Boundary homogenization for a sphere with an absorbing cap of arbitrary size

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This paper focuses on trapping of diffusing particles by a sphere with an absorbing cap of arbitrary size on the otherwise reflecting surface. We approach the problem using boundary homogenization which is an approximate replacement of non-uniform boundary conditions on the surface of the sphere by an effective uniform boundary condition with appropriately chosen effective trapping rate. One of the main results of our analysis is an expression for the effective trapping rate as a function of the surface fraction occupied by the absorbing cap. As the cap surface fraction increases from zero to unity, the effective trapping rate increases from that for a small absorbing disk on the otherwise reflecting sphere to infinity which corresponds to a perfectly absorbing sphere. The obtained expression for the effective trapping rate is applied to find the rate constant describing trapping of diffusing particles by an absorbing cap on the surface of the sphere. Finally, we find the capacitance of a metal cap of arbitrary size on a dielectric sphere using the relation between the capacitance and the rate constant of the corresponding diffusion-limited reaction. The relative error of our approximate expressions for the rate constant and the capacitance is less than 5% over the entire range of the cap surface fraction from zero to unity. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4968598>]

I. INTRODUCTION

Researchers and engineers frequently face the problem of trapping of diffusing particles by patchy surfaces which contain absorbing patches on the otherwise reflecting surface. Examples include electric current through an array of microelectrodes,¹ reactions on supported catalysts,² transport through porous membranes,³ water exchange in plants,⁴ ligand binding to cell surface receptors,⁵ ligand accumulation in cell culture assays,⁶ to mention just a few. This is a notoriously complicated problem because one has to deal with non-uniform boundary conditions: absorbing on the patches and reflecting on the rest of the boundary.

Boundary homogenization is an approximate method which significantly simplifies the solution of such problems. Its main idea is to replace the non-uniform boundary conditions on the surface by a uniform boundary condition with an appropriately chosen effective surface trapping rate. The observation underlying this idea is that sufficiently far from the boundary, diffusive fluxes lose their lateral components and become directed normal to the boundary. As a consequence, they are indistinguishable from the fluxes to the uniform *partially absorbing* boundary characterized by the effective trapping rate, κ , that enters into the boundary condition on the surface.

A computer-assisted boundary homogenization approach has been proposed to determine this effective trapping rate.^{7–9} The approach involves two steps: (1) to write κ as the product of a dimensional factor and a dimensionless function of the

surface fraction σ occupied by the absorbing patches and (2) to find a relatively simple expression for this function by approximating the values of the trapping rate, κ , obtained numerically for various values of σ . Earlier, this approach was used to determine the dependence $\kappa(\sigma)$ for surfaces with non-overlapping identical circular absorbing patches whose radius was small compared to the curvature radius of the surface.^{7–9} In fact, this was homogenization of flat surfaces. Recently, the approach was utilized to find $\kappa(\sigma)$ for striped cylindrical surfaces.¹⁰

Here we apply computer-assisted boundary homogenization to obtain $\kappa(\sigma)$ for a sphere containing a single absorbing cap of arbitrary size on the otherwise reflecting surface as illustrated in Fig. 1. Our main result is a simple formula for $\kappa(\sigma)$ in Eq. (4). This formula is used to evaluate the rate constant that describes trapping of diffusing particles by a sphere with an absorbing cap which occupies the fraction σ of the otherwise reflecting surface of the sphere. A simple expression for this rate constant, which covers the entire range of σ , $0 \leq \sigma \leq 1$, is another main result of this paper, given in Eq. (11). Next, we take advantage of the relation between the rate constant and the capacitance of a metal cap occupying the surface fraction σ of the dielectric sphere. This allows us to find an approximate formula for the capacitance of the cap using the obtained formula for the rate constant. The expression for the capacitance of the cup, which works over the entire range of σ , is given by Eq. (16). This is the third main result of this work. The relative error of the expressions for the rate constant and the capacitance is less than 5% over the entire range of the cap surface fraction from zero to unity.

FIG. 1. Spheres with absorbing caps, shown in brown. The cap size increases from left to right. The most right sphere is perfectly absorbing.

The outline of the present paper is as follows. The formula for the effective trapping rate $\kappa(\sigma)$ is obtained and analyzed in detail in Section II. The two above mentioned applications are discussed in Section III.

