Diffusion-Controlled Reactions over Fluctuating Barriers

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Motivation

- Motivated by recent studies on tunable nano-reactors with thermosensitive polymer shell a simplified system of diffusing particles in the vicinity of a spherical sink shielded by a metastable potential barrier is investigated.
  We derive an implicit solution for the resulting Fokker-Planck equation to obtain the diffusion-controlled reaction rate.
- The system shows resonant activation as previously seen with thermally activated escape over fluctuating barriers.
- We find that this resonant activation phenomenon is crucially depending on the barrier curvature.

System description

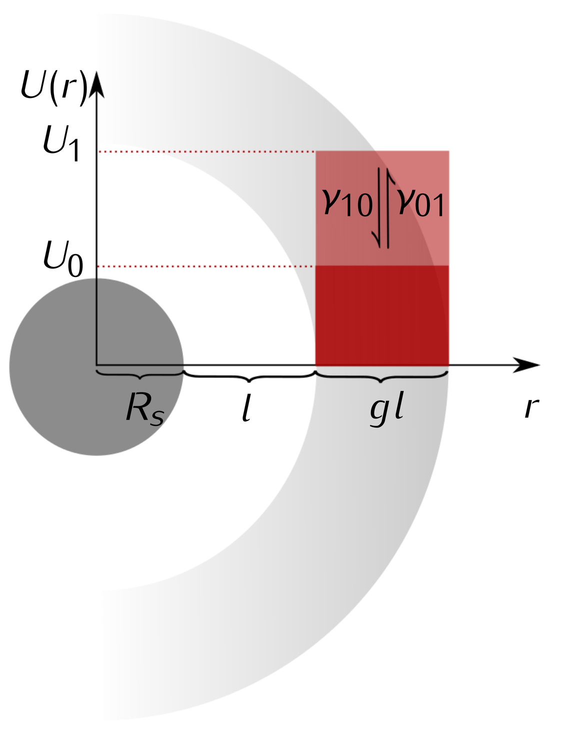
- The system consists of a spherical sink of Radius R_s enclosed by a radially symmetric, boxcar shaped potential barrier.

$$U_n(r) = \begin{cases} 0 & : 1 < r \leq 1 + l \\ U_n & : 1 + l < r \leq 1 + l + gl \\ 0 & : 1 + t + gl < r \end{cases} \quad (1)$$

- The probabilities P_n for the barrier to be in one of the states $U_n \in [U_0, \cdots U_N]$ follow a Master equation with a rate matrix that obeys detailed balance:

$$\frac{\partial \mathbf{P}}{\partial t} = \mathbb{W}\mathbf{P}; \quad W_{mn} P_n^{(eq)} = W_{nm} P_m^{(eq)} \quad (2)$$

- Sink and barrier are embedded in a bath of Brownian particles.
- $K_B T$ and R_s are set to be one.



Reaction-Diffusion approach

- The combined Markov Process on $\mathbb{R}^3 \times [0, \cdots N]$ can be described in terms of particle densities $\rho_n(\vec{r})$

$$\frac{\partial}{\partial t}\rho(\vec{r}, n, t) = \{\mathbb{F} + \mathbb{W}\}\, \rho(\vec{r}, n, t). \quad (3)$$

- Where $\mathbb{F}$ is a diagonal Fokker-Planck operator.

$$\mathbb{F} = \mathrm{diag}\left[\vec{\nabla}\frac{1}{\gamma}\left(\vec{\nabla}U_n(r)\right) + D\vec{\nabla}^2\right]. \quad (4)$$

- The absorption rate is equal to the total Flux through the sink surface:

$$K = \int_{\partial Sink} \vec{J} d\vec{A} = 4\pi D R_s^2 \sum_{n=1}^{N} \frac{\partial}{\partial r}\bigg|_{R_s} \rho_n(r) \quad (5)$$

Expansion in Eigenfunctions of $\mathbb{W}$

- Since $\mathbb{W}$ satisfies detailed balance it can be symmetrized by the similarity transform $\mathbb{T} = \delta_{nm}[P_m^{(eq)}]^{1/2}$,
- The symmetric matrix $\mathbb{S} = \mathbb{T}^{-1}\mathbb{W}\mathbb{T}$ can be diagonalized by an orthogonal transformation $\mathbb{O}$. Its Eigenvalues are $\lambda_0 = 0$ and $\lambda_{i>0} < 0$.
- We exploit the fact that $\mathbb{F}$ is invariant under these transformations for $r \neq 1+l, r \neq 1+l+gl$ and write eq. (3) in terms of the transformed particle densities $\tilde{\rho} = \mathbb{T}^{-1}\mathbb{O}^{\dagger}\rho$.
- The piecewise solution in $\tilde{\rho}_n$ then reads:

