Boundary Homogenization for Trapping Rates of Two Patchy Objects

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Abstract

Many processes in chemical and biological physics involve two diffusing particles binding or a diffusing particle binding to a surface. It is often the case that one or both of the interacting surfaces are not uniformly reactive but instead have localized areas of reactivity. Mathematical models of such reactions take the form of a diffusion equation with mixed boundary conditions corresponding to the behavior of the heterogeneous or "patchy" surfaces. These models are commonly studied using boundary homogenization to replace the mixed boundary conditions by an effective uniform boundary condition identified by a single trapping rate parameter. In this work, we consider two patchy spherical particles and use a quasi-chemical formalism to derive a simple analytical approximation for the trapping rate as a function of the reactive surface area fractions and the homogenized trapping rates of each particle in the case of small areas of reactivity. We confirm this result by using matched asymptotic analysis to formally derive the homogenized trapping rate for two patchy particles as well as applying and confirming our result for the system of a patchy sphere and a patchy plane. We further verify this result through numerical calculations via kinetic Monte Carlo algorithms.

Problem Statement

The goal of this project is to derive homogenized trapping rates for models of two partially-reactive objects, via both a heuristic approximation method and formal matched asymptotic analysis.

Trapping Rates and Survival Probabilities

We study models of two reactive objects, where reactions occur if and only if two constraints are met:

- Proximity constraint
- Orientation constraint

Survival Probability

The survival probability $S(r, \Theta, t)$ is the probability that a reaction has not yet occurred by time t, given initial relative distance r and relative orientation Θ

$$\partial_t S(r,\Theta,t) = D\Delta S(r,\Theta,t), \quad r > R,$$
$$\lim_{r\to\infty} S(r,\Theta,t) = 1,$$
$$S(r,\Theta,t) = 1, \quad r > R,\ t = 0,$$
$$\partial_r S(r,\Theta,t) = \kappa S(r,\Theta,t), \quad r = R$$

for reaction radius R, total translational diffusivity D, and trapping rate κ.

Homogenization of "Patchy" Objects

"Patchy" Objects

"Patchy" particles and planes have small reactive sites on the boundary but are reflective otherwise

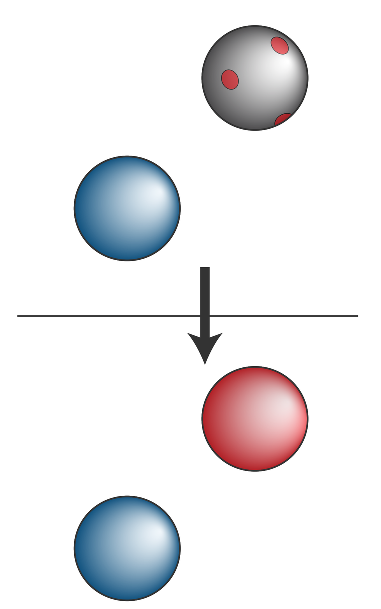
Reaction occurs when touching if and only if the contact location is reactive on both objects

Interactions between patchy objects require complex mixed Dirichlet-Neumann boundary conditions.

We want to simplify these boundary conditions by homogenizing the boundary to have a single trapping rate $0 < \kappa < +\infty$ that captures the behavior of the boundary at far-field.

Prior work on boundary homogenization of patchy objects has only involved one patchy object and one fully-reactive object, but many systems involve two patchy objects.

What are the homogenized trapping rates for models with two patchy objects?

