Boundary homogenization for trapping by patchy surfaces

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We analyze trapping of diffusing particles by nonoverlapping partially absorbing disks randomly located on a reflecting surface, the problem that arises in many branches of chemical and biological physics. We approach the problem by replacing the heterogeneous boundary condition on the patchy surface by the homogenized partially absorbing boundary condition, which is uniform over the surface. The latter can be used to analyze any problem (internal and external, steady state, and time dependent) in which diffusing particles are trapped by the surface. Our main result is an expression for the effective trapping rate of the homogenized boundary as a function of the fraction of the surface covered by the disks, the disk radius and trapping efficiency, and the particle diffusion constant. We demonstrate excellent accuracy of this expression by testing it against the results of Brownian dynamics simulations.
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I. INTRODUCTION

Problems where diffusing particles are trapped by patchy surfaces are abundant in chemical and biological physics. Ligand binding to cell surface receptors,[1,2] reactions on supported catalysts,[3] electric current through arrays of microelectrodes,[4] and water exchange in plants[5] are just a few from a long list of practical examples. Patchy cells, electrodes, or catalysts can be modeled as reflecting surfaces covered by partially absorbing traps.[6] In this paper we consider the case of randomly distributed, nonoverlapping circular traps. We approach the problem by replacing the heterogeneous boundary condition on the patchy surface by the homogenized partially absorbing boundary condition, which is uniform over the surface (Fig. 1). This uniform boundary condition is universal in the sense that it can be used to analyze both internal and external problems in which diffusing particles come to the trapping surface from inside a cavity or from its outside. In addition this boundary condition can be used to analyze both steady state and time-dependent problems.

Boundary homogenization discussed below belongs to a class of methods called "effective medium theories."[7–9] These theories treat phenomena in micro-non-uniform random/regular media by replacing the real medium by a fictitious uniform medium with prescribed effective parameters. The specific feature of the problem under study is that we homogenize nonuniform boundary condition. The idea underlying homogenization in our case is that nonuniformity of the boundary manifests itself only near the surface. The memory about local properties of the boundary decays with the distance from the boundary and the fields of fluxes and concentrations become uniform in lateral directions.

We use a computer-assisted boundary homogenization procedure to evaluate the effective trapping rate of the surface. Our main result is the expression for the effective trapping rate given in Eq. (5.1) with function $F(\sigma)$ defined in Eq. (3.3). This expression shows how the trapping rate depends on the fraction of the surface covered by the disks, the disk radius and trapping efficiency, and the particle diffusion constant. To obtain this result, we first construct an approximating formula that fits the effective trapping rates deduced from simulations with perfectly absorbing disks. A conventional "addition of resistances" trick is then used to extend this formula to partially absorbing disks. Excellent accuracy of this approximation is demonstrated by testing it against the results of Brownian dynamics simulations (Figs. 2 and 3).

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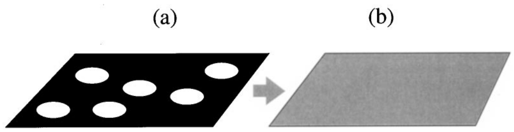

FIG. 1. Schematic representation of the homogenization procedure. The original heterogeneous boundary condition on the surface (a) is replaced by the homogenized partially absorbing boundary condition (b) characterized by the uniform trapping rate κ. On the heterogeneous surface, the boundary condition is $D\nabla_{\mathbf{n}}G(\mathbf{r},t|\mathbf{r}_0)=\kappa_{disk}G(\mathbf{r},t|\mathbf{r}_0)$ on the trap surfaces and $\nabla_{\mathbf{n}}G(\mathbf{r},t|\mathbf{r}_0)=0$ otherwise, where $G(\mathbf{r},t|\mathbf{r}_0)$ is the particle propagator and $\mathbf{n}$ is the surface normal vector. The boundary condition over the entire homogenized surface is given by $D\nabla_{\mathbf{n}}G(\mathbf{r},t|\mathbf{r}_0)=\kappa G(\mathbf{r},t|\mathbf{r}_0)$.

II. SUMMARY OF RESULTS FOR SURFACES COVERED BY PERFECTLY ABSORBING DISKS

The homogenization of the boundary condition on a reflecting surface randomly covered by nonoverlapping perfectly absorbing disks was first introduced by Shoup and Szabo[10] in their intuitively appealing derivation of the Berg and Purcell (BP) result for the stationary flux of diffusing particles to a reflecting[1] sphere covered by small perfectly absorbing disks. When analyzing ligand binding to cell surface receptors BP approximated a cell with N receptors by a reflecting sphere of radius R with N small perfectly absorbing disks of radius a on the surface, $a \ll R$. Ligands were modeled as point Brownian particles with diffusion constant D, which were trapped upon the first contact with disk-shaped receptors.

