Suppression of thermally activated escape by heating

Sebastian Getfert and Peter Reimann

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Overdamped Langevin equation

Consider one-dimensional noisy dynamics

$$\mathbf{m\ddot{x}(t) = -U'(x(t),t) - \boldsymbol{\eta}(t)\dot{x}(t) + \sqrt{2\boldsymbol{\eta}(t)k_B T(t)}\boldsymbol{\xi}(t)}$$

$\xi(t)$ Gaussian , $\langle\xi(t)\rangle = 0$, $\langle\xi(t)\xi(t')\rangle = \delta(t-t')$

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Examples:

- Colloidal particles in a force field
- Chemical reactions
- Cold atoms in optical lattices

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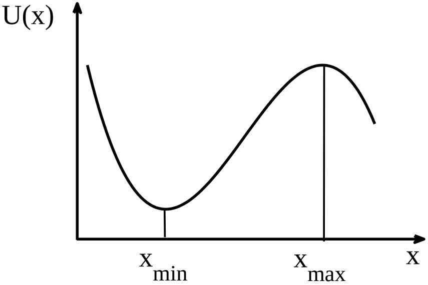
Overdamped limit: $m \to 0 \quad \Rightarrow$

$$\mathbf{\eta(t)\dot{x}(t) = -U'(x(t),t) + \sqrt{2\eta(t)k_B T(t)}\xi(t)}$$

Thermally activated escape

- t-independent η and T
- metastable potential $U(x)$
  $\Rightarrow$ simple deterministics
- probability density $\rho(x, t)$



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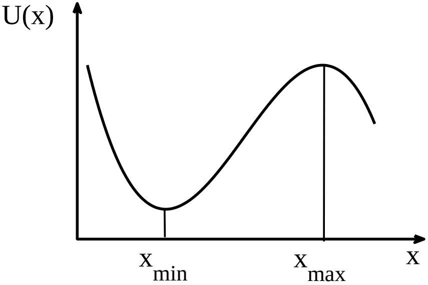

- survival probability: $n(t) := \int_{-\infty}^{x_{\max}} dx\, \rho(x,t)$
- instantaneous escape rate: $\Gamma(t) := -\dot{n}(t)/n(t)$
- for $\Delta U := U(x_{\max}) - U(x_{\min}) \gg k_B T$ and large t

$$\Gamma(t) \simeq \frac{|U''(x_{\max})\, U''(x_{\min})|^{1/2}}{2\pi\eta} \exp\left(-\Delta U/k_B T\right)$$

Time dependent case

- general case, treated in Phys. Rev. E 80, 030101 (2009)

$$\eta(\mathbf{t})\dot{x}(t) = -U'(x(t), \mathbf{t}) + \sqrt{2\eta(\mathbf{t}) k_B T(\mathbf{t})}\xi(t)$$

- simplest non-trivial case, treated in this talk

$$\dot{\mathbf{x}}(\mathbf{t}) = -\mathbf{U}'(\mathbf{x}(\mathbf{t})) + \sqrt{\mathbf{2Dg(t)}}\xi(\mathbf{t}) \ ,$$

$$\lim_{t\to\infty} \frac{1}{t} \int_0^t dt \, g(t) = 1 \ , \quad g(t) > 0$$

D: noise strength, small parameter

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D: noise strength, small parameter

- Fokker-Planck-eq. for conditional prob. $\boldsymbol{\rho}(\mathbf{x},\mathbf{t}|\mathbf{x_0},\mathbf{t_0})$

$$\frac{\partial}{\partial \mathbf{t}}\rho(\mathbf{x},\mathbf{t}|\mathbf{x_0},\mathbf{t_0}) = \frac{\partial}{\partial \mathbf{x}}\left(\mathbf{U}'(\mathbf{x}) + \mathbf{Dg}(\mathbf{t})\frac{\partial}{\partial \mathbf{x}}\right)\rho(\mathbf{x},\mathbf{t}|\mathbf{x_0},\mathbf{t_0})$$

Rate formula

- survival probability: $n(t) := \int_{-\infty}^{x_{\max}} dx\ \rho(x, t|x_0, t_0)$
- instantaneous escape rate: $\Gamma(t) := -\dot{n}(t)/n(t)$
- with Fokker-Planck-equation:

$$\dot{n}(t) = Dg(t)\frac{\partial\rho\left(x_{\max}, t|x_0, t_0\right)}{\partial x_{\max}}$$