$$\tilde{\rho}_1^{(j)}(r) = c_{1,1}^{(j)} + c_{1,2}^{(j)}\frac{1}{r}$$
$$\tilde{\rho}_{i\neq 1}^{(j)}(r) = c_{i,1}^{(j)}\frac{1}{r}\exp\left[-r\sqrt{\frac{\lambda_i}{D}}\right] + c_{i,2}^{(j)}\frac{1}{r}\exp\left[r\sqrt{\frac{\lambda_i}{D}}\right] \quad (6)$$

- Coefficients $c_{i,k}^{(j)}$ are derived from the system of linear equations emerging from boundary conditions and fit conditions @ $r = 1 + l$ and $r = 1 + l + gl$.

Boundary and Fit Conditions

- Fit conditions are obtained by integrating over a box including the jump discontinuity of the potential and then taking the limit of the box size to zero:

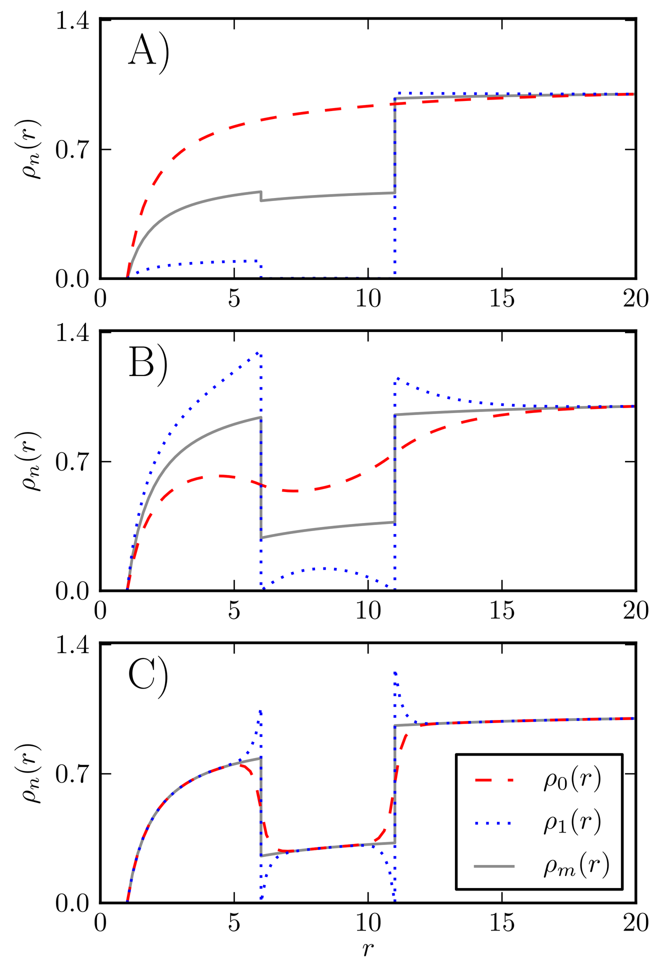
$$\rho^{(I)}(1 + l) = \mathrm{diag}\left[\exp\{U_n\}\right]\rho^{(II)}(1 + l); \qquad \vec{\nabla}\rho^{(I)}\Big|_{1+l} = \vec{\nabla}\rho^{(II)}\Big|_{1+l}. \quad (7)$$

- Boundary conditions at $r = 1$ and $r \to \infty$ are

$$\rho^{(I)}(1) = 0; \qquad \lim_{r\to\infty}\rho(r) = \mathbf{P}^{(eq)}. \quad (8)$$

- The total density at infinity is thereby set to one.

Density profiles



Examples of density profiles for symmetric $\gamma_{10} = \gamma_{01} = \gamma$ and attractive metastable barrier.

- The figure shows density profiles for the active $\rho_0(r)$ and inactive $\rho_1(r)$ state of the barrier, as well as the mean density profile.
- The three figures differ in the ratio of diffusion constant of the Brownian particles to the switching rate which influences the decay length of the influence of the potential (comp. eq. (6))

$$r_d = \sqrt{\frac{D}{\lambda_1}} = \sqrt{\frac{D}{2\gamma}} \quad (9)$$

Obviously, this decay length gives the radial range of the influence of the potential.