BP derived an approximate expression for the stationary flux of particles to the trap-covered sphere, J_N^{BP}:

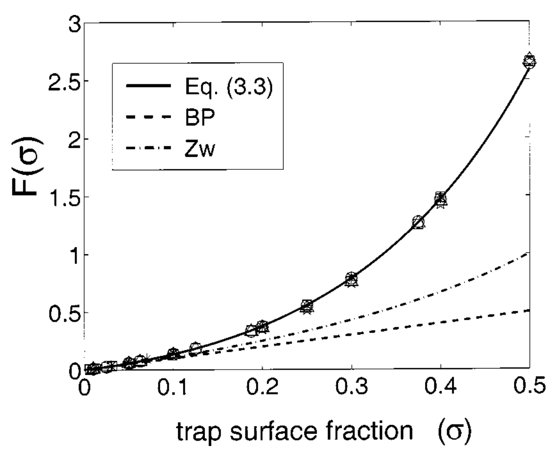

FIG. 2. Function $F(\sigma)$ obtained from simulations and predicted by the Berg–Purcell (BP) and Zwanzig (Zw) formulas given in Eq. (3.2) and the approximation in Eq. (3.3). In simulations with spherical geometry we chose $D=1$ and $R=1$. Simulations were run with disks of radii $a=0.025$ (□), 0.05 (○), 0.1 (△), and 0.2 (☆); the surface fraction σ was varied from 0.01 to 0.5. The values of $F(\sigma)$ were computed from $\langle t\rangle$ determined from simulations with 10^5 diffusing particles. For each of the particles the simulations were run with a new random disks' configuration. In simulations with planar geometry (*), we take $a=1$ and determine $F(\sigma)$ from $\langle t\rangle$ found in simulations with 10^5 diffusing particles in the regime when $\langle t\rangle$ linearly depends on L ($L=1000$). In these simulations, 200 traps were generated using the random sequential addition algorithm in a periodic geometry. The size of the unit cell was computed from the trap surface fraction. With 200 traps, averaging over trap configurations did not lead to improvement of results. In both cases, the relative error of simulation results is within 5%.

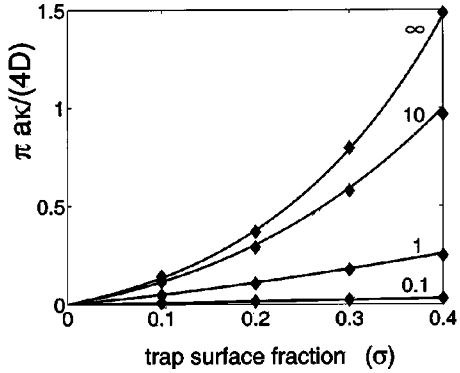

FIG. 3. Dimensionless effective trapping rates $\pi a\kappa/4D$ obtained from simulations with partially absorbing disks and predicted by Eq. (5.1) with $F(\sigma)$ given in Eq. (3.3). The results are presented for disks with $\kappa_{disk}=0.1$, 1, and 10. The upper curve corresponds to perfectly absorbing disks ($\kappa_{disk}=\infty$).

$$J_N^{BP}=k_N^{BP}c_\infty, \quad k_N^{BP}=k_{Sm}\frac{Nk_{disk}}{k_{Sm}+Nk_{disk}}. \tag{2.1}$$

Here c_∞ is the ligand concentration at infinity. The BP rate constant k_N^{BP} is written in the Collins–Kimball form, i.e., as a product of the Smoluchowski rate constant, $k_{Sm}=4\pi DR$, and the trapping probability for a particle that starts from the surface of a uniformly absorbing sphere of radius R having the surface trapping rate $\kappa_{BP}=Nk_{disk}/(4\pi R^2)$. In these equations $k_{disk}=4Da$ is the stationary rate constant for a perfectly absorbing disk of radius a located on the otherwise reflecting plane.[11] These results were tested by Brownian dynamics simulations.[12]

We can write the BP result for the effective trapping rate in the form

$$\kappa_{BP}=\frac{4D}{\pi a}\sigma, \quad \sigma=\frac{Na^2}{4R^2}, \tag{2.2}$$

where σ is the trap-covered fraction of the spherical surface and $4D/(\pi a)$ is the ratio of k_{disk} to the disk area. Using an effective medium treatment, Zwanzig (Zw) extended the BP result to arbitrary surface coverages:[7]

$$\kappa_{Zw}=\frac{1}{1-\sigma}\kappa_{BP}=\frac{4D}{\pi a}\frac{\sigma}{1-\sigma}. \tag{2.3}$$

A simple derivation of this formula is given in Appendix A.

