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Note: Effect of a small surface defect on the Smoluchowski rate constant and capacitance of a spherical capacitor

Leonardo Dagdug,[1] Alexander M. Berezhkovskii,[2] and Vladimir Yu. Zitserman[3]
[1]*Departamento de Fisica, Universidad Autonoma Metropolitana-Iztapalapa, 09340 Mexico City, Mexico*
[2]*Mathematical and Statistical Computing Laboratory, Division of Computational BioScience, Center for Information Technology, National Institutes of Health, Bethesda, Maryland 20819, USA*
[3]*Joint Institute for High Temperatures, Russian Academy of Sciences, Izhorskaya 13, Bldg. 2, Moscow 125412, Russia*

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This paper focuses on how a small reflecting disk on the perfectly absorbing surface of a spherical sink affects the rate constant, defined as the ratio of the steady-state flux of non-interacting point particles diffusing toward the sink to the particle concentration at infinity. Here, to our knowledge for the first time, we derive an asymptotically exact analytical solution for the rate constant when the ratio of the disk and sink radii tends to zero. In the absence of the disk, the rate constant is given by the Smoluchowski formula, $k_{Sm} = 4\pi DR$, where D and R are the particle diffusivity and sink radius. To characterize the effect we consider the ratio of the rate constant k_b in the presence of a small reflecting disk of radius b, $b \ll R$, to k_{Sm}. As we will see, this ratio, denoted by f_b, and sometimes referred to in the literature[1–15] as the steric factor, is given by

$$f_b = k_b/k_{Sm} = 1 - (1/3\pi)\ (b/R)^3. \tag{1}$$

Note that the same expression gives the ratio of the capacitance of a metallic sphere of radius R with a small circular dielectric disk of radius b on its surface to the capacitance of the defect-free metallic sphere of the same radius. Denoting the former and latter capacitances by C_b and C_0, we can write

$$C_b/C_0 = f_b = 1 - (1/3\pi)\ (b/R)^3. \tag{2}$$

Before deriving the relation in Eq. (1), we indicate that the steric factor has a probabilistic interpretation. This factor is the trapping probability for a particle starting from the surface of the sphere, averaged over the uniform distribution of the particle starting point over the surface. We use this to write the steric factor as

$$f_b = 1 - P_{esc}A_{disk}\big/A_{sphere} = 1 - P_{esc}b^2\big/\left(4R^2\right), \tag{3}$$

where $A_{disk} = \pi b^2$ and $A_{sphere} = 4\pi R^2$ are the disk and sphere areas, respectively, and P_{esc} is the probability that the particle starting from the disk escapes to infinity, averaged over the disk surface. Comparison of Eqs. (1) and (3) shows that the escape probability is given by

$$P_{esc} = (4/3\pi)\ (b/R). \tag{4}$$

This is another interesting result of this work.

To derive the expression for the steric factor in Eq. (1), we have to solve the Laplace equation with a reflecting boundary condition on the disk and an absorbing boundary condition on the rest of the sphere. This is a mixed boundary value problem. A classic example of such a problem is the problem of a small absorbing disk on the otherwise reflecting sphere. The Hill-Berg-Purcell[3,4] solution for the rate constant in this case is equivalent to the Weber solution for the capacitance of a metallic disk in electrostatics.[16,17] It is worth noting that the problem of a small reflecting disk on the otherwise absorbing surface is much more complex than the problem of a small absorbing disk on the otherwise reflecting sphere. While the latter problem can be solved by standard methods of mathematical physics, these methods fail to solve the former problem. Therefore, we derive the expression in Eq. (1), by means of a more sophisticated approach based on dual series relations.[18]

We use the version of the formalism proposed by Traytak,[12] who studied trapping of diffusing particles by a sphere with axially symmetric perfectly absorbing and reflecting parts separated by an arbitrary polar angle θ_0, $0 \leq \theta_0 \leq \pi$; the surface was perfectly absorbing for $0 \leq \theta \leq \theta_0$ and perfectly reflecting for $\theta_0 < \theta \leq \pi$. Starting from the dual series relations,[18] Traytak showed that the steric factor $f(\theta_0)$ is one half of an auxiliary function $X_0(\theta_0)$, $f(\theta_0) = X_0(\theta_0)/2$. This function satisfies an infinite system of inhomogeneous linear equations for functions $X_l(\theta_0)$, $l = 0, 1, 2, \ldots$,

$$X_l(\theta_0) - \sum_{m=0}^{\infty} Q_{lm}(\theta_0)\, q_m X_m(\theta_0) = Q_{l0}(\theta_0), \qquad l = 0, 1, 2, \ldots, \tag{5}$$

where $q_l = 1/[2(l+1)]$ and the matrix element $Q_{lm}(\theta_0)$ is given by

$$Q_{lm}(\theta_0) = \frac{1}{\pi}\left\{\left[\theta_0 + \frac{\sin[(2l+1)\theta_0]}{2l+1}\right]\delta_{lm} + \left[\frac{\sin[(l+m+1)\theta_0]}{l+m+1} + \frac{\sin[(l-m)\theta_0]}{l-m}\right](1-\delta_{lm})\right\}. \tag{6}$$

In the general case, this infinite system of equations is solved numerically. However, as shown below, when the disk is small, it is possible to find two leading terms of the solution for $X_0(\theta_0)$ analytically by the perturbation theory.

