Unified Approach to Spherically Symmetric Diffusion

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The general form of the Green's-function solution for the spherically symmetric Smoluchowski equation serves as a unified starting point for deriving identities. This approach enables one to obtain a nonlinear differential equation for the dependence of the Green's function on the location of the boundary, relations between Green's-function solutions for various boundary conditions, and their asymptotic expansions.

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Spherically symmetric diffusion outside a sphere plays an important role in the study of diffusion-influenced reactions, for example, as a model for geminate pair recombination [1]. When a spherically symmetric potential is introduced, one obtains a Smoluchowski equation [2] that cannot, in general, be analytically solved. One can, however, obtain asymptotic solutions such as the long-time behavior of the time-dependent rate coefficient [3]. As an aid to this end, Sibani and Pedersen [4] have derived, using renewal arguments, a Riccati equation for the dependence of the time-dependent rate coefficient on the sphere's radius. This equation has been recently generalized by Agmon and Szabo [5], who have also obtained identities connecting solutions for different boundary conditions. Such identities have previously been derived [6–8] by various methods, such as renewal arguments [9]. The present Letter further generalizes the approach [5] to the Green's-function solution, which depends on a single unknown function. By manipulating this solution and eliminating the unknown function, the most general form of the above-mentioned identities may be obtained.

The spherically symmetric Smoluchowski equation [1,2] for diffusion outside a d-dimensional sphere,

$$\frac{\partial\rho(r,t\,|\,r_0)}{\partial t}=\frac{\partial}{\partial r}D(r)e^{-V(r)}\frac{\partial}{\partial r}e^{V(r)}\rho(r,t\,|\,r_0)\equiv\mathcal{L}_r\rho(r,t\,|\,r_0),\quad r\geq a\,,\qquad(1)$$

describes the time (t) evolution of the radial probability density, $\rho(r,t|r_0)\equiv\gamma_d r^{d-1}p(r,t|r_0)$, where $p(r,t|r_0)$ is the probability density for a particle to be located a distance r from the origin by time t given that it was initially ($t=0$) located at r_0. $\gamma_d\equiv 2\pi^{d/2}\Gamma(d/2)=1$, 2π, and 4π for $d=1$, 2, and 3, respectively. $D(r)>0$ is a diffusion coefficient tending to a constant value at large distances, $D(r)\to D_\infty$ as $r\to\infty$. $V(r)\equiv U(r)/k_BT-(d-1)\ln r$, where $U(r)$ denotes a spherically symmetric potential of interaction, k_B is Boltzmann's constant, and T is the absolute temperature. It is assumed that $U(r)\to 0$ as $r\to\infty$. $\mathcal{L}_r$ stands for the Smoluchowski operator in the variable r. The initial condition imposed on Eq. (1) is therefore that of a δ function,

$$\rho(r,0|r_0)=\delta(r-r_0)\,.\qquad(2)$$

Hence $\rho(r,t|r_0)$ is the Green's function for the Smoluchowski equation.

The most general form for the boundary condition at $r=a$ to be considered below is the "radiation" boundary condition [1]

$$R(t\,|\,r_0)\equiv D(a)e^{-V(a)}\frac{\partial}{\partial r}e^{V(r)}\rho(r,t\,|\,r_0)\Big|_{r=a}=\kappa\rho(a,t\,|\,r_0)\,,\qquad(3)$$

in which case we [5] denote the solution by $\rho_{\rm rad}(r,t|r_0)$. In the special case that $\kappa=0$, it reduces to the solution for a reflecting boundary condition, $\rho_{\rm ref}(r,t|r_0)$, while for $\kappa=\infty$, Eq. (3) reduces to an absorbing boundary condition, $\rho_{\rm abs}(a,t|r_0)=0$. Whenever the boundary condition is not explicitly noted, the result is understood to be generally valid. In the opposite limit of $r\to\infty$ the solution vanishes, $\rho(r,t|r_0)\to 0$. In general, $\rho(r,t|r_0)$ depends on the two variables r and t, as well as on two parameters, r_0 and a. The dependence on r_0 enters through the initial condition, Eq. (2), while the dependence on a is implicit through the boundary condition, Eq. (3). The latter can be stressed by using the notation $\rho(r,t|r_0;a)$ whenever appropriate.