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- for weak noise $D \ll \Delta U$ and not too large t: $n(t) \simeq 1 \Rightarrow$

$$\mathbf{\Gamma(t) = -Dg(t)\frac{\partial\rho\left(x_{\max}, t|x_0, t_0\right)}{\partial x_{\max}}}$$

- simplest and most relevant case $x_0 = x_{\min}$

Time discretization

Noisy dynamics: $\dot{x}(t) = -U'(x(t)) + \sqrt{2Dg(t)}\,\xi(t)$

Discretization: $t_n := n \cdot \Delta t \;, \quad n = 0, ..., N \;, \quad x_n := x(t_n) \;,$

$$\frac{x_{n+1} - x_n}{\Delta t} = -U'(x_n) + \sqrt{2Dg(t_n)}\,\frac{W_n}{\Delta t}$$

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$$\Leftrightarrow \quad W_n = \frac{\Delta t}{\sqrt{2Dg(t_n)}}\left[\frac{x_{n+1}-x_n}{\Delta t} + U'(x_n)\right]$$

Discrete Wiener process $\quad \rho(W_n) = \frac{1}{\sqrt{2\pi\Delta t}}\ \exp\{-\frac{W_n^2}{2\Delta t}\}$

$$\Rightarrow \quad \rho(x_{n+1}, t_{n+1}|x_n, t_n) = C\ \exp\{-\tfrac{1}{D}\,\Delta t\ L_n\}$$

$$L_n := \frac{1}{4\,g(t_n)}\ \left[\frac{x_{n+1}-x_n}{\Delta t} + U'(x_n)\right]^2$$

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Chapman-Kolmogorov $\rho(x_{n+2}, t_{n+2}|x_n, t_n) =$

$$= \int dx_{n+1}\ \rho(x_{n+2}, t_{n+2}|x_{n+1}, t_{n+1})\ \rho(x_{n+1}, t_{n+1}|x_n, t_n)$$

$$\Rightarrow \rho(x_N, t_N|x_0, t_0) = \int dx_1 \cdots dx_{N-1}\, C^{N-1}\ \exp\{-\tfrac{1}{D}\sum_{n=0}^{N} \Delta t\ L_n\}$$

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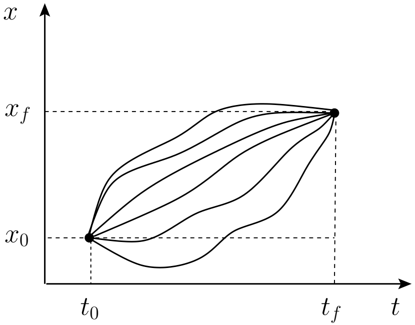
Continuous time limit $\Delta t \to 0$, $N \to \infty$

Path integrals

"Sum" over all "paths" $x(t)$ with $x(t_0) = x_0$ and $x(t_f) = x_f$



$$\rho(\mathbf{x_f}, \mathbf{t_f} | \mathbf{x_0}, \mathbf{t_0}) = \int_{\substack{\mathbf{x(t_0)=x_0} \\ \mathbf{x(t_f)=x_f}}} \mathcal{D}\mathbf{x(t)}\ \mathbf{e}^{-\mathbf{S[x(t)]/D}}$$

Action: $S[x(t)] := \int_{t_0}^{t_f} dt\ L(x(t), \dot{x}(t), t)$

Lagrangian: $L(x, \dot{x}, t) := \frac{1}{4g(t)}[\dot{x} + U'(x)]^2$

Saddle point approximation

- path $x^*(t)$ minimizes $S[x(t)] \;\Rightarrow\; \boldsymbol{\delta \mathbf{S}[\mathbf{x}^*(\mathbf{t})] = 0}$

  $\Rightarrow\;$ $x^*(t)$ solves corresponding Euler-Lagrange equation

- Noise strength D small $\Rightarrow$

  path integral dominated by $x^*(t)$ and its neighborhood

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  path integral dominated by $x^*(t)$ and its neighborhood