Fig. 3: Density profiles for barrier with $U_0 = 0$, $U_1 = 10$, $l = 5$ and $g = 1$. A: $r_d = 25$, B: $R_d = 2.5$, C: $R_d = 0.25$

Absorption Rates - Resonant Activation

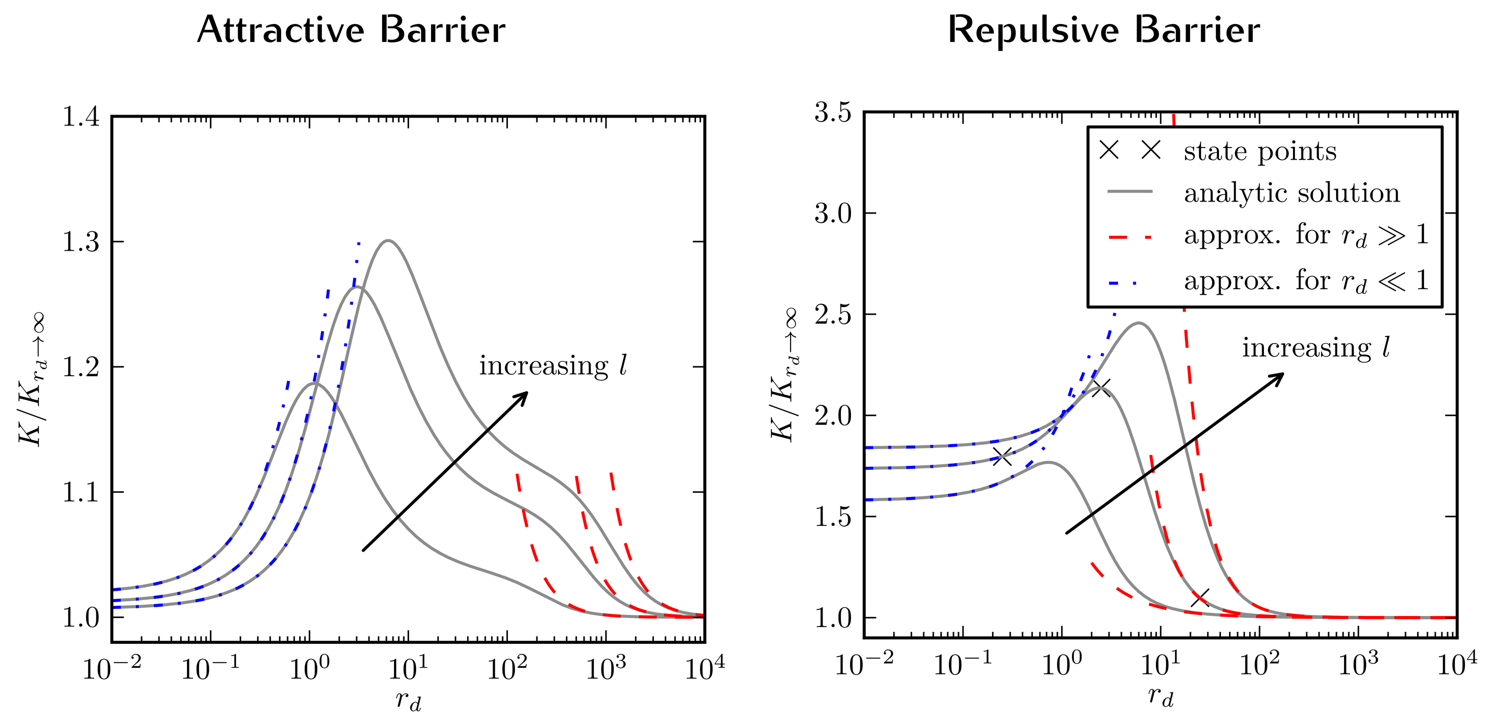


Fig. 6: normalized absorption rate vs. decay length for attractive fluctuating barrier. Parameters are $U_1 = 10, -10$, $U_0 = 0$, $g = 1$ and $l = 2, 5, 10$.

Breathing Barrier $U_1 < 0$: the barrier collects particles while at an active state and releases them when its state changes.

Pumping Barrier $U_1 > 0$: particles can cross the outer barrier border while it is down and get lifted up when the barrier state changes.

The absorption rate profiles exhibit a resonant peak depending on decay length and size of the barrier. Similar phenomena are found in escape over fluctuating barriers. The resonant peak follows a power law:

$$r_d^{(res)} = Cl^{\kappa} \quad (10)$$

with $C \approx 1$ and $\kappa \approx 2/5$. Also for fixed gap to width ratio g of the barrier, the resonant rate $K^{(res)}$ converges to a finite value.