II. RESULTS

To find the dependence $\kappa(\sigma)$, we determined the mean lifetime of a particle diffusing in a spherical layer between two concentric spheres. The outer sphere of radius R_{out} was a reflecting boundary for the particle. The inner sphere of radius R , $R < R_{out}$, contained an absorbing cap that occupied fraction σ of its otherwise reflecting surface, as shown in Fig. 2. The particle starting point was uniformly distributed over the inner-sphere surface. The mean lifetime, $\tau_{sim}(\sigma)$, was obtained by averaging the lifetime over 10^6 realizations of the particle trajectory, including those that started from the cap and were instantly trapped. The lifetime for such realizations was zero. For realizations that started from the reflecting part of the surface, the particle lifetimes were obtained from the Brownian dynamics simulations.

FIG. 2. Two concentric spheres of radii R and R_{out} , $R < R_{out}$. The inner sphere contains an absorbing cap, shown in brown, on the otherwise reflecting surface. The outer sphere is a reflecting boundary for diffusing particles.

The mean lifetime obtained from the simulations was compared with its counterpart predicted by the theory assuming that the inner surface was uniform and partially absorbing with the trapping rate κ . This mean lifetime, denoted by $\tau_{theory}(\kappa)$, is given by (see the derivation in the Appendix)

$$\tau_{theory}(\kappa) = \frac{1}{3\kappa R^2} (R_{out}^3 - R^3). \quad (1)$$

Assuming that the two mean lifetimes were equal, $\tau_{sim}(\sigma) = \tau_{theory}(\kappa)$, we found $\kappa(\sigma)$ by the relation

$$\kappa(\sigma) = \frac{1}{3\tau_{sim}(\sigma)R^2} (R_{out}^3 - R^3). \quad (2)$$

According to Eq. (2), $\kappa(\sigma)$ is a function of R_{out} . This is indeed the case for not too large R_{out} . However, as R_{out} increases, $\kappa(\sigma)$ becomes independent of R_{out} approaching its plateau value which is the effective trapping rate of interest. This is illustrated in Table I which shows the R_{out} -dependences of $\kappa(\sigma)$ for $\sigma = 0.25, 0.5$, and 0.75 . The table presents dimensionless effective trapping rates, $\tilde{\kappa}(\sigma)$, defined as the product of $\kappa(\sigma)$ and the inverse of the dimensional factor D/R , where D is the particle diffusivity,

$$\tilde{\kappa}(\sigma) = \frac{R\kappa(\sigma)}{D}, \quad (3)$$

at several values of the outer sphere radius, $R_{out} = R(1 + j)$, $j = 0.5, 1, 2, \dots, 8$. One can see that $\tilde{\kappa}(\sigma)$ first increases with R_{out} and then becomes practically R_{out} -independent.

The plateau values of $\tilde{\kappa}(\sigma)$ obtained from the simulations at $\sigma = 0.05, 0.10, 0.15, \dots, 0.95$ are collected in Table II. We used these values to find a formula that approximates $\tilde{\kappa}(\sigma)$ over the entire range of σ from zero to unity,

$$\tilde{\kappa}(\sigma) = \frac{R\kappa(\sigma)}{D} = \frac{2}{\pi} \sqrt{\sigma} \frac{1 + 2.6\sqrt{\sigma} - 3.2\sigma^2}{(1 - \sigma)^{3/2}}. \quad (4)$$

This formula is one of the main results of this work. It fits $\tilde{\kappa}(\sigma)$ obtained from the simulations with the relative error of less than 5% for all σ , except $\sigma = 0.05$, where the relative error is about 6%.