It is convenient to Laplace transform the above equations, defining $\hat\rho(r,s|r_0)\equiv\int_0^\infty dt\,e^{-st}\rho(r,t|r_0)$ for $0\leq s<\infty$. In Laplace space, the Smoluchowski equation becomes an ordinary differential equation,

$$s\hat\rho(r,s\,|\,r_0)-\delta(r-r_0)=\mathcal{L}_r\hat\rho(r,s\,|\,r_0),\quad r\geq a\,,\qquad(4)$$

with boundary conditions transformed accordingly. The inhomogeneous, δ-function term comes from the initial condition, Eq. (2). One may similarly absorb the initial condition into Eq. (1) by adding $\delta(t)\delta(r-r_0)$ to its right-hand side (rhs).

The starting point for all subsequent derivations is the general form of the solution to Eq. (4), as obtained from properties of ordinary differential equations and Green's functions [10]. Assume that $f(r)$ is a solution of the homogeneous part of Eq. (4), i.e., for $r\neq r_0$. (This solution depends parametrically on s but not on a.) Then, it is well known [10] that $f(r)I(r;a)$ is a second, linearly independent solution of the second-order homogeneous equation, where

$$I(r;a)\equiv\int_a^r dx\,[D(x)e^{V(x)}f(x)^2]^{-1}.$$

This may be checked by direct differentiation. Furthermore, let $f(r)$ obey the outer boundary condition, namely, $f(r)\to 0$ as $r\to\infty$. Then $y_1(r)\equiv f(r)$ is the solution in the outer region, $r>r_0$. The solution in the inner region, $r<r_0$, denoted by $y_2(r)$, can always be written as a linear combination of the two above-mentioned solutions. Therefore $y_2(r)=f(r)[\alpha(a)+I(r;a)]$, where $\alpha(a)$ is a constant which will depend on the boundary condition imposed at $r=a$. The solutions y_1 and y_2 are again linearly independent since their Wronskian [10], $W(y_1,y_2)\equiv y_1y_2'-y_2y_1'$, differs from zero everywhere. Specifically, $W(y_1,y_2)=-[D(r_0)e^{V(r_0)}]^{-1}$. Given $y_1(r)$ and $y_2(r)$, it is standard technique [10] to obtain the solution of the inhomogeneous equation (4):

$$-D(r_0)W(y_1,y_2)\hat\rho(r,s\,|\,r_0)=\begin{cases}y_1(r)y_2(r_0), & \text{if } r\ge r_0,\\ y_1(r_0)y_2(r), & \text{if } r\le r_0.\end{cases}$$

Therefore

$$\hat\rho(r,s\,|\,r_0;a)=f(r)f(r_0)e^{V(r_0)}[\alpha(a)+I(r,r_0;a)],$$
$$I(r,r_0;a)\equiv\int_a^{\min(r,r_0)}dx\,[D(x)e^{V(x)}f(x)^2]^{-1}. \tag{5}$$

Equation (5) reveals the usual properties of the Green's function, which is continuous at $r=r_0$, but whose first derivative is discontinuous there [due to the function $I(r,r_0)$]. Expressing the solution in terms of a generally unknown function $f(r)$ may seem futile [5]: Whenever Eq. (4) admits an analytic solution, so is $f(r)$. The importance of Eq. (5) is in cases where no analytic solutions exist, as it allows the derivation of many useful identities.

First, consider the dependence on the parameters r_0 and a. Equation (5) implies that the Green's function obeys the symmetry relation

$$\hat\rho(r,s\,|\,r_0)e^{-V(r_0)}=\hat\rho(r_0,s\,|\,r)e^{-V(r)}.$$

Evidently, this relation holds in the time domain as well, where it is known as *detailed balancing*. Insertion in Eq. (4) shows that the r_0 dependence can be described by

$$s\hat\rho(r,s\,|\,r_0)-\delta(r-r_0)=e^{V(r_0)}\frac{\partial}{\partial r_0}D(r_0)e^{-V(r_0)}\frac{\partial}{\partial r_0}\hat\rho(r,s\,|\,r_0)\equiv\mathcal{L}_{r_0}^\dagger\hat\rho(r,s\,|\,r_0),\quad r_0\ge a, \tag{6}$$

which is the well-known [1] "backward" Kolmogorov equation. $\mathcal{L}_{r_0}^\dagger$ denotes the adjoint Smoluchowski operator in r_0, and the boundary condition transforms accordingly [11,12].

