},t|\alpha),\ \ \mathbf{x}\in\Sigma_\alpha(t)\equiv\Sigma\setminus\cup_{\beta\neq\alpha}\mathcal{B}_\beta(t)$$

$$\rho(\mathbf{x},t|\alpha) = 0,\ \ \mathbf{x}\in\partial\mathcal{B}_\beta(t),\ \beta\neq\alpha$$

$$\rho(\mathbf{x},t+T|\alpha) = \rho(\mathbf{x},t|\alpha),$$

$$k_\alpha(t) \equiv \sum_{\beta\neq\alpha} k_{\beta,\alpha}(t)$$

$$\frac{\partial}{\partial t}\bar\rho(\mathbf{x},t|\alpha) = L(t)\bar\rho(\mathbf{x},t|\alpha),\quad \bar\rho(\mathbf{x},t|\alpha) = 0,\ \ \mathbf{x}\in\partial\mathcal{B}_\beta(t),\ \beta\neq\alpha$$

$$\rho(\mathbf{x},t|\alpha) = N_\alpha^{-1}(t)\bar\rho(\mathbf{x},t)$$

$$k_\alpha(t) = -\dot N_\alpha(t)/N_\alpha(t)$$

Flux-over-population rate

$$k_{\beta,\alpha}(t) = \underbrace{\int_{\partial\mathcal{B}_\beta(t)} d\mathbf{S}\cdot\mathbf{j}(\mathbf{x},t|\alpha)}_{\text{flux of } \rho(\mathbf{x},t|\alpha) \text{into } \mathcal{B}_\beta(t)} \Big/ \underbrace{\int_{\Sigma_\alpha(t)} d\mathbf{x}\rho(\mathbf{x},t|\alpha)}_{=1,\text{ population}}$$

$$j_i(\mathbf{x},t|\alpha) = K_i(\mathbf{x},t)\rho(\mathbf{x},t|\alpha) - \sum_l \frac{\partial}{\partial x_l} D_{i,l}(\mathbf{x},t)\rho(\mathbf{x},t|\alpha)$$

Remarks

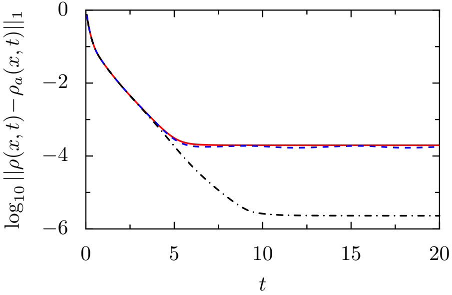
(i) $\rho(\mathbf{x},t|\alpha)$: Kramers' current carrying prob. density for a time-homogeneous process

(ii) In the time-homogeneous case the "flux over the barrier" is conveniently determined at a saddle point. In the periodic case only the flux that directly leads to "products" gives the correct time-dependent rate. Only averages over a period are insensitive to the choice of the boundary.

Decoration of metastable states

Decoration of the metastable state probabilities $p_\alpha(t)$ with $\rho(\mathbf{x}, t|\alpha)$:

$$\rho_a(\mathbf{x}, t) = \sum_\alpha \rho(\mathbf{x}, t|\alpha) p_\alpha(t)$$



$A = 0.1,\ D = 0.025,$
$\Omega = 1$
$||f||_1 = \int |f(x)| dx$

Semi-adiabatic limit and frozen detailed balance[3]

$$T,\; k^{-1}(t) \gg \tau$$

$$k_{\alpha,\beta}(t) = \cancel{\int_\Sigma d\mathbf{x}\, \frac{\partial \chi_\alpha(\mathbf{x},t)}{\partial t} \rho(\mathbf{x},t|\beta)} + \int_\Sigma d\mathbf{x}\, \chi_\alpha(\mathbf{x},t) L(t) \rho(\mathbf{x},t|\beta)$$