The formula in Eq. (4) is constructed so that to reproduce a known asymptotic behavior of $\kappa(\sigma)$ as $\sigma \rightarrow 0$. In this limiting case, the cap is an absorbing disk of radius $a = 2R\sqrt{\sigma}$, which is much smaller than R . Since the trapping of diffusing particles by such a cap is described by the Hill rate constant,¹¹ $4Da$, $\tilde{\kappa}(\sigma)|_{\sigma \rightarrow 0}$ is the ratio of this rate constant to the sphere surface area, $4\pi R^2$,

$$\tilde{\kappa}(\sigma)|_{\sigma \rightarrow 0} = \frac{a}{\pi R} = \frac{2}{\pi} \sqrt{\sigma}. \quad (5)$$

TABLE I. The effective trapping rate, $\tilde{\kappa}(\sigma)$, given by Eq. (2), as a function of $R_{out} = R(1 + j)$ at $\sigma = 0.25, 0.5$, and 0.75 .

			j								
			0.5	1	2	3	4	5	6	7	8
σ	0.25	$\tilde{\kappa}(\sigma)$	0.519	0.775	0.946	1.001	1.027	1.020	1.034	1.029	1.038
	0.50	$\tilde{\kappa}(\sigma)$	1.353	1.949	2.341	2.441	2.501	2.537	2.539	2.553	2.564
	0.75	$\tilde{\kappa}(\sigma)$	4.197	5.458	6.128	6.346	6.371	6.401	6.441	6.408	6.470

TABLE II. The plateau values of $\tilde{\kappa}(\sigma)$ obtained from the simulations at different values of the cap surface fraction, σ .

σ	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5
$\tilde{\kappa}(\sigma)$	0.26	0.44	0.63	0.82	1.03	1.26	1.52	1.82	2.15	2.55
σ	0.55	0.6	0.65	0.7	0.75	0.8	0.85	0.9	0.95	
$\tilde{\kappa}(\sigma)$	2.99	3.56	4.26	5.27	6.44	8.36	11.23	16.94	2945.41	

As $\sigma \rightarrow 1$, the effective trapping rate, Eq. (4), diverges as $1/(1 - \sigma)^{3/2}$. A rationale for this asymptotic behavior is provided in Sec. III.

It is interesting to compare the dependences $\tilde{\kappa}(\sigma)$ for spheres with absorbing patches of different shapes. Such a comparison is presented in Fig. 3, where the solid curve is $\tilde{\kappa}(\sigma)$ in Eq. (4), and the dashed curve is $\tilde{\kappa}(\sigma)$ for small non-overlapping identical absorbing circular patches of radius a_1 randomly distributed over the surface of the sphere (see Fig. 4), given by⁸

$$\tilde{\kappa}(\sigma) = \frac{\kappa(\sigma)R}{D} = \frac{4R}{\pi a_1} \sigma \frac{1 + 0.34\sqrt{\sigma} + 0.58\sigma^2}{(1 - \sigma)^2}. \quad (6)$$

In the latter case, the right dimensional factor for $\kappa(\sigma)$ is D/a_1 . For the sake of comparison with $\tilde{\kappa}(\sigma)$ in Eq. (4), in Eq. (6) we use the same non-dimensionalizing factor R/D as in Eq. (4). As a result, the right-hand side of Eq. (6) is the product of a dimensionless function of σ and the dimensionless factor

FIG. 3. Comparison of different σ -dependences of the effective trapping rate, $\tilde{\kappa}(\sigma)$. The solid curve is $\tilde{\kappa}(\sigma)$ for an absorbing cap occupying the surface fraction σ of the otherwise reflecting sphere (see Fig. 1), given by Eq. (4). The dashed curve is $\tilde{\kappa}(\sigma)$ for small non-overlapping identical absorbing circular patches of radius a_1 randomly distributed over the surface of the sphere (see Fig. 4), given by Eq. (6), with $a_1 = 0.05R$. Circles in Fig. 3 are the values of $\tilde{\kappa}(\sigma)$ for a sphere with absorbing rings of different sizes (see Fig. 5). The values of $\tilde{\kappa}(\sigma)$ obtained numerically for the internal problem, where particles diffusing inside the sphere are trapped by the absorbing cap occupying the fraction σ of the surface, are shown by squares.

R/a_1 . The dashed curve in Fig. 3 shows $\tilde{\kappa}(\sigma)$ in Eq. (6) for $a_1/R = 0.05$.

Circles in Fig. 3 are the values of $\tilde{\kappa}(\sigma)$ for a sphere with absorbing rings of different sizes (see Fig. 5). These values were obtained numerically using the same methodology as that described above for absorbing caps. As might be expected, the dashed curve goes above the solid one, and the circles are in between. Such mutual arrangement between the two curves and the circles is due to the fact that delocalization of the absorbing regions at fixed σ decreases their mutual screening effect that, in turn, leads to the increase in the effective trapping rate $\kappa(\sigma)$. One can clearly see this from Eq. (6). Decreasing the patch radius a_1 at a fixed value of σ , one can make $\tilde{\kappa}(\sigma)$ arbitrarily large at an arbitrarily small value of σ .