- Saddle point (Gaussian) approximation

$$\boldsymbol{\rho(x_f, t_f | x_0, t_0) = \frac{e^{-S[x^*(t)]/D}}{\sqrt{4\pi D Q(t_f)}}[1 + \mathcal{O}(D)]}$$

  $Q(t)$: solution of a linear ODE

Recall: $\Gamma(t_f) = -Dg(t_f)\frac{\partial\rho(x_{\max},t_f|x_{\min},t_0)}{\partial x_{\max}}$

For $x(t_0) = x_{\min}$ and $x(t) = x_{\max}$, quite "different" paths $x(t)$ may yield almost the same $S[x(t)] = \int_{t_0}^{t_f} dt\ \frac{[\dot{x}(t)+U'(x(t))]^2}{4g(t)}$

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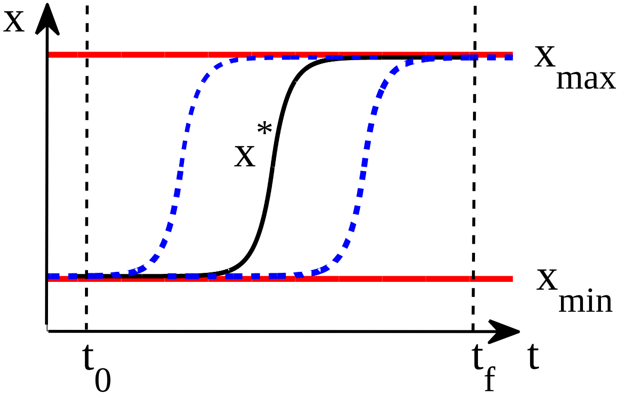
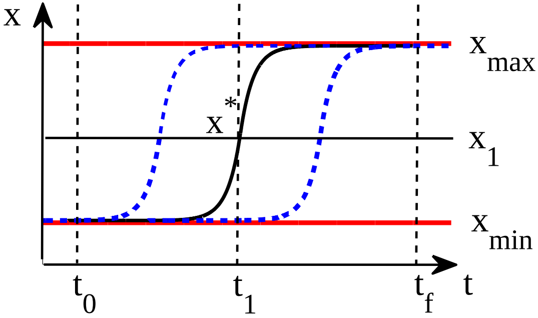


$\Rightarrow$ Saddle point approximation fails even for quite small D

Idea: impose extra condition $x(t_1) = x_1$ and integrate over t_1



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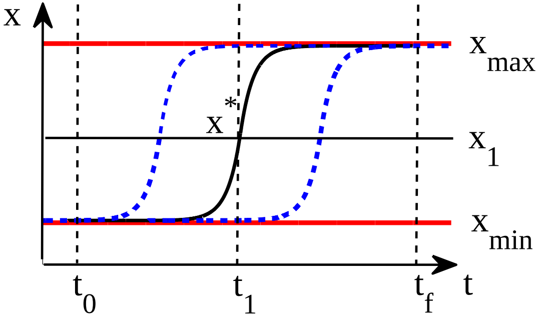

Def.: $h(t_1)\,dt_1 :=$ probability that $x(t)$ crosses x_1 for the first time during $[t_1, t_1 + dt_1]$, given $x(t_0) = x_{\min}$

$$\Rightarrow \quad \boldsymbol{\rho\,(x_{\max}, t | x_{\min}, t_0) = \int_{t_0}^{t} \rho(x_{\max}, t | x_1, t_1)\; h(t_1)\, dt_1}$$

Main idea: $h(t_1)\,dt_1$ and $\rho(x_1, t_1|x_{\min}, t_0)\,dx_1$ approximately "count the same events" if $dx_1 = \dot{x}^*(t_1)\,dt_1$ and D small $\Rightarrow$

$$\boldsymbol{\rho}\,(\mathbf{x}_{\max}, \mathbf{t}|\mathbf{x}_{\min}, \mathbf{t_0}) = \int_{\mathbf{t_0}}^{\mathbf{t}} \boldsymbol{\rho}(\mathbf{x}_{\max}, \mathbf{t}|\mathbf{x_1}, \mathbf{t_1})\,\boldsymbol{\rho}(\mathbf{x_1}, \mathbf{t_1}|\mathbf{x}_{\min}, \mathbf{t_0})\,\dot{\mathbf{x}}^*(\mathbf{t_1})\,\mathbf{dt_1}$$