In contrast to the backward equation, little is said in the literature about the dependence on the boundary location a. Using Eq. (5), it is possible to obtain the following nonlinear *boundary equation* for a reflecting sphere,

$$\partial\hat\rho_{\rm ref}(r,s\,|\,r_0;a)/\partial a=s\hat\rho_{\rm ref}(r,s\,|\,a;a)\hat\rho_{\rm ref}(a,s\,|\,r_0;a), \tag{7}$$

which is valid for $r>a$. In the time domain, Eq. (7) becomes a convolution relation,

$$\partial\rho_{\rm ref}(r,t\,|\,r_0;a)/\partial a=\int_0^t d\tau\,\rho_{\rm ref}(r,t-\tau\,|\,a;a)\partial\rho_{\rm ref}(a,\tau\,|\,r_0;a)/\partial\tau. \tag{8}$$

It attributes the variation in $\rho_{\rm ref}(r,t\,|\,r_0)$, caused by a change in the reflective sphere radius, to all those stochastic trajectories which enter the spherical shell between a and $a+da$ at some intermediate time. The restriction to a reflective sphere is no limitation since, as we shall see below, any solution of interest may be related to the reflective solution.

Boundary equations of the type (7) may be obtained by *invariant imbedding* techniques [13], for example, through the appropriate Cauchy system. In the unified approach presented here, a straightforward derivation begins by imposing a reflecting boundary condition on Eq. (5). For $\kappa=0$ and $r_0>a$, Eq. (3) becomes

$$0=D(a)e^{-V(a)}\frac{\partial}{\partial r}e^{V(r)}f(r)[\alpha_{\rm ref}(a)+I(r;a)]\bigg|_{r=a}=\alpha_{\rm ref}(a)D(a)e^{-V(a)}\frac{\partial}{\partial r}e^{V(r)}f(r)\bigg|_{r=a}+[e^{V(a)}f(a)]^{-1}. \tag{9}$$

Subsequently, (the left-hand side of) Eq. (9) is differentiated with respect to a, yielding

$$0=\frac{\partial[\alpha_{\rm ref}(a)+I(r;a)]}{\partial a}D(a)e^{-V(a)}\frac{\partial}{\partial r}e^{V(r)}f(r)\bigg|_{r=a}+\mathcal{L}_r\{f(r)[\alpha_{\rm ref}(a)+I(r;a)]\}|_{r=a}. \tag{10}$$

The first term on the rhs is now simplified using (the rhs of) Eq. (9), while for the second term one uses the fact that $f[\alpha+I]$ solves the homogeneous part of Eq. (4) with $I(a;a)=0$. Subsequently,

$$\frac{\partial[\alpha_{\rm ref}(a)+I(r,r_0;a)]}{\partial a}=se^{V(a)}f(a)^2\alpha_{\rm ref}(a)^2=s\alpha_{\rm ref}(a)\hat\rho_{\rm ref}(a,s\,|\,a;a). \tag{11}$$

The replacement of $I(r;a)$ by $I(r,r_0;a)$ follows the application of a similar procedure to the adjoint equation. Now, on the one hand, differentiation of Eq. (5) with respect to a gives

$$\frac{\partial\hat\rho(r,s\,|\,r_0;a)}{\partial a}=\frac{\hat\rho(r,s\,|\,r_0;a)}{\alpha(a)+I(r,r_0;a)}\frac{\partial[\alpha(a)+I(r,r_0;a)]}{\partial a}. \tag{12}$$

On the other hand, by setting $r_0=a$ or $r=a$ in Eq. (5) one finds

$$\hat{\rho}(r,s|a;a)\hat{\rho}(a,s|r_0;a) = \frac{\hat{\rho}(r,s|r_0;a)}{\alpha(a)+I(r,r_0;a)}\hat{\rho}(a,s|a;a)\alpha(a). \quad (13)$$

For a reflecting boundary condition, insertion of Eqs. (11) and (13) into Eq. (12) eliminates the unknown function $f(a)$, thus leading to Eq. (7).