It is worth mentioning that $\tilde{\kappa}(\sigma)$ for a sphere with small absorbing patches, Eq. (6), works equally well for both external and internal problems, where the particles diffuse outside and inside the sphere, respectively. However, $\tilde{\kappa}(\sigma)$ for a sphere with an absorbing cap, Eq. (4), works only for the external problem. In Fig. 3, we show $\tilde{\kappa}(\sigma)$ obtained numerically for the internal problem (where particles diffusing inside the sphere are trapped by the absorbing cap that occupies the fraction σ of the spherical surface) by squares. One can see that they are below the solid curve representing $\tilde{\kappa}(\sigma)$ in Eq. (4). In this respect, boundary homogenization for a sphere with a cap differs from that for a striped cylindrical tube, where the same effective trapping rate works for both internal and external problems.¹⁰

III. APPLICATIONS AND CONCLUDING REMARKS

One can use the effective trapping rate to find the rate constant that characterizes trapping of diffusing particles by an immobile sphere with an absorbing cap of arbitrary size. This problem attracted attention of many researchers.^{11–23} Analytical and numerical results obtained in some of the papers cited above are compared in Ref. 21.

To find the rate constant, we took advantage of the Collins-Kimball formula²⁴ that describes trapping of diffusing particles by a uniform partially absorbing sphere. This

FIG. 4. Small non-overlapping absorbing circular patches, shown in brown, randomly distributed over the surface of the otherwise reflecting sphere. The surface fraction, σ , of the patches on the left sphere is lower than that on the right sphere.

formula gives the Collins-Kimball (CK) rate constant, k_{CK} , as the product of the Smoluchowski (Sm) rate constant, k_{Sm} , and the trapping probability, P_{tr} , which is the probability to be trapped for a particle that starts from the surface of the sphere,

$$k_{CK} = k_{Sm}P_{tr}. \quad (7)$$

For a sphere of radius R , k_{Sm} and P_{tr} are given by

$$k_{Sm} = 4\pi DR \quad (8)$$

and

$$P_{tr} = \frac{\kappa R/D}{1 + \kappa R/D}, \quad (9)$$

where D is the particle diffusivity and κ is the surface trapping rate.

Substituting in Eq. (9) $\tilde{\kappa}(\sigma)$ in Eq. (4), we arrive at the expression for the trapping probability as a function of σ ,

$$P_{tr}(\sigma) = \frac{2\sqrt{\sigma}(1 + 2.6\sqrt{\sigma} - 3.2\sigma^2)}{\pi(1 - \sigma)^{3/2} + 2\sqrt{\sigma}(1 + 2.6\sqrt{\sigma} - 3.2\sigma^2)}. \quad (10)$$

This together with Eqs. (7) and (8) allows us to find the rate constant, $k(\sigma)$, for the trapping of diffusing particles by a sphere with an absorbing cap that occupies the fraction σ of the surface of the sphere, which can be arbitrary, $0 < \sigma \leq 1$,

$$k(\sigma) = k_{Sm}P_{tr}(\sigma) = \frac{8\pi DR\sqrt{\sigma}(1 + 2.6\sqrt{\sigma} - 3.2\sigma^2)}{\pi(1 - \sigma)^{3/2} + 2\sqrt{\sigma}(1 + 2.6\sqrt{\sigma} - 3.2\sigma^2)}. \quad (11)$$

When $\sigma = 1$, the rate constant $k(\sigma)$ reduces to the Smoluchowski rate constant in Eq. (8), since $P_{tr}(\sigma)|_{\sigma=1} = 1$. In the opposite limiting case, $\sigma \rightarrow 0$, where the cap is a small

disk of radius $a = 2R\sqrt{\sigma}$, $a \ll R$, the trapping probability, Eq. (10), takes the form $P_{tr}(\sigma) = (2/\pi)\sqrt{\sigma}$, and the rate constant $k(\sigma)$ reduces to the Hill rate constant, $k(\sigma) = 4Da$. The latter rate constant describes trapping of diffusing particles by an absorbing disk of radius a on the otherwise reflecting flat wall.