frozen detailed balance: $L(t)\rho_{\text{eq}}(\mathbf{x},t) = \rho_{\text{eq}}(\mathbf{x},t) L^+(t)$

$$\begin{aligned}
\rho(\mathbf{x},t|\alpha) &= \chi_\alpha(\mathbf{x},t)\rho_{\text{eq}}(\mathbf{x},t) \\
\cancel{\frac{\partial}{\partial t}\chi_\alpha(\mathbf{x},t)} &= L^+(t)\chi_\alpha(\mathbf{x},t) + \cancel{\text{source- and sink-terms}} \\
\chi_\alpha(\mathbf{x},t) &= \delta_{\alpha,\beta} \quad \text{for } \mathbf{x} \in \mathcal{A}_\beta(t)
\end{aligned}$$

[3] P. Talkner, New J. Phys. **1**, 4 (1999);
P. Talkner, J. Łuczka, PRE **69** , 046109 (2004)

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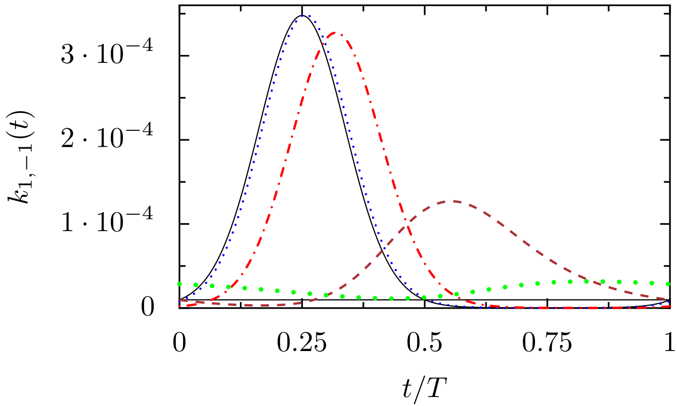
Example



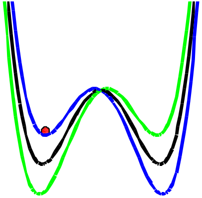
A=0.1, D= 0.025 $\Omega = 0,\ 10^{-3},\ 10^{-2},\ 0.1,\ 0.5,\ 1,\ \infty$

Conclusion of part 1

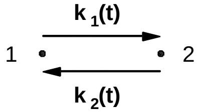
Large-time dynamics of the conditional probability $\rho(\mathbf{x}, t|\mathbf{y}, s)$ is determined by
(1) the transitions between metastable states governed by a master equation with time-dependent rates
(2) the localizing functions $\chi_\alpha(\mathbf{x}, t)$
(3) the state specific probabilities $\rho(\mathbf{x}, t|\alpha)$.
Absorbing boundary approximation yields specific probabilities and localizing functions.
Rates then are given by flux-over-population expressions.
Slow driving: Semi-adiabatic approximation

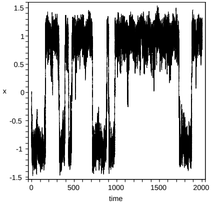
P. Talkner, J. Łuczka, PRE **69**, 046109 (2004).
C. Kim, P. Talkner, E.K. Lee, P. Hänggi, Chem. Phys. **370**, 277 (2010).

Rates and point-process of transition times[4]



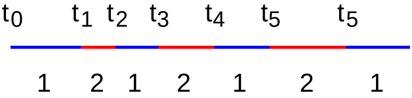
$$\dot{x}(t) = -\partial V(x,t)/\partial x + \sqrt{2/\beta}\,\xi(t)$$