To reduce Eq. (7) to the case that the final location is on the reflecting sphere, $r=a$, the chain rule for differentiation is applied, namely,

$$\partial\hat{\rho}(a,s|r_0;a)/\partial a = [\partial\hat{\rho}(r,s|r_0;a)/\partial a + \partial\hat{\rho}(r,s|r_0;a)/\partial r]|_{r=a}.$$

This gives

$$e^{-V(a)}\frac{\partial e^{V(a)}\hat{\rho}_{\rm ref}(a,s|r_0;a)}{\partial a} = s\hat{\rho}_{\rm ref}(a,s|a;a)\hat{\rho}_{\rm ref}(a,s|r_0;a). \quad (14)$$

Similarly, setting $r_0=a$ gives

$$\partial\hat{\rho}_{\rm ref}(r,s|a;a)/\partial a = s\hat{\rho}_{\rm ref}(r,s|a;a)\hat{\rho}_{\rm ref}(a,s|a;a). \quad (15)$$

Finally, equating both initial and final distances to a gives

$$e^{-V(a)}\frac{\partial e^{V(a)}\hat{\rho}_{\rm ref}(a,s|a;a)}{\partial a} = s\hat{\rho}_{\rm ref}(a,s|a;a)^2 - D(a)^{-1}. \quad (16)$$

The last term on the rhs is obtained by noting that when either the initial or the final location is on the boundary,

$$\left.\frac{\partial\hat{\rho}_{\rm ref}(a,s|r_0;a)}{\partial r_0}\right|_{r_0=a} = e^{-V(a)}\left.\frac{\partial e^{V(r)}\hat{\rho}_{\rm ref}(r,s|a;a)}{\partial r}\right|_{r=a} = \alpha_{\rm ref}(a)f(a)\left.\frac{\partial e^{V(t)}f(r)}{\partial r}\right|_{r=a} = -D(a)^{-1}. \quad (17)$$

The latter follows from Eq. (5) and (9), using $I(a,r_0;a) = I(r,a;a)=0$. Equation (17) implies that the full form of the reflective boundary condition for the Green's function is $R(t|r_0) = -\delta(t)\delta(r_0-a)$. Indeed, when the initial location is on the boundary, the derivative cannot vanish at $t=0$.

Starting from Eq. (5), the derivation of identities connecting solutions for various boundary conditions is straightforward. For an absorbing boundary $\rho_{\rm abs}(a,t|r_0) = \rho_{\rm abs}(r,t|a)=0$, so that $\alpha_{\rm abs}=0$ and Eq. (5) simplifies to $\hat{\rho}_{\rm abs}(r,s|r_0) = f(r)f(r_0)e^{V(r_0)}I(r,r_0;a)$. It follows from Eqs. (5) and (13) that

$$\hat{\rho}_{\rm abs}(r,s|r_0) = \hat{\rho}(r,s|r_0) - \hat{\rho}(r,s|a)\hat{\rho}(a,s|r_0)/\hat{\rho}(a,s|a), \quad (18)$$

which is most useful for a reflecting boundary condition imposed on the rhs. For the more general radiation boundary condition, Eq. (3), the Laplace-transformed solution may be written as a linear combination of those for reflecting and absorbing boundaries, namely,

$$\hat{\rho}_{\rm rad}(r,s|r_0) = \beta\hat{\rho}_{\rm ref}(r,s|r_0) + (1-\beta)\hat{\rho}_{\rm abs}(r,s|r_0)$$

Indeed, by inserting into Eq. (5) one concludes that $\beta=\alpha_{\rm rad}/\alpha_{\rm ref}$. By applying the boundary condition, Eq. (3), and using Eqs. (18) and (17) one finds that $\beta=[1+\kappa\hat{\rho}_{\rm ref}(a,s|a)]^{-1}$. Hence

$$\hat{\rho}_{\rm rad}(r,s|r_0) = \hat{\rho}_{\rm ref}(r,s|r_0) - \frac{\kappa\hat{\rho}_{\rm ref}(r,s|a)\hat{\rho}_{\rm ref}(a,s|r_0)}{1+\kappa\hat{\rho}_{\rm ref}(a,s|a)}. \quad (19)$$