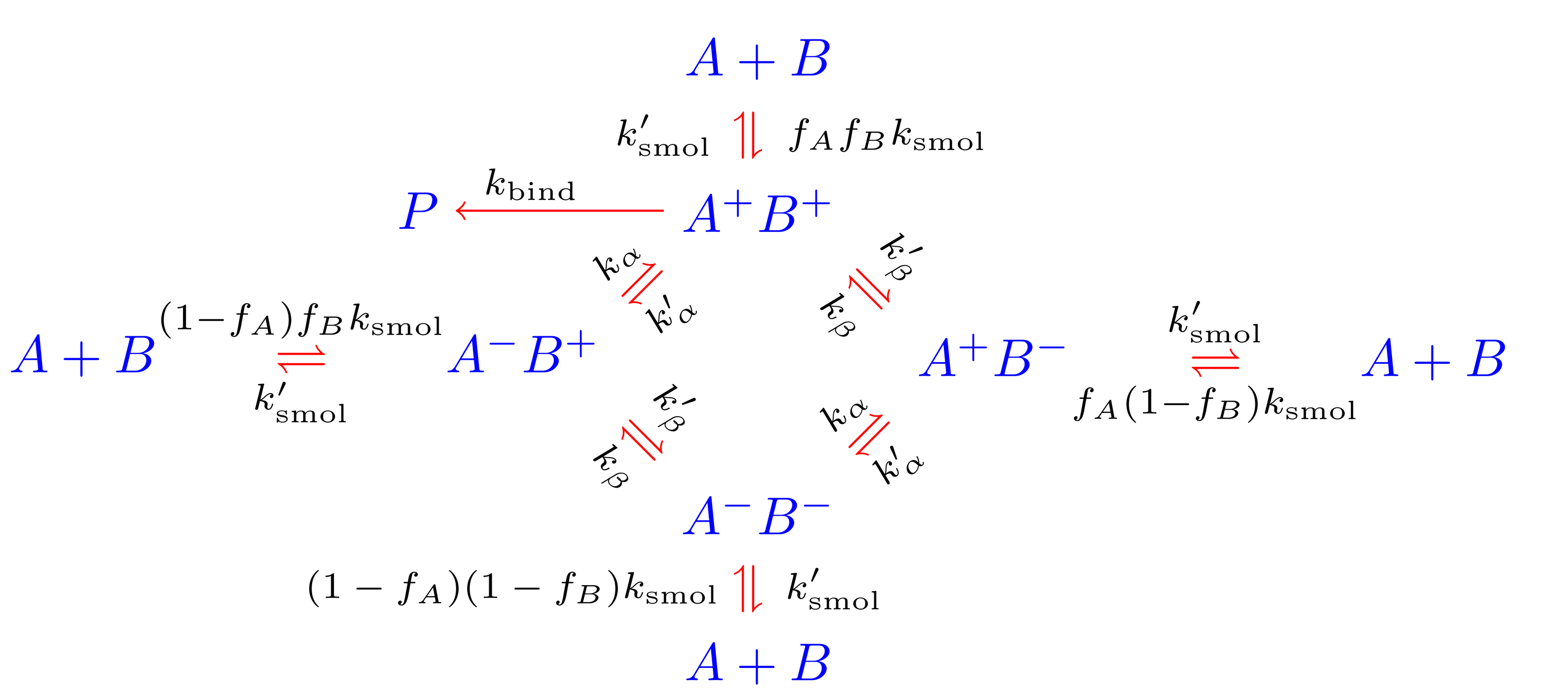


Quasi-Chemical Formalism

The quasi-chemical formalism is a heuristic approach to derive binding rates developed by Šolc and Stockmayer [6]. This formalism reduces the model of continuous diffusion to a discrete 6-state model. We use it to derive approximate trapping rate formulas for two patchy objects which rely on κ_A and κ_B: trapping rates where the A particle is partially-reactive and the B is fully reactive and vice versa.

Assumptions:

- Mass-action kinetics for two particles diffusing in 3D
- f_A and f_B: fraction reactive surface areas for the A and B particles
- Assume reaction occurs immediately upon contact: $k_{\text{smol}}/k_{\text{bind}} \to 0$



- P: product
- $A+B$: particles are far away
- $A^{\pm}B^{\pm}$: particles are close
- A^+B^+: both particles with correctly aligned reactive sites
- A^-B^-: both particles with no correctly aligned reactive sites
- A^+B^-: A particle with a correctly aligned reactive site, B particle without correctly aligned reactive site
- A^-B^+: A particle without correctly aligned reactive site, B particle with a correctly aligned reactive site