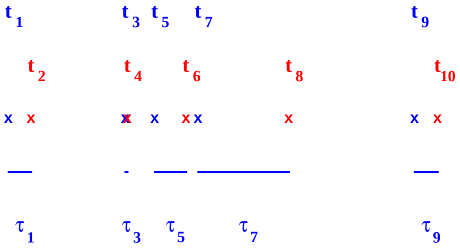
$$k_i(t) = \frac{\omega_i(t)\omega_b(t)}{2\pi} e^{-\beta\Delta V_i(t)}$$

$$\dot{p}_1(t) = -k_1(t)p_1(t) + k_2(t)p_2(t), \quad \dot{p}_2(t) = k_1(t)p_1(t) - k_2(t)p_2(t)$$



[4] P. Talkner, Physica A **325**, 124 (2003);
P. Talkner, L. Machura, P. Hänggi, J. Łuczka, New J. Phys. **7**, 14 (2005)

Transition times



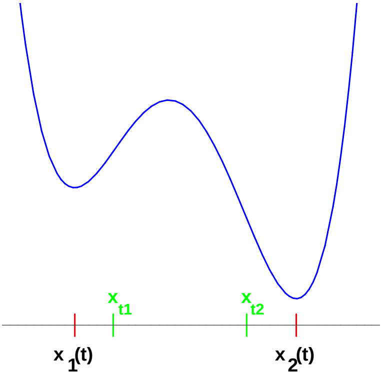
$1 \longrightarrow 2$

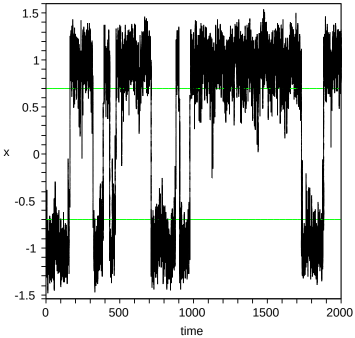
$2 \longrightarrow 1$

residence times in 1

Transition times constitute two alternating point processes $\{t_1, t_2, t_3, t_4 \ldots\}$

Langevin simulation of transition times





register alternating crossing times of thresholds x_{t1} and x_{t2}

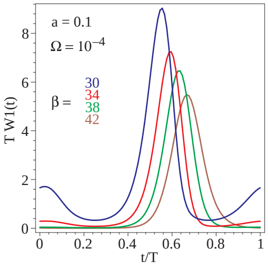
Entrance time density

$$W_1(t)dt = \#\{\text{transitions into state 1 within [t,t+dt]}\}$$

$$W_1(t) = k_2(t)p_2(t) \qquad \text{entrance time density}$$

$$f_{1,1}(t,s) = k_2(t)p(2,t|1,s)k_2(s)p_2(s)$$
$$f_{1,2}(t,s) = k_2(t)p(2,t|2,s)k_1(s)p_1(s)$$

joint densities of entrances into states 1 and 1 (2) at times t and s, respectively.
$p_\alpha(t)$: asymptotic, periodic solution of master equation.
$p(\alpha, t|\alpha', s)$: prob. α at t conditioned on α' at s.
Beginning of a hierarchy of joint n-time entrance densities.



P. Talkner, Physica A **325**, 124 (2003)

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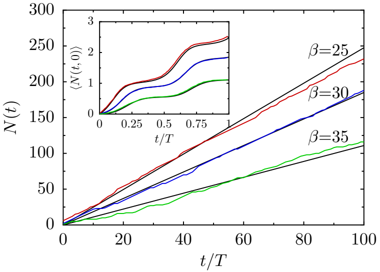
Counting process and Rice phase

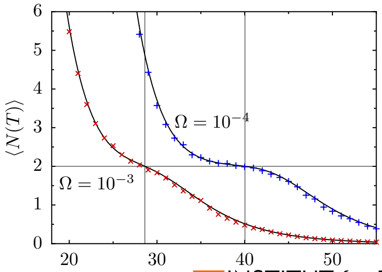
$N(t,s) = \#\{\text{transitions in } (s,t)\}$: counting process

