Simple formulas for the trapping rate by nonspherical absorber and capacitance of nonspherical conductor

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This note deals with the rate coefficient, $k(t)$, that determines the survival probability, $S(t)$, of an immobile absorber which instantly annihilates at the first contact with one of the freely diffusing point particles

$$S(t) = \exp\left[-c\int_0^t k(t')dt'\right]. \tag{1}$$

Here c is the concentration of the diffusing particles, which are assumed to be uniformly distributed in space at $t=0$. For a spherical absorber of radius a the exact solution for the rate coefficient was found by Smoluchowski[1]

$$k_{\mathrm{sph}}(t) = 4\pi a^2\sqrt{\frac{D}{\pi t}} + 4\pi Da. \tag{2}$$

In what follows we suggest an approximate formula for $k(t)$ that generalizes the Smoluchowski solution to nonspherical absorbers whose boundaries are not too rough. This formula has been tested by comparison with known analytical and numerical results as well as numerical results obtained by the authors. Comparison shows that the formula provides a reasonable approximation for the rate coefficient.

It is not obvious how to generalize the expression for the rate coefficient in Eq. (2) to the case of nonspherical absorbers. However, this expression looks quite general and suggestive for generalization if one writes it in terms of the surface area, A, of the absorber

$$k(t) = A\sqrt{\frac{D}{\pi t}} + \sqrt{4\pi A}D. \tag{3}$$

This formula (i) reduces to the exact solution as $t\to 0$, $k(t) = A\sqrt{D/\pi t}$, and (ii) satisfies the general relation,[2] which gives the asymptotic long-time behavior of the rate coefficient in terms of the plateau value $k_\infty = k(\infty)$,

$$k(t) = k_\infty\left[1 + \frac{k_\infty}{4\pi D\sqrt{\pi D t}}\right], \quad t\to\infty. \tag{4}$$

Below we first compare the approximate formula for the plateau value

$$k_\infty = \sqrt{4\pi A}D, \tag{5}$$

which we will call the rate constant, with known analytical and numerical results as well as with our numerical results obtained by a finite difference method. Then we compare the rate coefficient in Eq. (3) with the time-dependent solution for $k(t)$ obtained numerically for two nonspherical targets.

There is a general relation between k_∞ and the capacitance, C, of the absorber, $k_\infty = 4\pi DC$. Therefore, the relation in Eq. (5) implies an approximate general formula for the capacitance

$$C = \sqrt{A/(4\pi)}. \tag{6}$$

This is another result of this note. We will use this formula when comparing with known results.

We begin with oblate spheroid, which is obtained by rotating an ellipse about its semiminor axis. The surface area of the oblate spheroid, A_{oblate}, is given by

$$A_{\mathrm{oblate}} = 2\pi a^2\left[1 + \frac{1-\varepsilon^2}{2\varepsilon}\ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right)\right], \tag{7}$$

where $\varepsilon = (1-a^2/b^2)^{1/2}$ is the eccentricity of the ellipse, $0\le\varepsilon\le 1$, a and b are the semimajor and the semiminor axes, respectively. The exact solution for the capacitance of the oblate spheroid is known,[3]

$$C_{\mathrm{oblate}}^{\mathrm{exact}} = \frac{a\varepsilon}{\arcsin(\varepsilon)}. \tag{8}$$

To compare the approximate general formula with the exact result consider the ratio $r_{\mathrm{oblate}}(\varepsilon) = k_{\mathrm{oblate}}^{\mathrm{approx}}/k_{\mathrm{oblate}}^{\mathrm{exact}} = C_{\mathrm{oblate}}^{\mathrm{approx}}/C_{\mathrm{oblate}}^{\mathrm{exact}}$ given by

$$r_{\mathrm{oblate}}(\varepsilon) = \frac{\arcsin(\varepsilon)}{\sqrt{2}\varepsilon}\left[1 + \frac{1-\varepsilon^2}{2\varepsilon}\ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right)\right]^{1/2}. \tag{9}$$

For $\varepsilon=0$ (sphere) the ratio is unity as it must be. The small-ε expansion of the ratio is given by

$$r_{\mathrm{oblate}}(\varepsilon) = 1 + \frac{2}{945}\varepsilon^6 + \frac{2}{675}\varepsilon^8 + \cdots. \tag{10}$$

The expansion begins with a term proportional to ε^6, and the coefficient of this term is very small. In the opposite limiting case, $b=0$ and $\varepsilon=1$, the spheroid reduces to the disk for

