Journal of Statistical Physics, Vol. 74, Nos. 3/4, 1994

A Comment on Early-Time Solutions of the Smoluchowski Equation

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Received December 31, 1992; final July 15, 1993

We present a simple derivation of classes of early-time solutions of the Smoluchowski equation in the presence of boundaries, simplifying and generalizing an analysis by van Kampen.

KEY WORDS: Eigenfunction expansions; Smoluchowski equation.

In a recent paper, motivated by applications to nucleation theory, van Kampen[1] has presented an approximation, valid at sufficiently early times, to the solution of a Smoluchowski equation. Specifically, he considered a one-dimensional Smoluchowski equation of the form

$$\frac{\partial p}{\partial t}=D\frac{\partial^2 p}{\partial x^2}+\frac{\partial}{\partial x}[U'(x)p] \tag{1}$$

where D is a diffusion constant and $U(x)$ is a two-body potential function. The probability density function $p(x, t\,|\,x_0)$ is the solution to this equation subject to the initial condition $p(x, 0\,|\,x_0)=\delta(x-x_0)$. The essence of van Kampen's paper is contained in a derivation of an approximation to $p(x, t\,|\,x_0)$ valid at sufficiently early times. In this note we present a simpler version of the proof, later extending it to the more general equation

$$\frac{\partial p}{\partial t}=\frac{\partial}{\partial x}\left[D(x)\frac{\partial p}{\partial x}\right]-\frac{\partial}{\partial x}[v(x)p] \tag{2}$$

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0022-4715/94/0200-0947$07.00/0

Our derivation is based on the asymptotic properties of eigenfunctions and eigenvalues of Sturm–Liouville equations.[2]

Let us first reproduce the van Kampen result and afterward discuss the extension to Eq. (2). We assume that the interval over which the diffusion process occurs is $(0, L)$, where at least one of the endpoints is a trapping point. A solution to Eq. (1) is equivalent to solving a Schrödinger equation, as may be seen by separating variables and writing

$$p(x, t \mid x_0) = e^{-\lambda t} e^{-U(x)/2D} \varphi(x) \tag{3}$$

We infer from this that $\varphi(x)$ can be chosen as the normalized solution to the eigenvalue equation

$$D\varphi''(x) + [\lambda - w(x)]\, \varphi(x) = 0 \tag{4}$$

where $w(x)$ is found in terms of the potential as

$$w(x) = \frac{[U'(x)]^2}{4D} - \frac{U''(x)}{2} \tag{5}$$

A formal expansion for $p(x, t \mid x_0)$ in terms of eigenfunctions is then

$$p(x, t \mid x_0) = e^{-[U(x) - U(x_0)]/2D} \sum_{n=0}^{\infty} e^{-\lambda_n t} \varphi_n(x_0)\, \varphi_n(x) \tag{6}$$

in which the λ's are arranged in ascending order. The early-time behavior of $p(x, t \mid x_0)$ will be influenced only by the behavior of the λ_n and $\varphi_n(x)$ in the limit of large n. The proof in ref. 2 is trivially extended to allow for the analysis of any homogeneous boundary condition, since the idea is that when $\lambda \gg 1$ in Eq. (4) the term $w(x)$ is negligible in comparison with λ. Van Kampen considered the case in which $x = 0$ is a reflecting point and $x = L$ is a trap, allowing us to write

$$\begin{aligned} \lambda_n &= \frac{\pi^2 D}{L^2}\left(n + \frac{1}{2}\right)^2 + O(1) \\ \varphi_n(x) &= \left(\frac{2}{L}\right)^{1/2} \cos\left[\frac{\pi(n + 1/2)x}{L}\right] + O\left(\frac{1}{\sqrt{\lambda_n}}\right) \end{aligned} \tag{7}$$

in the large-n limit. Although these approximations are independent of the function $w(x)$, corrections to these asymptotic results will depend on this function.

On inserting the lowest order terms in Eq. (7) into the expansion in Eq. (6) and, consistent with this replacement, changing the sum to an integral, we find

$$p(x, t \mid x_0) \sim \frac{1}{(4\pi Dt)^{1/2}} \exp\left[-\frac{U(x)-U(x_0)}{2D} - \frac{(x-x_0)^2}{4Dt}\right] \tag{8}$$

at early times. The probability density for the first passage time to the trap at $x = L$ can be calculated from

$$f(t \mid x_0) = -D \left.\frac{\partial p}{\partial x}\right|_{x=L} \sim \frac{L-x_0}{2(4\pi Dt^3)^{1/2}} \exp\left[-\frac{U(L)-U(x_0)}{2D} - \frac{(L-x_0)^2}{4Dt}\right] \tag{9}$$

where we have neglected a term proportional to $U'(L)/(2D)$ in comparison to $(L-x_0)^2/(4Dt)$ because of the assumption of early times. The expression in this last equation coincides with the result found by van Kampen.