$\Phi(t,s) = \pi N(t,s)$: generalized Rice phase

Callenbach et al. PRE **65**, 051110 (2002)

$$\langle N(t,s)\rangle = \int_s^t dt'\; W(t'), \quad W(t) = W_1(t) + W_2(t)$$





SYNCHRONIZATION at SR: $\langle N(T,0)\rangle = 2$

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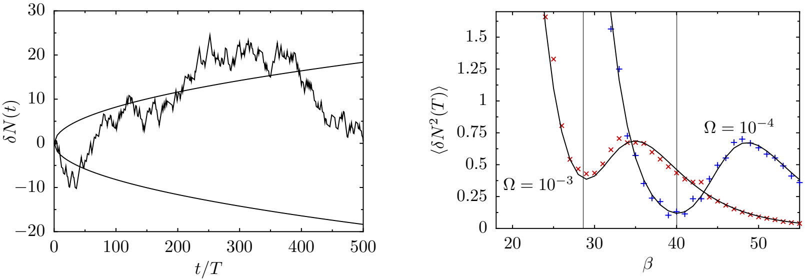
Phase diffusion

$$\langle N^2(t,s)\rangle = \langle N(t,s)\rangle + 2\int_s^t dt' \int_s^{t'} ds'\, f(t',s')$$

$$\langle \delta N^2(t,s)\rangle \equiv \langle (N(t,s) - \langle N(t,s)\rangle)^2\rangle \sim D(s)(t-s) \quad \text{for } t-s \to \infty$$



P. Talkner, Ł. Machura, M. Schindler, P. Hänggi, J. Łuczka, New J. Phys. **7**, 14 (2005); J. Casado-Pascual et al. PRE **71**, 011101 (2005)

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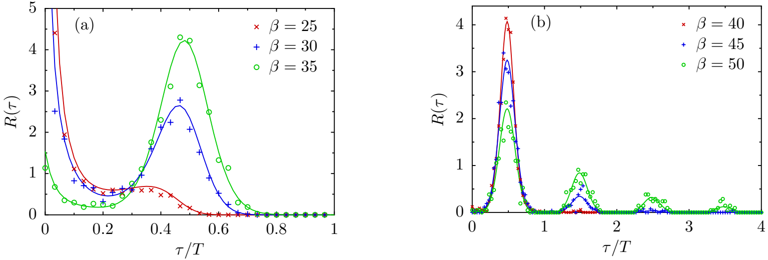
Residence time distributions

$$R_\alpha(\tau) = \frac{\int_0^T ds\, P_\alpha(s+\tau|s) W_\alpha(s)}{\int_0^T dt W_\alpha(t)}$$

$$P_\alpha(t|s) = \exp\{-\int_s^t dt'\, k_\alpha(t')\}$$ waiting time distribution in α



L. Gammaitoni, F. Marchesoni, S. Santucci, PRL **74**, 1052 (1995)

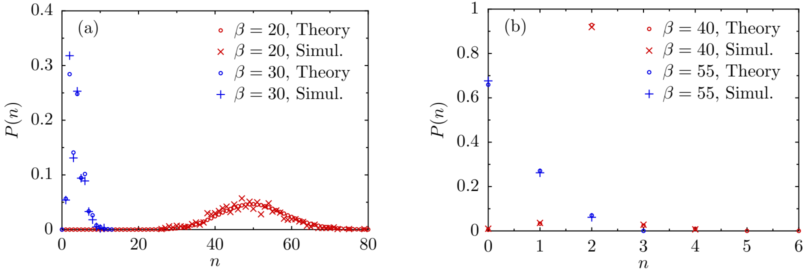
Counting statistics

$$p_\alpha(n;t,s) = \text{Prob}\left\{z(s)=\alpha \text{ and } n \text{ transitions in } (s,t)\right\}$$

$$\begin{aligned}\frac{\partial}{\partial t}p_\alpha(n+1;t,s) &= -k_{\alpha_{n+1},\alpha_n}(t)p_\alpha(n+1;t,s)\\ &\quad +k_{\alpha_n,\alpha_{n-1}}(t)p_\alpha(n;t,s)\end{aligned}$$