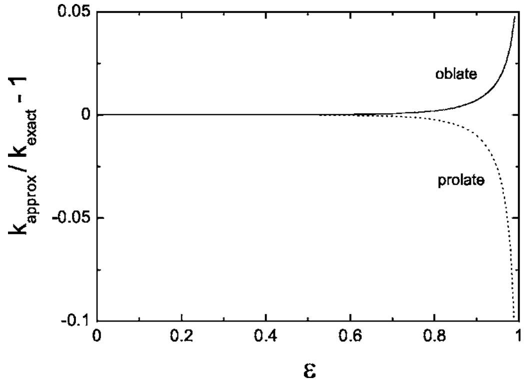

FIG. 1. Relative error of the approximate formula (5) for oblate (solid line) and prolate (dotted line) spheroidal absorbers as a function of the eccentricity.

which the capacitance is known, $C_{\text{disk}}=2a/\pi$. In this case the ratio is approximately 1.1. Thus for oblate spheroid the approximate formulas works reasonably well over the entire range of ε. The dependence of $r_{\text{oblate}}(\varepsilon)-1$ is shown in Fig. 1.

Next we compare our approximate formulas with the exact results for prolate spheroid obtained by rotating the ellipse about the semimajor axis. The area and capacitance[3] of this spheroid, respectively, are

$$A_{\text{prolate}}=2\pi a^2\sqrt{1-\varepsilon^2}\left[\sqrt{1-\varepsilon^2}+\frac{\arcsin(\varepsilon)}{\varepsilon}\right] \tag{11}$$

and

$$C_{\text{prolate}}^{\text{exact}}=\frac{2a\varepsilon}{\ln[(1+\varepsilon)/(1-\varepsilon)]}. \tag{12}$$

The ratio, analogous to that discussed for the oblate spheroid, is given by

$$r_{\text{prolate}}(\varepsilon)=\frac{1}{2\sqrt{2}\varepsilon}\ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right)\times\left[1-\varepsilon^2+\frac{1}{\varepsilon}\sqrt{1-\varepsilon^2}\arcsin(\varepsilon)\right]^{1/2}. \tag{13}$$

Again, the ratio is unity for $\varepsilon=0$ (sphere). The small-ε expansion of the ratio is

$$r_{\text{prolate}}(\varepsilon)=1-\frac{2}{945}\varepsilon^6-\frac{16}{4725}\varepsilon^8+\cdots. \tag{14}$$

As for oblate spheroid, the expansion begins with a term proportional to ε^6, and the coefficient of this term is very small. As $\varepsilon\to 1$ both the area in Eq. (11) and the capacitance in Eq. (12) tend to zero. In this limiting case Eq. (13) takes the form

$$r_{\text{prolate}}(\varepsilon)=\frac{\sqrt{\pi\sqrt{2}}}{4}(1-\varepsilon)^{1/4}\ln\left(\frac{2}{1-\varepsilon}\right), \tag{15}$$

and also tends to zero as $\varepsilon\to 1$. As an estimate we indicate that for $b=0.1a(\varepsilon\approx 0.995)$ the ratio is approximately 0.85, while the rate constant and the capacitance decrease approximately three times compared to their values for the sphere of radius $a(\varepsilon=0)$. The dependence of $r_{\text{prolate}}(\varepsilon)-1$ is shown in Fig. 1.

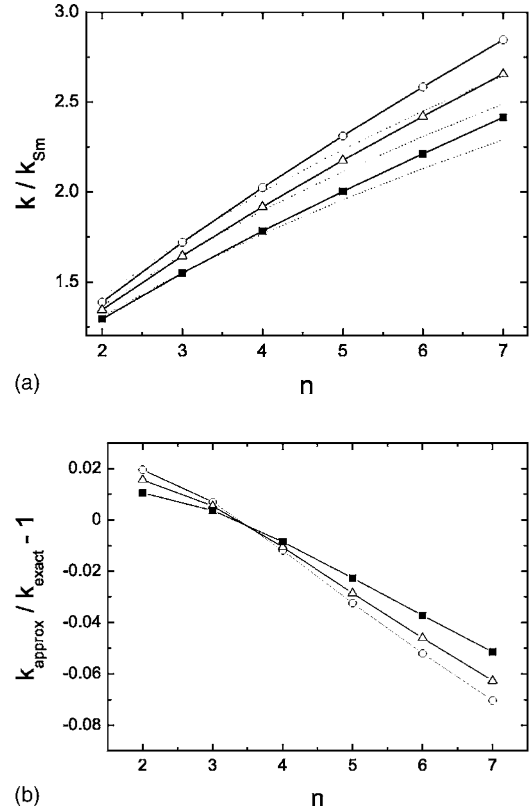

FIG. 2. (a) Stationary rate constant k for a linear "molecule" absorber composed of n overlapping spheres normalized to the Smoluchowski rate constant, $k_{\text{Sm}}=4\pi Da$, for one sphere of radius a. Symbols show numerically exact results for the following intersphere separations: $L/a=2$ (circles), $L/a=\sqrt{3}$ (triangles), and $L/a=\sqrt{2}$ (squares). Predictions of the approximate formulas are illustrated by dotted lines. (b) Relative error of the approximate formulas (5) for a linear "molecule" absorber as a function of the number n of composing spherical units. Symbols correspond to different intersphere separations.