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$$\boldsymbol{\rho\,(\mathbf{x}_{\max}, \mathbf{t}|\mathbf{x}_{\min}, \mathbf{t}_0) = \int_{\mathbf{t}_0}^{\mathbf{t}} \rho(\mathbf{x}_{\max}, \mathbf{t}|\mathbf{x}_1, \mathbf{t}_1)\,\rho(\mathbf{x}_1, \mathbf{t}_1|\mathbf{x}_{\min}, \mathbf{t}_0)\,\dot{\mathbf{x}}^*(\mathbf{t}_1)\,\mathbf{dt}_1}$$

Rigorous calculations: S. Getfert, PhD Thesis 2009

Similar concepts:

N. Berglund and B. Genz, J. Stat. Phys. 114, 1577 (2004);

N. Berglund and B. Genz, Europhys. Lett. 70, 1 (2005)

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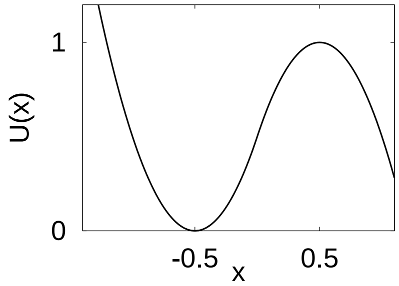
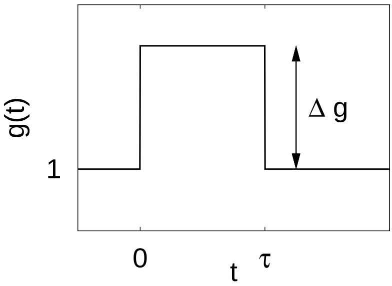
Previous problems of saddle point approximation absent for $\rho(x_{\max},t|x_1,t_1)$ and $\rho(x_1,t_1|x_{\min},t_0)$

$\Rightarrow$ $\boldsymbol{\Gamma(\mathbf{t}) = -\mathbf{D}\mathbf{g}(\mathbf{t})\,\frac{\partial\rho(\mathbf{x}_{\max},\mathbf{t}|\mathbf{x}_{\min},\mathbf{t_0})}{\partial\mathbf{x}_{\max}}}$ "straightforward"

Example 1: Temperature pulse

- piecewise parabolic potential
- $g(t)$ with single pulse: duration τ, amplitude $\mathbf{\Delta g = 1}$





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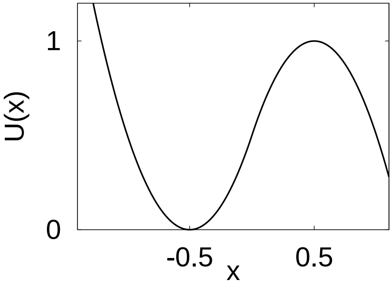
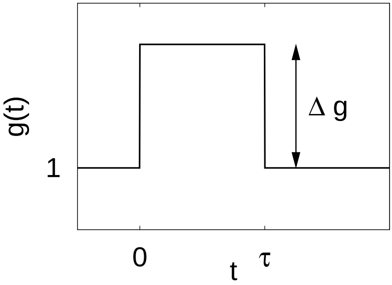


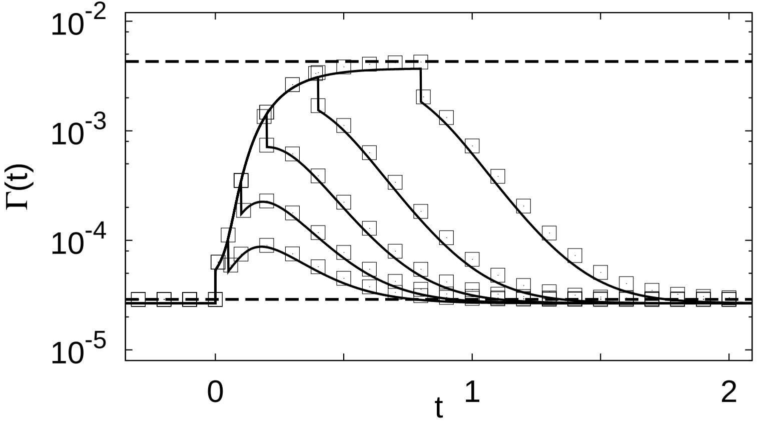


$$\Gamma(t) = -Dg(t) \int_{t_0}^{t} \frac{\partial \rho(x_{max}, t | x_1, t_1)}{\partial x_{max}} \, \rho(x_1, t_1 | x_0, t_0) \, \dot{x}^*(t_1) \, dt_1$$