In the literature on the theory of diffusion-controlled reactions with anisotropic reactivity, many authors refer to the ratio of $k(\sigma)$ to the Smoluchowski rate constant as the steric factor, $f = k(\sigma)/k_{Sm}$. Very accurate values of f obtained numerically for a wide range of σ are published in Ref. 21. Since the steric factor is identical to our $P_{tr}(\sigma)$, in Table III we compare the values of $P_{tr}(\sigma)$ given by Eq. (10) with the values of f reported in Ref. 21. The comparison shows that the relative error of the values of $P_{tr}(\sigma)$ predicted by Eq. (10) does not exceed 5%.

The formula for $k(\sigma)$ in Eq. (11) has advantages over other results for this rate constant reported in the literature. (1) The formula gives the rate constant as a relatively simple function of σ , whereas some authors give $k(\sigma)$ as an infinite series in the Legendre polynomials. (2) The formula predicts $k(\sigma)$ with the relative error that does not exceed 5% over the entire range of σ , $0 < \sigma \leq 1$. (3) $k(\sigma)$ in Eq. (11) has the correct asymptotic behavior as $\sigma \rightarrow 0$, whereas some of the reported results reproduce the correct asymptotic behavior in this limiting case only approximately.

Expression for the trapping probability, Eq. (10), allows us to shed some light on the asymptotic behavior of the effective trapping rate, $\tilde{\kappa}(\sigma)$, in Eq. (4), as $\sigma \rightarrow 1$. The trapping probability, Eq. (10), in this limiting case takes the form

$$P_{tr}(\sigma)|_{\sigma \rightarrow 1} = 1 - \frac{5\pi}{4}(1 - \sigma)^{3/2}. \quad (12)$$

FIG. 5. Spheres with absorbing rings, shown in brown. The ring size increases from left to right. The most right sphere is perfectly absorbing.

TABLE III. The comparison of the values of the trapping probability, $P_{tr}(\sigma)$, given by Eq. (10) with the values of the steric factor, f , reported in Ref. 21.

σ	0.011	0.043	0.095	0.165	0.249	0.345	0.448	0.551	0.654	0.750	0.834	0.904	0.956	0.988
Eq. (10)	0.080	0.174	0.279	0.389	0.496	0.600	0.696	0.780	0.851	0.908	0.950	0.978	0.993	0.999
Reference 21	0.079	0.178	0.288	0.401	0.507	0.602	0.685	0.755	0.814	0.864	0.907	0.945	0.976	0.995

The escape probability, $P_{esc}(\sigma)$, for a particle starting from the surface of the sphere is $P_{esc}(\sigma) = 1 - P_{tr}(\sigma)$. As $\sigma \rightarrow 1$, this probability, according to Eq. (12), reduces to

$$P_{esc}(\sigma)\big|_{\sigma \rightarrow 1} = 1 - P_{tr}(\sigma)\big|_{\sigma \rightarrow 1} = \frac{5\pi}{4} (1 - \sigma)^{3/2}. \quad (13)$$

A particle has a chance to escape from the sphere only if it starts from the reflecting part of the surface. Since the particle starting point is uniformly distributed over the surface of the sphere, the escape probability is the product of the probability to start from the reflecting part of the surface, which is equal to $1 - \sigma$, and the conditional (c) probability to escape starting from the reflecting part. Denoting the latter probability by $P_{esc}^{(c)}(\sigma)$, we find that, as $\sigma \rightarrow 1$, this probability, according to Eq. (13), is given by

$$P_{esc}^{(c)}(\sigma)\big|_{\sigma \rightarrow 1} = \frac{5\pi}{4} \sqrt{1 - \sigma}. \quad (14)$$

When $\sigma \rightarrow 1$, the reflecting part of the surface is a small disk of radius b , $b = 2R\sqrt{1 - \sigma} \ll R$. The conditional escape probability in Eq. (14) can be written in terms of the ratio b/R as

$$P_{esc}^{(c)}(b/R)\big|_{b/R \rightarrow 0} = \frac{5\pi}{8} \frac{b}{R}. \quad (15)$$