Formulas for Combining Trapping Rates

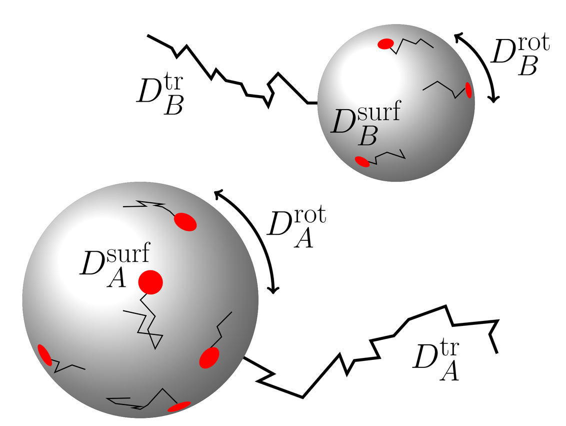
Using this formalism, we derive the following approximation for the trapping for two partially-reactive particles, with non-dimensionalized individual trapping rates $\psi_A = \frac{R\kappa_A}{D}$ and $\psi_B = \frac{R\kappa_B}{D}$:

$$\kappa \approx \frac{D}{R}\frac{\psi_A\psi_B(\psi_A f_B(1-f_A)+\psi_B f_A(1-f_B)-f_A f_B)}{(f_A+(1-f_A)\psi_A)(f_B+(1-f_B)\psi_B)+(1+\psi_A+\psi_B)(\psi_A f_B(1-f_A)+\psi_B f_A(1-f_B)-f_A f_B)}$$

We can further assume that $f_A, f_B \ll 1$ since in many cases the reactive patches are small. This allows us to simplify the formula to:

$$\kappa \approx \kappa_A f_B + \kappa_B f_A$$

Model for Two Patchy Particles



- N_A and N_B patches of nondimensional size ε
- Sum of radii R
- $D^{\text{tr}} = D^{\text{tr}}_A + D^{\text{tr}}_B$
- $D_A = \frac{R^2 D^{\text{rot}}_A + D^{\text{surf}}_A}{D^{\text{tr}}}$
- $D_B = \frac{R^2 D^{\text{rot}}_B + D^{\text{surf}}_B}{D^{\text{tr}}}$
- React upon contact if and only if patches touch
- Relative initial position $\mathbf{r}$
- Initial patch locations Θ

Let S be the survival probability. Then S satisfies the diffusion equation:

$$\partial_t S(\mathbf{r},\Theta,t) = \mathbb{L}S(\mathbf{r},\Theta,t), \quad (\mathbf{r},\Theta) \in \Omega,$$
$$S = 0, \quad (\mathbf{r},\Theta) \in \partial\Omega_A, \qquad \partial_r S = 0, \quad (\mathbf{r},\Theta) \in \partial\Omega_R,$$
$$\mathbb{L} := D^{\text{tr}}\Delta_3 + R^{-2}D^{\text{surf}}_A \sum_{n=1}^{N_A} \mathcal{L}_{A,n} + R^{-2}D^{\text{surf}}_B \sum_{m=1}^{N_B} \mathcal{L}_{B,m},$$

ignoring rotational diffusion, where $\Delta_3, \mathcal{L}_{A,n}, \mathcal{L}_{B,m}$ are appropriate Laplace or Laplace-Beltrami operators and the boundary $\partial\Omega$ is divided into absorbing $\partial\Omega_A$ and reflecting $\partial\Omega_R$ portions.