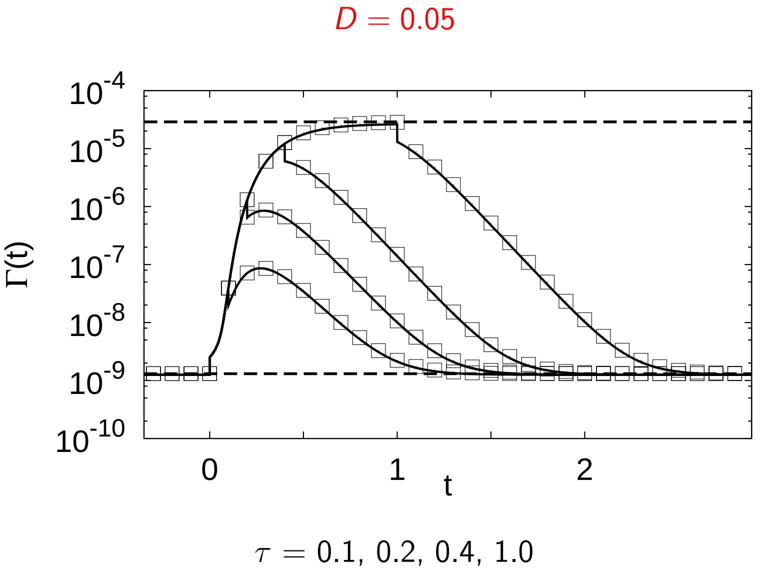
$\Rightarrow$ closed analytical expression for integrand

numerical evaluation of integral

$D = 0.1$



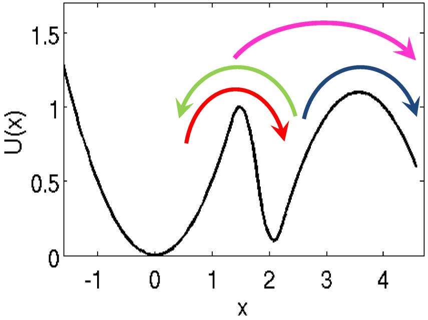
$\tau = 0.05,\ 0.1,\ 0.2,\ 0.4,\ 0.8$

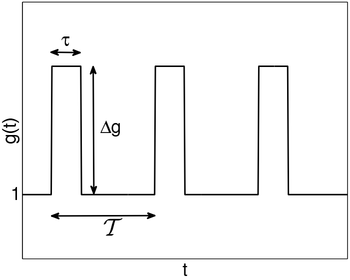


$D = 0.05$
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
Γ(t)
0
1
2
t
$\tau = 0.1,\ 0.2,\ 0.4,\ 1.0$

