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Calculation of the second term of the exact Green's function of the diffusion equation for diffusion-controlled chemical reactions

Ianik Plante *

Wyle Science, Technology & Engineering Group, 1290 Hercules, Houston, TX 77058, USA

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ABSTRACT

The exact Green's function of the diffusion equation (GFDE) is often considered to be the gold standard for the simulation of partially diffusion-controlled reactions. As the GFDE with angular dependency is quite complex, the radial GFDE is more often used. Indeed, the exact GFDE is expressed as a Legendre expansion, the coefficients of which are given in terms of an integral comprising Bessel functions. This integral does not seem to have been evaluated analytically in existing literature. While the integral can be evaluated numerically, the Bessel functions make the integral oscillate and convergence is difficult to obtain. Therefore it would be of great interest to evaluate the integral analytically. The first term was evaluated previously, and was found to be equal to the radial GFDE. In this work, the second term of this expansion was evaluated. As this work has shown that the first two terms of the Legendre polynomial expansion can be calculated analytically, it raises the question of the possibility that an analytical solution exists for the other terms.

1. Introduction

1.1. The Green's function of the diffusion equation for partially diffusion-controlled chemical reactions

The exact Green's function of the diffusion equation (GFDE) for interparticle diffusion is used as the gold standard to validate chemical theories [1,2] and, therefore, is of great importance for radiation chemistry codes [3]. The GFDE is used in the chemistry code included in the software RITRACKS [4] as a probability distribution for a particle initially located at position (r_0, θ_0, ϕ_0) in a spherical coordinate system, to be located at position (r, θ, ϕ) at time t. The GFDE is considered exact for a 2-particle system. This GFDE is given by [5,6]

$$p_{\text{ex}}(r,\theta,\phi,t|r_0,\theta_0,\phi_0) = \frac{1}{4\pi\sqrt{rr_0}}\sum_{n=0}^{\infty}(2n+1)P_n(\cos\gamma)\int_0^{\infty} e^{-u^2Dt}uF_{n+1/2}(u,r)F_{n+1/2}(u,r_0)du, \tag{1}$$

where D is the sum of the diffusion coefficients of the reacting particles, $P_n(x)$ are the Legendre polynomials, and

$$F_\upsilon(u,r) = \frac{(2\sigma k_a+1)\left[J_\upsilon(ur)Y_\upsilon(u\sigma) - Y_\upsilon(ur)J_\upsilon(u\sigma)\right] - 2u\sigma\left[J_\upsilon(ur)Y'_\upsilon(u\sigma) - Y_\upsilon(ur)J'_\upsilon(u\sigma)\right]}{\sqrt{\left[(2\sigma k_a+1)J_\upsilon(u\sigma) - 2u\sigma J'_\upsilon(u\sigma)\right]^2 + \left[(2\sigma k_a+1)Y_\upsilon(u\sigma) - 2u\sigma Y'_\upsilon(u\sigma)\right]^2}}. \tag{2}$$

In the latter equation, $J_\upsilon(z)$ and $Y_\upsilon(z)$ are Bessel functions [7]; σ is the reaction radius; k_a is the reaction rate constant; r_0 and r are the interparticle distances at times 0 and t; and

$$\cos(\gamma) = \cos(\theta)\cos(\theta_0) + \sin(\theta)\sin(\theta_0)\cos(\phi-\phi_0). \tag{3}$$

In Eq. (3), θ_0 and ϕ_0 are the interparticle vector angles at the initial time, and θ and ϕ are the corresponding angles at time t, and γ is the angle between the initial and final interparticle vectors.

* Tel.: +1 281 244 6426.
E-mail address: Ianik.Plante-1@nasa.gov.

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1.2. Particular cases

For free diffusion ($k_a = 0, \sigma \to 0$), $F_{n+1/2}(u,r) \to J_{n+1/2}(ur)$, so that the integral in Eq. (1) can be evaluated directly:

$$p_{fr}(r,\theta,\phi,t|r_0,\theta_0,\phi_0) = \frac{1}{4\pi\sqrt{rr_0}}\sum_{n=0}^{\infty}(2n+1)P_n(\cos\gamma)\frac{1}{2Dt}\exp\left(-\frac{r^2+r_0^2}{4Dt}\right)I_{n+1/2}\left(\frac{rr_0}{2Dt}\right). \quad (4)$$

Using the identity [7]

$$\exp(z\cos\gamma) = \sqrt{\frac{\pi}{2z}}\sum_{n=0}^{\infty}(2n+1)P_n(\cos\gamma)I_{n+1/2}(z), \quad (5)$$

Eq. (4) can be rewritten

$$p_{fr}(r,\theta,\phi,t|r_0,\theta_0,\phi_0) = \frac{1}{(4\pi Dt)^{3/2}}\exp\left(-\frac{r^2+r_0^2-2rr_0\cos\gamma}{4Dt}\right). \quad (6)$$

This is indeed the GFDE for free diffusion.