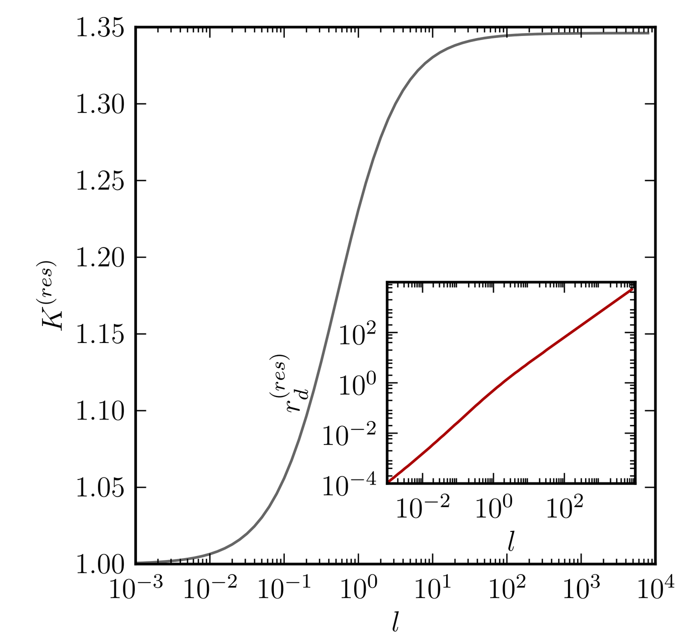
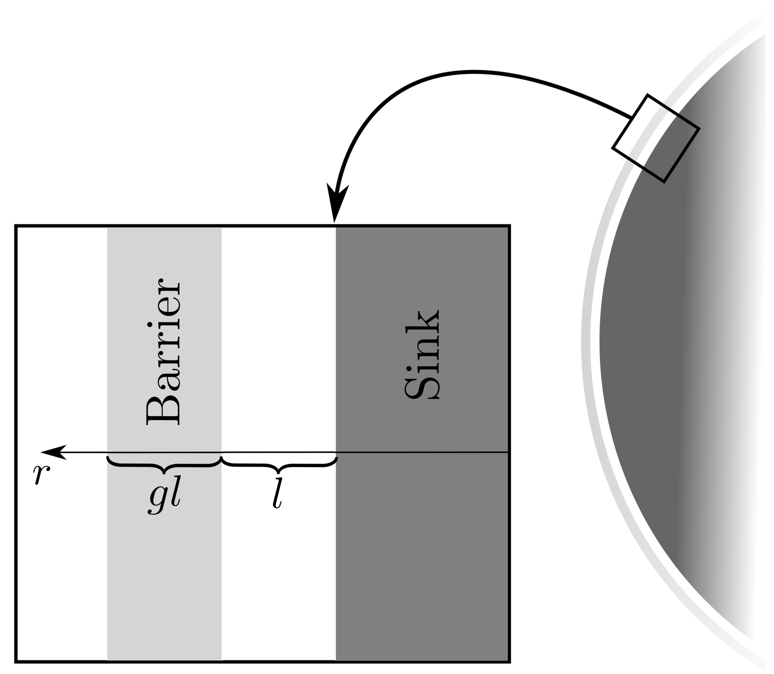


Fig. 7: Resonant decay length $r_d^{(res)}$ and absorption rate $K^{(res)}$ for repulsive parrier $U_1 = 10$ and $g = 1$

Limit $l \ll 1 \rightarrow$ No Resonant Activation

In the limit of $t \gtrsim 0$ the system can locally be approximated by a metastable barrier in front of an absorbing wall.



In this case, the problem is one dimensional on the microscopic level of a particle right at the potential barrier.

For the absorption rate there are three fundamentally different cases:

- The finite barrier $|U_1| < 0$

$$K \approx 4\pi D\left(1 - \frac{1}{2}\left(e^{U_1} - 1\right)gl + \mathcal{O}(l^2)\right)$$

- The ideal attractive barrier $U_1 \to -\infty$

$$K \approx 4\pi D\left(1 + \frac{gl}{4} + \mathcal{O}(l^2)\right)$$

- The ideal repulsive barrier $U_1 \to \infty$

$$K \approx 4\pi D\left(\frac{1 + r_d}{1 + 2r_d} - \frac{(g+1)l}{(2r_d + 1)^2} + \mathcal{O}(l^2)\right)$$

All of these expressions have in common, that they do *not have a maximum* but are either constant or in the last case interpolate monotonously between two values.

The curvature of the potential barrier must therefore be a crucial criterion for resonant activation to take place.