A Spectral Approach for Computing Survival Probabilities and Residence Times in Model Porous Media

B. T. Nguyen[1] and D. S. Grebenkov[1]

[1]Laboratoire de Physique de la Matière Condensée, CNRS – Ecole Polytechnique, 91128 Palaiseau France

Diffusion is a fundamental transport mechanism in physics, chemistry and biology [1, 2]. During the diffusive exploration, particles may encounter traps, reactive regions or relaxing sinks which are distributed either in the bulk, or on the interface. While staying inside or in vicinity of these specific zones, particles may disappear with a given rate. This is a common mathematical model for many biological and industrial systems, e.g.

1. chemical reactors with heterogeneous spatial distributions of catalytic germs [3];
2. biological cells with specific arrangements of organelles [4, 5];
3. mineral porous media with relaxing agents in nuclear magnetic resonance (NMR) experiments [6].

We propose a spectral approach for computing and investigating the survival probability inside a bounded isolated medium [7]. Traps, reactive regions or relaxing sinks are represented through a spatially heterogeneous trapping, reaction or relaxation rate $B(\mathbf{r})$. The reaction term in the diffusion-reaction equation is treated as a "perturbation" to the Laplace operator. Two infinite-dimensional matrices Λ and $\mathcal{B}$ represent respectively the Laplace operator and the reaction rate $B(\mathbf{r})$ in the Laplacian basis [8, 9]:

$$\Lambda_{m,m'} = \delta_{m,m'}\lambda_m, \qquad \mathcal{B}_{m,m'} = \int\limits_\Omega d\mathbf{r}\; u^*_m(\mathbf{r})B(\mathbf{r})u_{m'}(\mathbf{r}), \tag{1}$$

where λ_m and $u_m(\mathbf{r})$ are the eigenvalues and eigenfunctions of the Laplace operator in a confining domain Ω. Once the matrices Λ and $\mathcal{B}$ are computed, analytically or numerically, the survival probability takes an explicit multi-exponential form:

$$S_h(t) = \sum_{m=0}^{\infty} A^h_m e^{-\gamma^h_m t}, \tag{2}$$

where h is the reaction "strength", $A^h_m = (UV^h_m)(V^h_m\tilde{U})$, γ^h_m and V^h_m are the eigenvalues and eigenvectors of the matrix $\Lambda + h\mathcal{B}$, and U and $\tilde{U}$ are the infinite-dimensional vectors representing the initial density of particles $\rho(\mathbf{r})$ and the weighting function $\tilde{\rho}(\mathbf{r})$:

$$U_m = \int\limits_\Omega d\mathbf{r}\; u^*_m(\mathbf{r})\rho(\mathbf{r}), \qquad \tilde{U}_m = \int\limits_\Omega d\mathbf{r}\; u_m(\mathbf{r})\tilde{\rho}(\mathbf{r}) \tag{3}$$

(in many practical situations, $\rho(\mathbf{r})$ and $\tilde{\rho}(\mathbf{r})$ are constant).

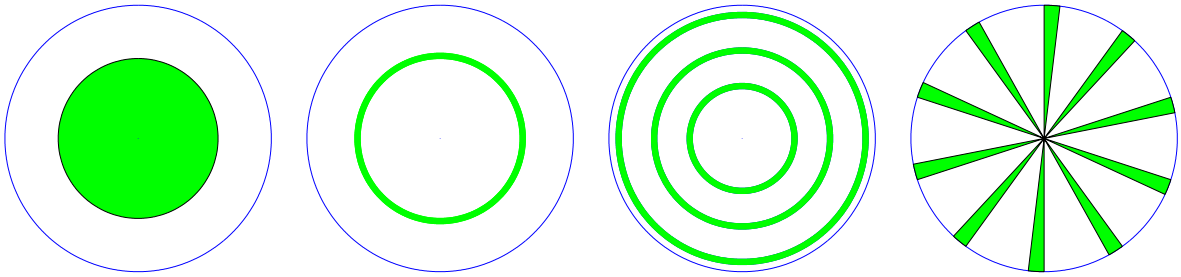

Figure 1: Several shapes of the reactive region A (in green) inside the unit disk, with $B(\mathbf{r}) = 1$ in the reactive region and 0 otherwise.

According to Eq. (2), the survival probability exhibits a mono-exponential decay in the long-time regime, and the decay constant is the smallest eigenvalue γ_0^h. Traditionally, γ_0^h is expected to be proportional to the total amount, or "strength", of traps, relaxing sinks or reactive regions. We aim at revealing subtle influences of a spatial heterogeneity $B(\mathbf{r})$ on the constant γ_0^h. For this purpose, we consider diffusion inside the unit disk which is filled with reactive regions of various shapes (Fig. 1). We search for configurations that provide the highest overall performance of a medium, aiming in future at design of efficient catalysts or diffusive exchangers via optimization of their geometrical shapes. Since the eigenvalues and eigenfunctions of the Laplace operator in the disk are known in a closed analytical form, the computation of the matrix $\mathcal{B}$ is reduced to a numerical integration of Bessel functions over reactive regions.

We show that a uniform filling of the disk provides the highest value for the overall reaction rate γ_0^h. Although the heterogeneity tends to reduce the reaction rate, reactive regions can still be heterogeneously arranged to get nearly optimal performances.

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