In a previous publication [8], the integral present in Eq. (1) was calculated for $n = 0$ and $k_a \geq 0$. The result is given by

$$\int_0^{\infty} e^{-u^2Dt}uF_{1/2}(u,r)F_{1/2}(u,r_0)du = \frac{1}{\sqrt{(rr_0)}}\frac{1}{\sqrt{4\pi Dt}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]+\exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\}$$
$$+\alpha\frac{1}{\sqrt{(rr_0)}}W\left(\frac{r+r_0-2\sigma}{\sqrt{4Dt}},\alpha\sqrt{Dt}\right), \quad (7)$$

where $W(x,y) = \exp(2xy+y^2)Erfc(x+y)$, and $\alpha = (k_a\sigma+1)/(\sigma)$. Interestingly, this corresponds to the radial Green's function. For $k_a \to \infty$, note that

$$\lim_{k_a\to\infty}\int_0^{\infty} e^{-u^2Dt}uF_{1/2}(u,r)F_{1/2}(u,r_0)du = \frac{1}{\sqrt{(rr_0)}}\frac{1}{\sqrt{4\pi Dt}}\left\{\exp\left[-\frac{(r-r_0)^2}{4Dt}\right]-\exp\left[-\frac{(r+r_0-2\sigma)^2}{4Dt}\right]\right\}. \quad (8)$$

The complex integral that appears in Eq. (1) does not seem to have been evaluated in the existing literature. In this paper, the integral is calculated directly for the second term ($n = 1$) of diffusion-controlled reactions ($k_a \to \infty$). Possible strategies to evaluate this integral for other values of n are discussed.

2. Calculation of the second term for $k_a \to \infty$

In this section, the second term of the expansion given in Eq. (1), i.e. for $n = 1$, is calculated. A numerical verification of each step is performed in the accompanying Mathematica document (see supplementary data, Appendix A). At this time it was only possible to calculate the integral for $k_a \to \infty$. The integral to evaluate is

$$I = \int_0^{\infty} e^{-u^2Dt}uF_{3/2}(u,r)F_{3/2}(u,r_0)du. \quad (9)$$

Using the definition of the Bessel functions, and the limit $k_a \to \infty$, the integral in Eq. (9) can be expressed with trigonometric functions:

$$I = \int_0^{\infty} e^{-u^2Dt}u\left[2\frac{u(\sigma-r)\cos[u(r-\sigma)]+(1+r\sigma u^2)\sin[u(r-\sigma])(u(\sigma-r_0)\cos[u(r_0-\sigma)]+(1+r_0\sigma u^2)\sin[u(r_0-\sigma)])}{(rr_0)^{3/2}\pi u^3(1+u^2\sigma^2)}\right]du. \quad (10)$$

2.1. Separation of the integral into integrable terms

Using basic trigonometric identities, the integral can be rewritten as the sum of four terms:

$$p_1 = \frac{1}{\pi(rr_0)^{3/2}}\int_0^{\infty} e^{-u^2Dt}u\frac{(1+rr_0u^2)\cos[u(r-r_0)]}{u^3}du. \quad (11a)$$

$$p_2 = \frac{1}{\pi(rr_0)^{3/2}}\int_0^{\infty} e^{-u^2Dt}u\frac{(-1+u^2(rr_0-2(r+r_0)\sigma+\sigma^2)-rr_0u^4\sigma^2)\cos[u(r+r_0-2\sigma])}{u^3(1+u^2\sigma^2)}du. \quad (11b)$$

$$p_3 = \frac{1}{\pi(rr_0)^{3/2}}\int_0^{\infty} e^{-u^2Dt}u\frac{u(r-r_0)\sin[u(r-r_0)]}{u^3}du. \quad (11c)$$

$$p_4 = \frac{1}{\pi(rr_0)^{3/2}}\int_0^{\infty} e^{-u^2Dt}u\left[u\frac{(-(r+r_0-2\sigma)+u^2(-2rr_0\sigma+(r+r_0)\sigma^2))\sin[u(r+r_0-2\sigma)]}{u^3(1+u^2\sigma^2)}\right]du. \quad (11d)$$