In the latter case, angle θ_0 is close to π, and it is convenient to introduce angle δ_0, defined as the angular size of

the reflecting disk, $\delta_0 = \pi - \theta_0 = b/R \ll 1$. Solving Eq. (5) by perturbation theory, we separate terms containing diagonal and non-diagonal matrix elements and write this equation as

$$\begin{aligned} &(1 - q_l Q_{ll}(\pi - \delta_0)) X_l(\pi - \delta_0) \\ &\quad - \sum_{m \neq l} Q_{lm}(\pi - \delta_0) q_m X_m(\pi - \delta_0) = Q_{l0}(\pi - \delta_0), \\ &\quad l = 0, 1, 2, ..., \end{aligned} \tag{7}$$

where the matrix element $Q_{lm}(\pi - \delta_0)$ is

$$\begin{aligned} Q_{lm}(\pi - \delta_0) = \frac{1}{\pi} \Bigg\{ &\left[\pi - \delta_0 + \frac{\sin[(2l+1)\delta_0]}{2l+1} \right] \delta_{lm} + (-1)^{l+m} \\ &\times \left[\frac{\sin[(l+m+1)\delta_0]}{l+m+1} - \frac{\sin[(l-m)\delta_0]}{l-m} \right] \\ &\times (1 - \delta_{lm}) \Bigg\}. \end{aligned} \tag{8}$$

In the absence of the defect, $\delta_0 = 0$, $Q_{lm}(\pi) = \delta_{lm}$, and Eq. (7) reduces to $(2l+1) X_l(\pi) = 2\delta_{l0}$. Solution of this equation provides the leading term of the perturbation theory expansion of $X_l(\pi - \delta_0)$, $X_l^{(0)}(\pi - \delta_0) = X_l(\pi) = 2\delta_{l0}$. Substituting $X_0(\pi) = 2$ into the relation $f(\theta_0) = X_0(\theta_0)/2$, we recover $f(0) = 1$, as it must be.

For small δ_0, the matrix element in Eq. (8) approximately is

$$\begin{aligned} Q_{lm}(\pi - \delta_0) = &\left[1 - (2l+1)^2 \frac{\delta_0^3}{6\pi} \right] \delta_{lm} \\ &+ (-1)^{l+m} (2l+1)(2m+1) \frac{\delta_0^3}{6\pi} (1 - \delta_{lm}). \end{aligned} \tag{9}$$

As a result, Eq. (7) reduces to

$$\begin{aligned} &\left[1 - q_l + q_l (2l+1)^2 \frac{\delta_0^3}{6\pi} \right] X_l(\pi - \delta_0) - (2l+1) \frac{\delta_0^3}{6\pi} \\ &\quad \times \sum_{m \neq l} (-1)^{l+m} (2m+1) q_m X_m(\pi - \delta_0) = \left(1 - \frac{\delta_0^3}{6\pi} \right) \delta_{l0}, \\ &\quad l = 0, 1, 2, ... \end{aligned} \tag{10}$$

We seek an asymptotic ($\delta_0 \to 0$) solution to this equation in the form

$$X_l(\pi - \delta_0) = X_l(\pi) + \left(\delta_0^3 / (6\pi) \right) \Delta X_l = 2\delta_{l0} + \left(\delta_0^3 / (6\pi) \right) \Delta X_l, \tag{11}$$

where factor ΔX_l is independent of δ_0. To determine this factor, we substitute $X_l(\pi - \delta_0)$ in Eq. (11) into Eq. (10). Keeping the terms of the order of δ_0^3 in the resulting equation, we find that ΔX_l satisfies

$$(1 - q_l) \Delta X_l = -2\delta_{l0} + (-1)^l (2l+1)(1 - \delta_{l0}). \tag{12}$$

Solving this equation and using the relation $1 - q_l = (2l+1)/[2(l+1)]$, we obtain

$$\Delta X_l = -4\delta_{l0} + (-1)^l 2(l+1)(1 - \delta_{l0}). \tag{13}$$

Substituting this into Eq. (11), we arrive at

$$\begin{aligned} X_l(\pi - \delta_0) = &2 \left[1 - \delta_0^3 / (3\pi) \right] \delta_{l0} \\ &+ (-1)^l 2(l+1) \left[\delta_0^3 / (6\pi) \right] (1 - \delta_{l0}). \end{aligned} \tag{14}$$

To determine the steric factor, we need to know $X_0(\pi - \delta_0)$, which is given by $X_0(\pi - \delta_0) = 2\left[1 - \delta_0^3/(3\pi)\right]$. Finally, we find the transmission factor using the relation $f(\theta_0) = X_0(\theta_0)/2$,

$$f_b = f(\theta_0 = \pi - \delta_0) = 1 - \delta_0^3 / (3\pi) = 1 - (1/3\pi)\ (b/R)^3. \tag{15}$$

This is the main result of this paper that allows one to find the rate constant which characterizes the trapping rate by a spherical absorber with a small reflecting circular disk on its otherwise perfectly absorbing surface, $k_b = f_b k_{Sm}$, as well as the capacitance of a metallic sphere containing a small dielectric circular disk on its surface, $C_b = f_b C_0$. The obtained asymptotic behavior of the steric factor has been used to find the asymptotically exact solution for the escape probability of a particle starting from the disk, Eq. (4), which is another result of this work.

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