This shows that when $b/R \rightarrow 0$, the conditional escape probability approaches zero linearly in b/R . This asymptotic behavior of $P_{esc}^{(c)}(b/R)$ is a consequence of the $1/(1 - \sigma)^{3/2}$ divergence of the effective trapping rate, $\tilde{\kappa}(\sigma)$, in Eq. (4), as $\sigma \rightarrow 1$. In other words, if the speculation above is correct, the $1/(1 - \sigma)^{3/2}$ divergence of $\kappa(\sigma)$ is due to the linear b/R asymptotic behavior of $P_{esc}^{(c)}(b/R)$ in Eq. (15). To our knowledge, an analytical solution for the conditional escape probability in the limiting case of $b \rightarrow 0$ is unknown.

Finally, we use $k(\sigma)$ in Eq. (11) to find the capacitance $C(\sigma)$ of a metal cap that occupies an arbitrary surface fraction σ of a dielectric sphere of radius R . The relation between the capacitance and the rate constant has the form $C(\sigma) = k(\sigma)/(4\pi D)$. This leads to

$$C(\sigma) = \frac{2\sqrt{\sigma} (1 + 2.6\sqrt{\sigma} - 3.2\sigma^2)}{\pi (1 - \sigma)^{3/2} + 2\sqrt{\sigma} (1 + 2.6\sqrt{\sigma} - 3.2\sigma^2)} R. \quad (16)$$

At $\sigma = 1$, this reduces to the capacitance of a metal sphere of radius R , $C(\sigma)|_{\sigma=1} = R$. As $\sigma \rightarrow 0$, $C(\sigma)$ in Eq. (16) reduces to the capacitance of a metal disk of radius a , $a = 2R\sqrt{\sigma}$, on a flat dielectric wall, $C(\sigma)|_{\sigma \rightarrow 0} = a/\pi$. Thus, Eq. (16) describes the transition of the capacitance between the two limiting cases of the metal sphere ($\sigma = 1$) and a small metal disk on the dielectric sphere ($\sigma \rightarrow 0$). Since the relation between the capacitance and the rate constant is an exact result, Eq. (16) describes the capacitance at arbitrary σ with the relative error less than 5%.

In summary, the main result of this paper is the expression in Eq. (4), which gives the effective uniform trapping rate of a sphere containing an absorbing cap of arbitrary size on the otherwise reflecting surface. This expression is used to find a formula for the rate constant, Eq. (11), that describes trapping of diffusing particles by an absorbing cap on the surface of the otherwise reflecting sphere. Next we take advantage of the relation between the capacitance of a metal cap on the surface of a dielectric sphere and the rate constant describing trapping of diffusing particles by an absorbing cap on the otherwise reflecting sphere. This relation is applied to find the capacitance, Eq. (16). Thus, the boundary homogenization approach allows us to find simple and accurate formulas for the rate constant and the capacitance.

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APPENDIX: DERIVATION OF EQ. (1)

Consider a particle diffusing in a spherical layer between two concentric spheres of radii R and R_{out} , $R < R_{out}$. The inner and outer spheres are partially absorbing and reflecting boundaries for the particle, respectively. The mean particle lifetime, considered as a function of its initial distance r_0 from the center of both spheres, denoted by $\tau(r_0)$, satisfies²⁵

$$\frac{D}{r_0^2} \frac{d}{dr_0} \left(r_0^2 \frac{d\tau(r_0)}{dr_0} \right) = -1, \quad (A1)$$

subject to the boundary conditions

$$\frac{d\tau(r_0)}{dr_0}\bigg|_{r_0=R_{out}} = 0, \quad D \frac{d\tau(r_0)}{dr_0}\bigg|_{r_0=R} = \kappa\tau(R), \quad (A2)$$

where D is the particle diffusivity, κ is the trapping rate of the inner sphere surface, and $\tau(R)$ is the mean lifetime of a particle that starts from this surface.

Integrating Eq. (A1) with the boundary condition at $r_0 = R_{out}$, we obtain

$$\frac{d\tau(r_0)}{dr_0} = \frac{1}{3Dr_0^2} (R_{out}^3 - r_0^3). \quad (A3)$$

We use this and the boundary condition at $r_0 = R$ to find $\tau(R)$. This leads to the expression for the mean lifetime of a

particle starting from the partially absorbing inner sphere given in Eq. (1).

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