III. EFFECTIVE TRAPPING RATE FOR SURFACES COVERED BY PERFECTLY ABSORBING DISKS

From dimensional arguments it follows that the trapping rate entering into the homogenized boundary condition, can be written as

$$\kappa=\frac{4D}{\pi a}F(\sigma), \tag{3.1}$$

where $F(\sigma)$ is a dimensionless function of the fraction of the surface covered by the traps. Thus, homogenization of the patchy surface reduces to finding a dimensionless function of the trap surface fraction. This function is universal for any surface if the boundary homogenization is justified. Whether this is really the case or not depends on the relation between the disk radius and characteristic lengths associated with the surface. The homogenization is justified when the smallest characteristic length is much greater than the disk radius.

Function $F(\sigma)$ tends to zero as $\sigma \to 0$ and to infinity as $\sigma \to 1$, since the plane becomes perfectly reflecting and absorbing in these limiting cases. Note that the trapping rate becomes infinite ($\kappa \to \infty$), when $a \to 0$ at $\sigma = \text{const}$. This means that the plane may act as perfectly absorbing when the disks cover only a very small fraction of its surface.

The Berg–Purcell and Zwanzig expressions for κ lead to $F(\sigma)$ of the form

$$F_{BP}(\sigma) = \sigma, \quad F_{Zw}(\sigma) = \frac{\sigma}{1-\sigma}. \tag{3.2}$$

While $F_{BP}(\sigma)$ describes only the limiting behavior of $F(\sigma)$ when $\sigma \ll 1$, $F_{Zw}(\sigma)$ captures both of the asymptotes: it reduces to $F_{BP}(\sigma)$ as $\sigma \to 0$ and diverges as $\sigma \to 1$. The range of applicability of $F_{Zw}(\sigma)$ is unknown. Our numerical results show that $F(\sigma)$ grows with σ much faster than it is predicted by $F_{Zw}(\sigma)$ (Fig. 2). We found that, over a wide range of σ, $F(\sigma)$ is accurately approximated by the following expression:

$$F(\sigma) = F_{Zw}(\sigma)(1+3.8\sigma^{1.25}) = \frac{\sigma}{1-\sigma}(1+3.8\sigma^{1.25}). \tag{3.3}$$

This is the main result of this paper. Function $F(\sigma)$ can be used to generalize the BP expression for the rate constant in Eq. (2.1):

$$k_N = k_{Sm} \frac{N k_{disk}\left[1+3.8\left(\dfrac{Na^2}{4R^2}\right)^{1.25}\right]}{k_{Sm}\left(1-\dfrac{Na^2}{4R^2}\right) + N k_{disk}\left[1+3.8\left(\dfrac{Na^2}{4R^2}\right)^{1.25}\right]}. \tag{3.4}$$

This rate constant reduces to k_{BP} when the trap surface fraction $\sigma = Na^2/(4R^2)$ is small compared to unity.

IV. COMPUTER-ASSISTED BOUNDARY HOMOGENIZATION

To find the approximating formula for $F(\sigma)$, we performed Brownian dynamics simulations in spherical and planar geometries. In simulations with spherical geometry, we computed the average lifetime of particles diffusing in a spherical cavity of radius R. The particles were initiated uniformly over the surface of the sphere and allowed to diffuse until they were trapped by perfectly absorbing nonoverlapping circular disks of radius a. The disks were randomly located on the surface of the sphere.

To determine $F(\sigma)$, we use the relation between the average particle lifetime in the spherical cavity with uniform partially absorbing wall and the wall trapping rate κ. As shown in Appendix B, for particles starting from the surface of the sphere, the average lifetime $\langle t \rangle$ is independent of the particle diffusion constant and given by

$$\langle t \rangle = \frac{R}{3\kappa}. \tag{4.1}$$

The boundary homogenization is justified when $a \ll R$. In this regime, we can use the expression for κ given in Eq. (3.1) in order to relate the average lifetime to $F(\sigma)$:

$$\langle t \rangle = \frac{\pi a R}{12 D F(\sigma)}. \tag{4.2}$$

This relation was used to determine $F(\sigma)$ from $\langle t \rangle$ found in simulations.