$$p_\alpha(n+1;s,s)=0 \quad p_\alpha(0;t,s)=P_\alpha(t|s)p_\alpha(s)$$

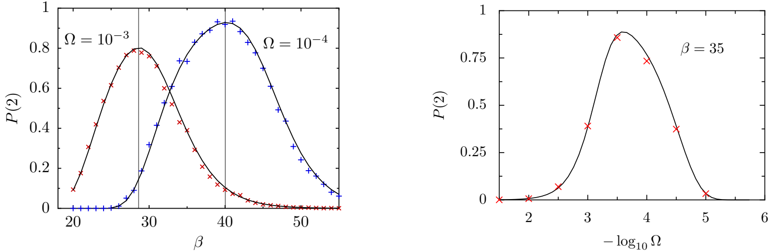
$$\alpha_n = \alpha \text{ for } n \;\; \bar{\alpha} \text{ for } n \text{ odd}$$



$$P(n) = p_1(n;T,0) + p_2(n;T,0)$$

Synchronization measure $P(2)$

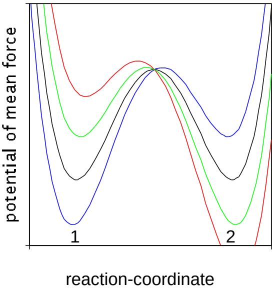
$$P(2) = \text{Prob}\,\{\text{two transitions per period}\}$$



$P(2)$ maximal at SR

BONA FIDE resonance

How often and how long?

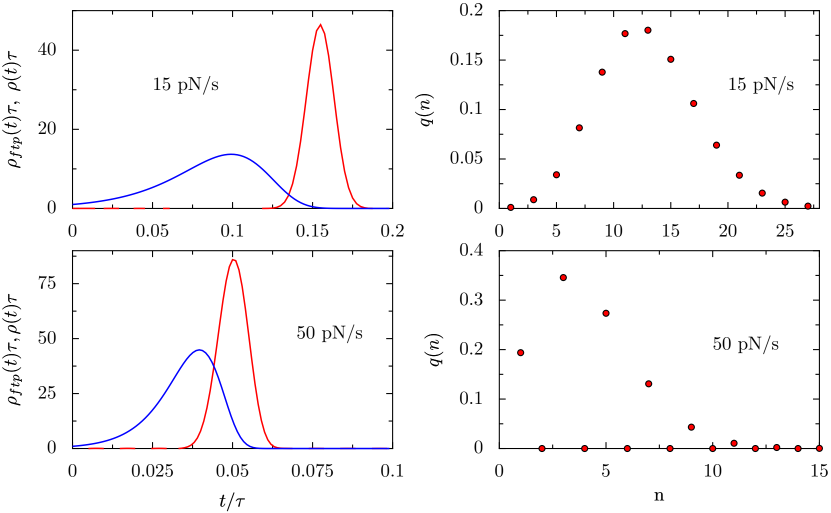


In a stretching experiment a force that increases with time is applied to a molecule. Often the process of conformational change induced by the applied force is considered as a first passage time problem.

$$k_1(t) = k_1^0 \exp\left[\lambda x_1 t/(k_B T)\right]$$
$$k_2(t) = k_2^0 \exp\left[-\lambda x_2 t/(k_B T)\right]$$

λ: speed of force increase

x_i: distance of the metastable state i from the barrier



$$\tau = 1/k_1^0 = 10s,\ k_2^0\tau = e^{10},\ x_1 = x_2 = 1nm$$

Conclusion of part 2

Transition rates determine

- Densities and correlations of transition times
  $\Longrightarrow$ average Rice phase and phase diffusion
- Residence time distributions
- Probabilities of numbers of transitions
- First passage times
- Total sojourn times of a state