Results on Two Patchy Particles

We perform formal matched asymptotic analysis to solve this BVP for patch size $\varepsilon \to 0$ and derive the homogenized survival probability $\overline{S}$ to find the trapping rate:

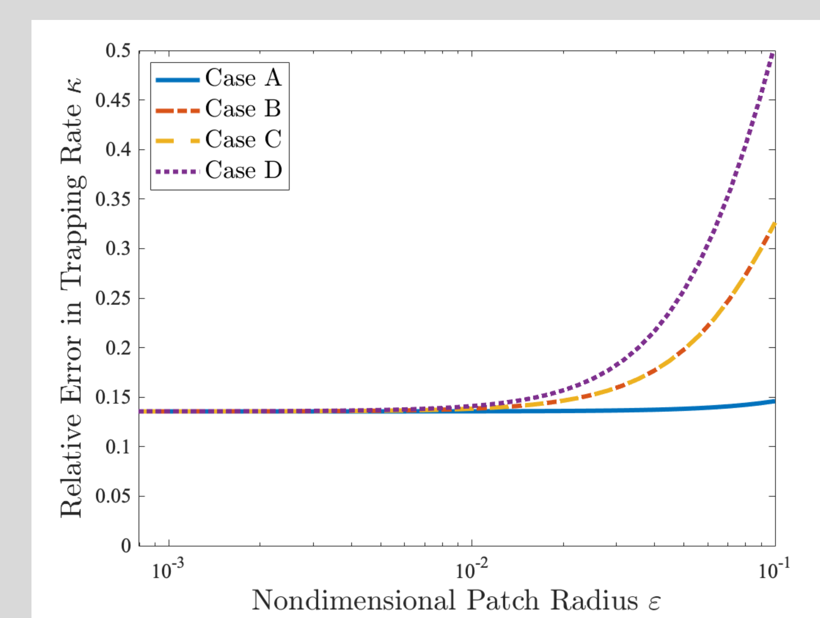
$$\kappa = \varepsilon^3 N_A N_B D^{\text{tr}}(D_A D_B + D_A + D_B)c_0/(4R), \quad \varepsilon \to 0$$

This depends on the numerically-calculated c_0, the capacitance of a particular 4D object in $\mathbb{R}^5$, which arises from the inner problem with stretched coordinates in distance and pair of patch locations.

Alternatively, we derive the following approximation for the trapping rate via quasi-chemical formalism and prior results [2]:

$$\kappa \approx \varepsilon^3 N_A N_B D^{\text{tr}}\left(\sqrt{1+D_A}+\sqrt{1+D_B}\right)/(4\pi R), \quad \varepsilon \to 0$$

Comparison Between Results



This figure compares the trapping rate κ from the hybrid asymptotic-numerical formula that uses the numerically-calculated c_0 and the quasi-chemical approximation. We have $R = D^{\text{tr}} = D_A = D_B = 1$ and:

- Case A: $N_A = N_B = 10$
- Case B: $N_A = 10, N_B = 500$
- Case C: $N_A = 500, N_B = 10$
- Case D: $N_A = N_B = 500$

References

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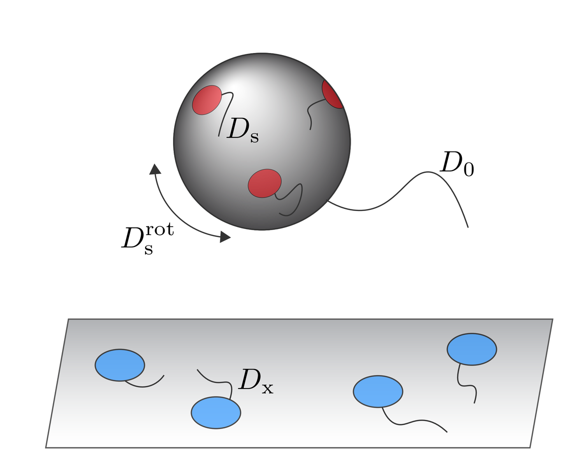
Model for a Patchy Particle and a Patchy Plane



- N_s patches on particle of nondimensional size ε
- Particle radius R
- λ patches per unit area on plane of nondimensional size ε
- $\overline{D}_s = \frac{R^2 D^{\text{rot}}_s + D_s}{D_0}$
- $\overline{D}_x = D_x/D_0$
- React upon contact if and only if patches touch
- Relative initial position X
- Initial patch locations Θ on the particle and U on the plane