The simulations were run with $D = R = 1$ and disks of radii $a = 0.025$, 0.05, 0.1, and 0.2. The surface fraction σ was varied from 0.01 to 0.5. The values of $F(\sigma)$ found in simulations with $a = 0.025$ and 0.05 are practically identical. This means that the boundary homogenization is justified when the disk radius is smaller than 0.05 of the radius of the sphere. These values were used to fit the simulation results by an approximating formula $F(\sigma) = F_{Zw}(\sigma)(1 + A\sigma^B)$. Fitting leads to $A = 3.8$ and $B = 1.25$ as given in Eq. (3.3). Figure 2 shows that Eq. (3.3) provides an extremely accurate approximation for numerically determined values of $F(\sigma)$. The difference between the approximation and numerical results grows with the disk radius. Systematic but small deviations from the formula have been found at $a = 0.1$ and 0.2 (the deviations are too small to be seen in Fig. 2).

In the planar geometry, we computed the average lifetime of particles diffusing in a layer of thickness L. The upper boundary of the layer was perfectly reflecting. The lower boundary was randomly covered by perfectly absorbing disks of unit radius, which did not overlap. The particles were initiated uniformly over the lower trap-covered boundary. To determine $F(\sigma)$, we took advantage of the fact that the average lifetime of particles starting from the uniformly absorbing lower boundary is given by

$$\langle t \rangle = \frac{L}{\kappa}, \tag{4.3}$$

where κ is the trapping rate of the boundary. This expression can be derived similarly to the analogous result in Eq. (4.1) for the spherical geometry.

To check the validity of the boundary homogenization, simulations were performed with layers of different heights. Simulations, from which we determined $F(\sigma)$, were done in the regime where the average lifetime linearly depends on the height of the layer. Assuming that the boundary homogenization is justified and that κ is given by the relation in Eq. (3.1), we can write

$$\langle t \rangle = \frac{\pi a L}{4 D F(\sigma)}. \tag{4.4}$$

As expected, the values of $F(\sigma)$ found in simulations fall right on top of the curve predicted by the approximation formula in Eq. (3.3) (Fig. 2).

V. PARTIALLY ABSORBING DISKS

We use the following approximation to find the effective trapping rate in the case when the disks are partially absorbing:

$$\frac{1}{\kappa}=\frac{\pi a}{4DF(\sigma)}+\frac{1}{\sigma\kappa_{disk}}. \tag{5.1}$$

Here, κ_{disk} is the trapping rate of the disk surface (not to be confused with $k_{disk}=4Da$). This formula interpolates the effective trapping rate between the limiting cases of perfectly absorbing and perfectly reflecting disks. Similar interpolation formula was suggested by Zwanzig and Szabo.[13] For perfectly absorbing disks ($\kappa_{disk}=\infty$) the formula leads to the expression for κ in Eq. (3.1). When the disks are perfectly reflecting ($\kappa_{disk}=0$) the effective trapping rate vanishes since the entire surface is perfectly reflecting. In the limiting case of small σ, $F(\sigma)=F_{BP}(\sigma)=\sigma$ and the relation in Eq. (5.1) takes the form

$$\frac{1}{\kappa}=\frac{1}{\sigma}\left(\frac{\pi a}{4D}+\frac{1}{\kappa_{disk}}\right), \tag{5.2}$$

which is the Zwanzig–Szabo generalization of the BP result in Eq. (2.2) to the case of partially absorbing disks.[13] When $\sigma\rightarrow 1$, $F(\sigma)\rightarrow\infty$ and κ approaches κ_{disk} as it should.

We have found that the approximation in Eq. (5.1) is in excellent agreement with the results of Brownian dynamics simulations of the trapping in planar geometry (Fig. 3). The simulations were performed similarly to the case of perfectly absorbing disks with particles initiated uniformly over the patchy surface. To deal with the partially absorbing boundary conditions on the disk surface, we used recently reported adaptive time-step algorithm that combines the first-passage time techniques with sampling of exact one-dimensional propagators.[14] The trapping rates were extracted from simulations using Eq. (4.3) as we did in the case of perfectly absorbing disks.