This result, previously derived by Szabo, Lamm, and Weiss [14], generalizes Eq. (18) to a partially absorbing boundary. The above results can be written in terms of reaction rates, Eq. (3). Use of Eq. (17) in Eqs. (18) and (19) gives

$$\hat{R}_{\rm abs}(s|r_0) = \hat{\rho}_{\rm ref}(a,s|r_0)/\hat{\rho}_{\rm ref}(a,s|a), \quad (20)$$

which generalizes to d dimensions a relation previously derived by van Kampen [15], and

$$\hat{R}_{\rm rad}(s|r_0) = \kappa\hat{\rho}_{\rm ref}(a,s|r_0)/[1+\kappa\hat{\rho}_{\rm ref}(a,s|a)]. \quad (21)$$

Since, by Eqs. (17) and (20),

$$-D(a)\partial\hat{R}_{\rm abs}(s|r_0)/\partial r_0|_{r_0=a} = \hat{\rho}_{\rm ref}(a,s|a)^{-1},$$

the combination of Eqs. (20) and (21) leads to the relation between radiation and absorbing rates as obtained by Pedersen [7] and Tachiya [8]. It therefore suffices to find a solution for the simplest boundary condition, either reflecting or absorbing.

An important role in diffusion theory [1] is played by the time-dependent rate coefficient [3,4] $k(t)$, which is defined as the reaction rate for an initial equilibrium distribution, $k(t) \equiv \gamma_d \int_a^\infty dr_0 r_0^{d-1} e^{-V(r_0)} R(t|r_0)$. Thus $k(t)$ involves differentiation of the Green's function with respect to r and its integration with respect to r_0. For an absorbing boundary in Laplace space, $\hat{\rho}_{\rm abs}(r,s|r_0)$ can be eliminated by Eq. (18). Subsequently, one may use identity (17) for the derivative of $\hat{\rho}_{\rm ref}(r,s|a)$ and

$$\int_a^\infty dr_0 e^{-V(r_0)}\hat{\rho}_{\rm ref}(r,s|r_0) = e^{-V(r)}/s \quad (22)$$

for the integral of $\hat{\rho}_{\rm ref}(a,s|r_0)$. This last identity follows by integration of Eq. (6). Therefore

$$s\hat{k}_{\rm abs}(s) = \gamma_d a^{d-1} e^{-V(a)}/\hat{\rho}_{\rm ref}(a,s|a). \quad (23)$$

Insertion into Eqs. (20) and (21) recasts the relation of radiative and absorptive solutions into a familiar form [5,6], while insertion into Eq. (16) yields the Riccati equation derived by Sibani and Pedersen [4],

$$\frac{\partial \hat{k}_{\rm abs}(s)}{\partial a} = -\gamma_d a^{d-1} e^{-V(a)} + \frac{s \hat{k}_{\rm abs}(s)^2 e^{V(a)}}{\gamma_d a^{d-1} D(a)}, \qquad (24)$$

which is therefore a special case of Eq. (7).

A practical application for Eq. (7) is in obtaining the long-time asymptotic solution to Eq. (6). This can be found in the case that $D(r) \to D_\infty$ and $V(r) \to 0$ for $r \to \infty$, in dimensions d for which the solution for D=const and $V=0$ is known analytically. The form of this solution in three dimensions [16] suggests the expansion

$$\hat{\rho}_{\rm ref}(r,s\,|\,r_0;a) \sim \sum_{n=0}^{\infty} g_n(r,r_0;a) s^{n/2}, \quad s \to 0\,. \qquad (25)$$

The coefficients g_n depend on the variables r, r_0, and a, but not the Laplace parameter s. By inserting expansion (25) into Eqs. (4), (6), and (7) and using the reflecting boundary condition [$\kappa=0$ in Eq. (3)], one obtains three hierarchies of equations in the above three variables, which may be solved sequentially for the coefficients g_n. The constants of integration are subsequently obtained by demanding that the solution reduces to the correct form in the limit of $r \to \infty$.

In conclusion, a unified approach for spherically symmetric diffusion invokes the general form for the Green's-function solution, Eq. (5), involving one unknown function which is independent of the inner boundary condition and a parameter which is determined by it. Using this approach, it is straightforward to derive some possibly new results [e.g., the *boundary equation* (7)] and many known identities, previously obtained by a variety of techniques. This eliminates much of the mystery and confusion attached to the subject of diffusion-influenced reactions. A similar approach may prove useful for other second-order differential equations of mathematical physics.

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