Example 2: suppression of escape by heating

- piecewise parabolic potential
- periodic temperature pulses



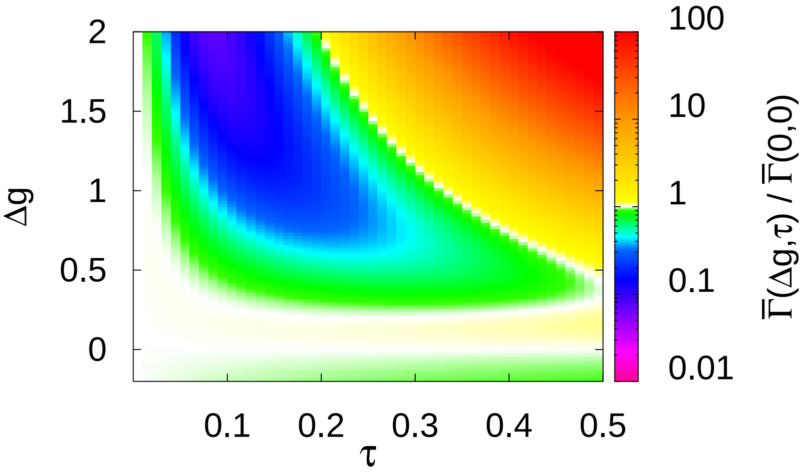


- Three single rates determined as before

  ⇒ **effective, time averaged rate Γ_{eff}**

Effective escape rates

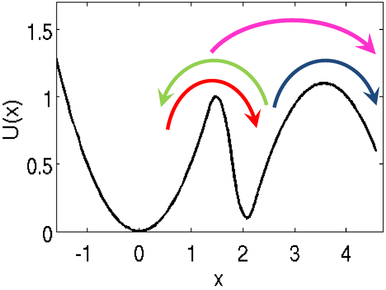
Noise strength $D = 0.05$, period $\mathcal{T} = 20$

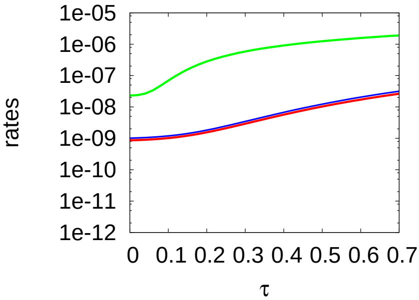


effective rate may decrease !

Explanation

Time averaged rates for $\Delta g = 1$:





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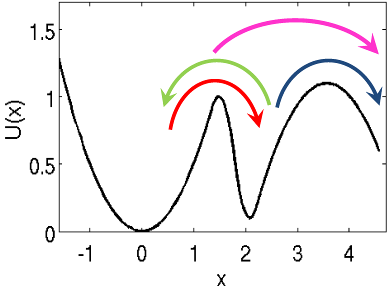

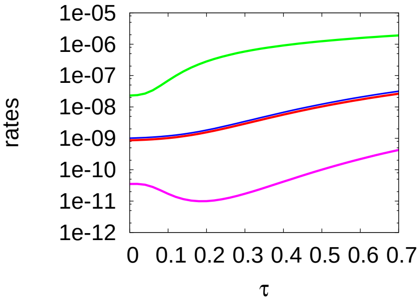

More details:

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Phys. Rev. E **80**, 030101(R) (2009)

Idee für neue Näherung

- Formal:

$$\rho(x_{\mathrm{max}}, t | x_{\mathrm{min}}, t_0) = \int_{t_0}^{t} dt_1 \; \Psi(x_1, t_1 | x_{\mathrm{min}}, t_0) \rho(x_{\mathrm{max}}, t | x_1, t_1)$$

- Erste-Passage-Zeitdichte:

$$\Psi(x_1, t_1 | x_{\mathrm{min}}, t_0) := -d/dt \, \mathrm{Prob}(x(t) < x_1 \, \forall \, t < t_1)$$

- Rate

$$\Gamma(t) = -Dg(t) \int_{t_0}^{t} dt_1 \; \Psi(x_1, t_1 | x_{\mathrm{min}}, t_0) \frac{\partial \rho \left(x_{\mathrm{max}}, t | x_1, t_1 \right)}{\partial x_{\mathrm{max}}}$$

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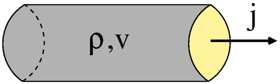
- Approximation $\Psi(x_1, t_1 | x_{\min}, t_0)$?

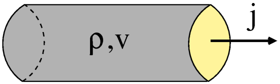
- Ziel: Drücke $\Psi(x_1, t_1|x_{\min}, t_0)$ durch Sattelpunktsnäherung für $\rho(x_1, t_1|x_0, t_0)$ aus.
- Einfachste Approximation:

$$\Psi(x_1, t_1|x_{\min}, t_0) \approx v_{typ}\rho(x_1, t_1|x_0, t_0)$$

v_{typ}: typische Geschwindigkeit



- Ziel: Drücke $\Psi(x_1, t_1|x_{\min}, t_0)$ durch Sattelpunktsnäherung für $\rho(x_1, t_1|x_0, t_0)$ aus.
- Einfachste Approximation:



$$\Psi(x_1, t_1|x_{\min}, t_0) \approx v_{typ}\rho(x_1, t_1|x_0, t_0)$$

v_{typ}: typische Geschwindigkeit

Gezeigt:

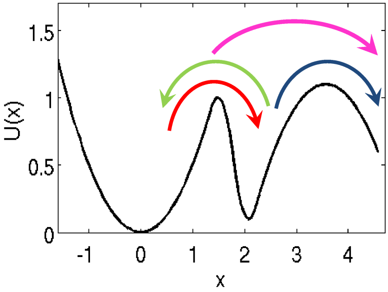
Falls Sattelpunktsnäherung für $\rho(x_1, t_1|x_0, t_0)$ anwendbar, ist

$$\Psi(x_1, t_1|x_{\min}, t_0) = \dot{x}^*(t_1|x_{\min}, t_0)\rho(x_1, t_1|x_0, t_0)$$

i.A. eine sehr gute Näherung. Dabei ist $\dot{x}^*(t_1|x_{\min}, t_0)$ die Geschwindigkeit des optimierenden Pfades.

Modell

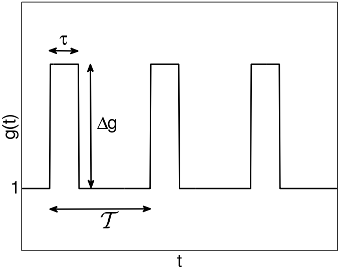
- Statisches Potential
- periodische, kurzzeitige Erhöhung Temperatur
- Wahrscheinlichkeit für Zustand i: $n_i(t)$
- Übergangsrate $i \rightarrow j$: $\Gamma_{i,j}(t)$
- Dynamik:



$$\frac{d}{dt}\mathbf{n}(t) = -\mathbf{G}(t)\mathbf{n}(t) \,,$$

$$\mathbf{n}(t) = \begin{pmatrix} n_1(t) \\ n_2(t) \end{pmatrix} \,,$$

$$\mathbf{G}(t) = \begin{pmatrix} \Gamma_{1,2}(t) + \Gamma_{1,0}(t) & -\Gamma_{2,1}(t \\ -\Gamma_{1,2} & \Gamma_{2,1}(t) \end{pmatrix} ,$$



Effektive Rate

- Annahme: $\int_0^{\mathcal{T}} dt\, \Gamma_{i,j}(t) \ll 1$
- Es reicht zeitgemittelte Größen zu betrachten:

$$\bar{n}_i(t) = 1/\mathcal{T} \int_{t-\mathcal{T}/2}^{t+\mathcal{T}/2} dt'\; n_i(t')\,, \qquad \bar{\Gamma}_{i,j} = 1/\mathcal{T} \int_0^{\mathcal{T}} dt\; \Gamma_{i,j}(t)$$

- Dynamik: $\frac{d}{dt}\bar{\mathbf{n}}(t) = -\bar{\mathbf{G}}\bar{\mathbf{n}}(t)$
- Effektive Entweichrate:

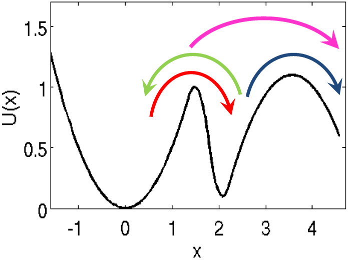
$$\bar{\Gamma} := \mathbf{min}(\mathrm{Eig}(\bar{\mathbf{G}}))$$

- Zugehöriger Eigenvektor: $\mathbf{n}_{eq}$

$$\Rightarrow \bar{\mathbf{n}}(t) \rightarrow n(t)\mathbf{n}_{eq} \text{ und } n(t) \propto e^{-\bar{\Gamma}t}$$

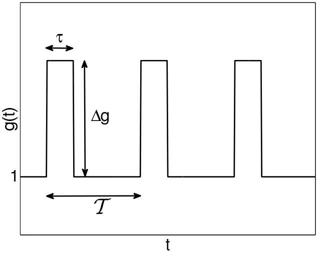
Beispiel

Stückweise parabolisches Potential:



$$\Delta U_{1\to 0} = 1$$
$$\Delta U_{1\to 2} = 0.9$$
$$\Delta U_{2\to 1} = 1$$

$$U''(x_{\min,2}) = -U''(x_{\max,1}) = 1$$
$$U''(x_{\min,1}) = -U''(x_{\max,2}) = 10$$



$$D = 0.05$$
$$\mathcal{T} = 20$$

Approximation der Raten wie gehabt!