VI. CONCLUDING REMARKS

We have combined dimensional arguments with Brownian dynamics simulations in order to homogenize boundary conditions on surfaces randomly covered by nonoverlapping circular traps. Our homogenization procedure requires the identity of the average lifetimes in the presence of patchy and homogenized boundaries. We have found that homogenized boundary excellently reproduces not only the average lifetime, but the survival probability as well. Figure 4 demonstrates excellent agreement of the survival probabilities found in simulations with patchy surfaces and those found for the problem with the homogenized boundaries.

The boundary homogenization discussed in this paper can be extended to a number of related problems with patchy surfaces. In particular, boundary homogenization can be carried out for surfaces with regular distributions of disk-shaped traps[8] as well as for surfaces regularly or randomly covered by hemispherical traps. A real patchy surface may be covered by nonidentical traps, e.g., the trap parameters (size and trapping rate) may fluctuate. Homogenization of such surfaces might be of use for the analysis of experiments with adherent

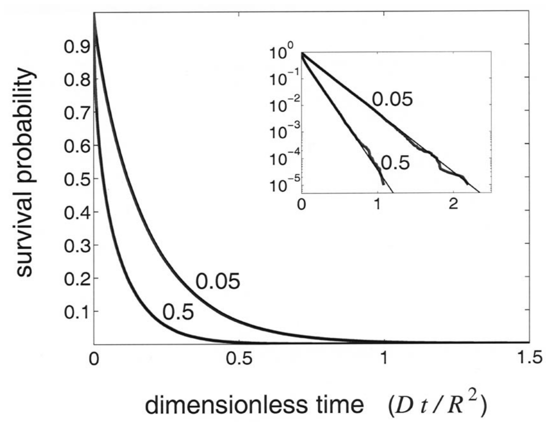

FIG. 4. Survival probabilities computed from simulations with the patchy surfaces (thick gray curve) and obtained solving the problem with homogenized boundaries (black curve). Logarithms of the survival probabilities are shown in the inset. Simulations were done in the spherical geometry with perfectly absorbing disks covering 5% and 50% of the surface of the sphere. Particle initial positions were uniformly distributed over the volume of the sphere. In the simulations, $R=D=1$ and $a=0.025$. Survival probabilities were computed on the basis of 10^5 trajectories. For the homogenized problem, the survival probability was found by numerical inversion of the Laplace transform in Eq. (B13).

cell cultures and cocultures.[14,15] In conclusion, we believe that boundary homogenization is a useful technique that significantly simplifies both analytical and numerical analysis of a large number of problems in which diffusing particles are trapped by patchy surfaces.

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APPENDIX A: ZWANZIG'S FORMULA FOR κ IN EQ. (2.3)

Consider a particle diffusing in a spherical cavity of radius R with N nonoverlapping small perfectly absorbing circular disks of radius a randomly located on its surface, $a \ll R$. The average lifetime of the particle, which starts from the cavity center $\langle t_N\rangle_{center}$ is given by

$$\langle t_N\rangle_{center}=\frac{R^2}{6D}+(1-\sigma)\langle t_N\rangle_{surf}\approx\frac{R^2}{6D}+\frac{1-\sigma}{N}\langle t_1\rangle_{surf}. \tag{A1}$$

Here $R^2/(6D)$ is the mean first-passage time from the cavity center to its wall [cf. Eq. (B10) from Appendix B with $r_0=0$ and $\kappa=\infty$], σ is the surface fraction covered by the disks, which is given in Eq. (2.2), and $\langle t_N\rangle_{surf}$ is the average lifetime on condition that the particle starting points are uniformly distributed over the reflecting part of the cavity wall. Equation (A1) accounts for the fact that the fraction σ of all trajectories lands right on the disks and is trapped instantly. For this fraction, the average lifetime is the mean first-passage time $R^2/(6D)$. In the second equality we have additionally assumed that $\langle t_N\rangle_{surf}\approx\langle t_1\rangle_{surf}/N$, i.e., the average lifetime in the presence of N disks is N times smaller than the average lifetime in the presence of the only disk. This is a reasonable approximation when N is not too large.

To estimate $\langle t_1 \rangle_{surf}$ we use the fact that when a is small enough, searching for the disk takes much more time than equilibration in the cavity with perfectly reflecting wall. Keeping this in mind, we can use the result from Grigoriev *et al.*[16] to write $\langle t_1 \rangle_{surf} = V_{cav}/(4Da)$, where $V_{cav} = 4\pi R^3/3$ is the cavity volume. Substituting this expression for $\langle t_1 \rangle_{surf}$ into Eq. (A1) we arrive at

$$\langle t_N \rangle_{center} = \frac{R^2}{6D} + \frac{(1-\sigma)\pi R^3}{3DaN}. \tag{A2}$$

Zwanzig's result for κ in Eq. (2.3) arises instantly if one compares this expression with the result in Eq. (B10) from Appendix B with $r_0 = 0$.