Another object for which an exact analytical solution for the capacitance is known is a dumbbell composed of two overlapping spheres (see Ref. 4 and references therein). We compare the approximate and exact expressions for the dumbbell made of two equal spheres of radius a at three intersphere separations: $L/a=2,\sqrt{3},\sqrt{2}$, where L is the distance between the centers of the spheres. The first case corresponds to two nonoverlapping spheres at contact. The surface area of the dumbbell, $A(L)$, is given by $A(L)=\pi a^2(1+L/2a)$. Exact values of the capacitance, $C(L)$, which will be used for comparison, can be found in Ref. 4. These value are $C(2a)=2a\ln 2$, $C(\sqrt{3}\,a)\approx 1.345\,a$, and $C(\sqrt{2}\,a)\approx 1.293\,a$. Using these values we obtain for the ratio, $r(L)$, of the approximate and exact expressions for the rate constant and the capacitance: $r(2a)\approx 1.02$, $r(\sqrt{3}\,a)\approx 1.01$, and $r(\sqrt{2}\,a)\approx 1.005$. As might be expected, the relative error of the prediction grows with separation and reaches its maximum at $L/a=2$ (contacting spheres) where it is about 2%.

We have also performed numerical analysis for a linear "molecule" composed of n overlapping equal-size spheres. Intersphere separations were the same as for the dumbbell

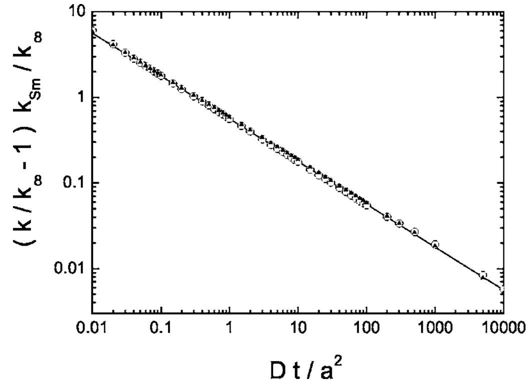

FIG. 3. Universal plot of the time-dependent rate coefficient $k(t)$ as a function of dimensionless time Dt/a^2 for two nonspherical absorbers: A dumbbell with intersphere separation $L/a=\sqrt{3}$ (circles) and a capped cylindrical rod of length $L/a=5$ (triangles).

model: $L/a=2,\sqrt{3},\sqrt{2}$. In our numerical procedure, we took advantage of the axial symmetry of the problem and used a finite difference method with adaptive triangular meshing to solve the corresponding two-dimensional partial differential equation. Relative error of the obtained stationary rate constant was 0.1%, which is sufficient to consider this to be essentially an exact result. Figure 2 illustrates the dependence of the stationary rate constant on the number of "atoms" in the "molecule" [Fig. 2(a)] and demonstrates the relative error of our approximate formula [Fig. 2(b)]. Note that for a "molecule" containing as many as seven "atoms," the rate constant almost triples the Smoluchowski value while the relative error of the approximate formula is within reasonable 7%.

The capacitance of a cube with side length a estimated by different methods is equal to $0.66a$ (see Ref. 4 and references therein). Comparison shows that Eq. (6) gives about 5% larger value of the capacitance.

Let us also consider a cylindrical rod of radius a and length L capped by semi-spheres. Our numerical analysis using a finite difference method shows that the accuracy of the approximate formula decreases with increasing rod length, as expected. However, for L as large as $10a$, where the rate constant is almost three times larger than that for a sphere, the relative error is only about 9%.

Finally, we analyze the accuracy of Eq. (4) for the time dependent rate coefficient. We choose two highly nonspherical objects, namely: the dumbbell composed of two overlapping spheres of radius a, with the distance $L=\sqrt{3}\,a$ between their centers, and a cylindrical rod of radius a and length $L=5a$ capped by semispheres. The symmetry of Eq. (4) allows us to plot it in a universal form, i.e., $[k(t)/k_\infty-1]k_{\mathrm{Sm}}/k_\infty$, where $k_{\mathrm{Sm}}=4\pi Da$ is the Smoluchowski rate constant, as a function of dimensionless time Dt/a^2. Numerical results were obtained by a finite difference method. Figure 3 shows remarkable accuracy of Eq. (4). Note that the plot covers six orders of magnitude in dimensionless time whereas the renormalized rate constant change covers four orders of magnitude.

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