Let S be the survival probability. Then S satisfies the diffusion equation:

$$\partial_t S(X,\Theta,U,t) = \mathbb{L}S(X,\Theta,U,t), \quad (X,\Theta,U) \in \Omega,$$
$$S = 0,\ (X,\Theta,U) \in \partial\Omega_A, \qquad \partial_x S = 0,\ (X,\Theta,U) \in \partial\Omega_R.$$
$$\mathbb{L} := D_0\Delta_3 + R^{-2}D_s \sum_{n=1}^{N} \mathcal{L}_n + D_x \sum_{m=1}^{\infty} \Delta_{2,m},$$

ignoring rotational diffusion, where $\Delta_3, \Delta_{2,m}, \mathcal{L}_n$ are appropriate Laplace or Laplace-Beltrami operators and the boundary $\partial\Omega$ is divided into absorbing $\partial\Omega_A$ and reflecting $\partial\Omega_R$ portions.

Results on a Patchy Particle and a Patchy Plane

We again perform formal matched asymptotic analysis to solve this BVP for patch size $\varepsilon \to 0$ and derive the homogenized survival probability $\overline{S}$ to find the trapping rate:

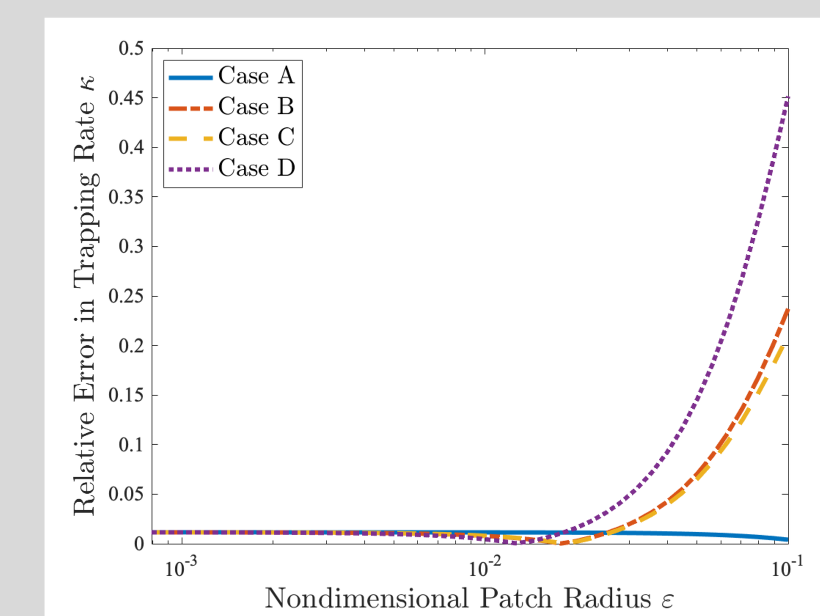
$$\kappa = \pi\varepsilon^3 \lambda N_s R D_0(\overline{D}_x \overline{D}_s + \overline{D}_s)c_1, \quad \varepsilon \to 0$$

This depends on the numerically-calculated c_1, the capacitance of a different particular 4D object in $\mathbb{R}^5$, which arises from the inner problem with stretched coordinates in distance and pair of patch locations.

Alternatively, we apply the quasi-chemical formalism and prior results [1, 3] by assuming the plane can be modeled as a spherical particle with radius $R_B \gg R$ to obtain the following approximation for the trapping rate:

$$\kappa \approx \varepsilon^3 \lambda N_s R D_0\left(\sqrt{1+\overline{D}_x}+\sqrt{\overline{D}_s}\right), \quad \varepsilon \to 0$$

Comparison Between Results



This figure compares the trapping rate κ from the hybrid asymptotic-numerical formula that uses the numerically-calculated c_1 and the quasi-chemical approximation. We have $R = D_0 = 1$, $D_x = 7/9$, and $D_s = 1$ and:

- Case A: $N_s = 10, \lambda = 0.1$
- Case B: $N_s = 500, \lambda = 0.1$
- Case C: $N_s = 10, \lambda = 50$
- Case D: $N_s = 500, \lambda = 50$

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