APPENDIX B: THE AVERAGE LIFETIME IN EQ. (4.1)

Consider a particle diffusing in a spherical cavity of radius R with a partially absorbing surface. The particle starts from the point located at distance r_0 from the cavity center. The particle propagator or Green's function $G(r,t|r_0)$ satisfies the diffusion equation,

$$\frac{\partial G}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial G}{\partial r} \right) \tag{B1}$$

with radiation boundary condition on the cavity wall,

$$-D \left. \frac{\partial G(r,t|r_0)}{\partial r} \right|_{r=R} = \kappa G(R,t|r_0) \tag{B2}$$

and the initial condition,

$$G(r,t|r_0) = \delta(r-r_0)/(4\pi r_0^2). \tag{B3}$$

The particle survival probability $S(t|r_0)$ is given by

$$S(t|r_0) = 4\pi \int_0^R r^2 G(r,t|r_0)\, dr. \tag{B4}$$

Respectively, its average lifetime is

$$\langle t(r_0) \rangle = \int_0^\infty t \left[-\frac{dS(t|r_0)}{dt} \right] dt = \int_0^\infty S(t|r_0)\, dt. \tag{B5}$$

The propagator considered as a function of r_0 satisfies

$$\frac{\partial G}{\partial t} = \frac{D}{r_0^2}\frac{\partial}{\partial r_0}\left(r_0^2 \frac{\partial G}{\partial r_0} \right), \tag{B6}$$

the initial condition in Eq. (B3) and radiation boundary condition on the wall

$$-D \left. \frac{\partial G(r,t|r_0)}{\partial r_0} \right|_{r_0=R} = \kappa G(r,t|R). \tag{B7}$$

Using the definitions in Eqs. (B4) and (B5) one can check that the average lifetime satisfies

$$\frac{D}{r_0^2}\frac{d}{dr_0}\left(r_0^2 \frac{d\langle t(r_0)\rangle}{dr_0} \right) = -1 \tag{B8}$$

and the boundary condition

$$-D \left. \frac{d\langle t(r_0)\rangle}{dr_0} \right|_{r_0=R} = \kappa \langle t(R) \rangle. \tag{B9}$$

Solving this equation one finds

$$\langle t(r_0) \rangle = \frac{R^2 - r_0^2}{6D} + \frac{R}{3\kappa}. \tag{B10}$$

For particles that start from the cavity wall this reduces to the expression for the average lifetime given in Eq. (4.1).

Finally we derive an expression for the Laplace transform of the survival probability for the case of uniform distribution of the particle starting points inside the sphere. It follows from Eqs. (B4) and (B6) that the Laplace transform of the survival probability, $\hat{S}(s|r_0) = \int_0^\infty \exp(-st) S(t|r_0)\, dt$, satisfies

$$\frac{D}{r_0^2}\frac{d}{dr_0}\left(r_0^2 \frac{d\langle \hat{S}(s|r_0)\rangle}{dr_0} \right) = s\hat{S}(s|r_0) - 1 \tag{B11}$$

with the boundary condition

$$-D \left. \frac{d\langle \hat{S}(s|r_0)\rangle}{dr_0} \right|_{r_0=R} = \kappa \langle \hat{S}(s|R) \rangle. \tag{B12}$$

Solving this equation and averaging the solution over the starting points one finds

$$\hat{S}_u(s) = 3\int_0^1 r_0^2 \hat{S}(s|r_0)\, dr_0 = \frac{1}{s}\left\{ 1 + \frac{3\tilde{\kappa}(\sqrt{\tilde{s}}\cosh\sqrt{\tilde{s}} - \sinh\sqrt{\tilde{s}})}{\tilde{s}[(1-\tilde{\kappa})\sinh\sqrt{\tilde{s}} - \sqrt{\tilde{s}}\cosh\sqrt{\tilde{s}}]} \right\}, \tag{B13}$$

where $\tilde{s} = sR^2/D$, $\tilde{\kappa} = \kappa R^2/D$, and subscript u indicates that this survival probability corresponds to the case of uniform distribution of the starting points. The survival probabilities for the problems with homogenized boundaries shown in Fig. 4 are obtained by inverting this Laplace transform.

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