Let us next consider the modification of this theory required to take into account a nonconstant diffusion constant as in Eq. (2). In this case a separation of variables of the solution to Eq. (2) as $p(x, t \mid x_0) = X(x) \exp(-\lambda t)$ leads to an eigenvalue equation for $X(x)$ which may be written as

$$[D(x)\, X']' - [v(x) X]' + \lambda X = 0 \tag{10}$$

This does not have the form of a Sturm–Liouville equation, but can be transformed into one for a function $Y(x)$ which is defined in terms of $X(x)$ by

$$X(x) = \exp\left(\int^x \frac{v(y)}{D(y)}\, dy\right) Y(x) = A(x)\, Y(x) \tag{11}$$

where $A(x)$ denotes the exponential term that is shown. The function $Y(x)$ is readily shown to satisfy the Sturm–Liouville equation

$$[A(x)\, D(x)\, Y'(x)]' + \lambda A(x)\, Y(x) = 0 \tag{12}$$

For convenience we define a function $g(x) = A(x)\, D(x)$, which is seen to be nonnegative. In the following exposition we will assume that it is, in fact, a strictly positive function.

For the sake of concreteness we will suppose that $x = 0$ and $x = L$ are trapping points and that $D(x)$ and $v(x)$ are continuous in the interval $(0, L)$. The presence of these trapping points requires that Eq. (10) be solved subject to the boundary conditions

$$X(0) = X(L) = 0 \tag{13}$$

or $Y(0) = Y(L) = 0$. Our consideration of this particular set of boundary conditions represents no real restriction, since similar results can be derived for any linear homogeneous boundary conditions which generate an eigenvalue problem. The motivation of the following proof lies in the observation that the behavior of the solution to Eq. (2) at early times is mainly determined by the large eigenvalues together with their associated eigenfunctions.

One can estimate these functions using theoretical results discussed in ref. 2. A first step in their argument requires the transformation of Eq. (5) to an equivalent equation having the form

$$\frac{d^2\Gamma}{d\xi^2} + [\lambda - r(\xi)]\Gamma = 0 \tag{14}$$

where ξ is a new spatial coordinate and $\Gamma(\xi)$ a new dependent variable. These are defined in terms of $g(x)$ and $A(x)$ by the relations

$$\xi = \int_0^x \left(\frac{A(z)}{g(z)}\right)^{1/2} dz, \qquad \Gamma(\xi) = [A(\xi)\, g(\xi)]^{1/4}\, Y(\xi) \tag{15}$$

and the function $r(\xi)$ that appears in Eq. (14) has the form

$$r(\xi) = \frac{\{[A(\xi)\, g(\xi)]^{1/4}\}''}{[A(\xi)\, g(\xi)]^{1/4}} \tag{16}$$

This function is not really needed in a derivation of the lowest-order approximation, but is required to calculate corrections to that approximation. The maximum value of the coordinate ξ will be denoted by ξ_m, which is found from Eq. (15) by setting $x = L$. Large-n approximations to λ and Γ are found, as before, by neglecting the term $r(\xi)$ in Eq. (14). The resulting set of eigenvalues and normalized eigenfunctions that satisfy the boundary conditions take the form

$$\begin{aligned} \lambda_n &= n^2 \frac{\pi^2}{\xi_m^2} + O(1) = \lambda_n^{(0)} + O(1) \\ \varphi_n(\xi) &= \left(\frac{2}{\xi_m}\right)^{1/2} \sin\left(\frac{n\pi\xi}{\xi_m}\right) + O\left(\frac{1}{\sqrt{\lambda_n}}\right) = \varphi_n^{(0)}(\xi) + O\left(\frac{1}{\sqrt{\lambda_n}}\right) \end{aligned} \tag{17}$$

Correction terms can be generated from the integral equation which forms the starting point of the analysis given in ref. 2. In the early-time regime we may approximate to the complete solution of Eq. (2) by the series

$$p(\xi, t \mid \xi_0) \sim \frac{2}{\xi_m} \sum_{n=1}^{\infty} \exp\left(-n^2 \frac{\pi^2}{\xi_m^2} t\right) \sin\left(\frac{n\pi\xi_0}{\xi_m}\right) \sin\left(\frac{n\pi\xi}{\xi_m}\right) \tag{18}$$

where x and x_0 have been replaced by ξ and ξ_0 as indicated by the transformation in Eq. (15).

The expansion in Eq. (18) can be identified with the solution to an ideal field-free diffusion equation (that is, one having a constant diffusion coefficient). The early-time approximation to $p(\xi, t \mid \xi_0)$ is again found by replacing the sum over n in Eq. (18) by an integral, which gives

$$p(\xi, t \mid \xi_0) = \frac{1}{(4\pi t)^{1/2}} \left(e^{-(\xi - \xi_0)^2/4t} - e^{-(\xi + \xi_0)^2/4t}\right) \tag{19}$$

The probability density function for the first passage time to the trap at $\xi = \xi_m$ is defined in terms of the flux through that point as in Eq. (9). The result of the calculation is, to lowest order,

$$f(t \mid \xi_0) = \frac{\xi_m - \xi_0}{(4\pi t^3)^{1/2}} \exp\left[-\frac{(\xi_m - \xi_0)^2}{4t}\right] \tag{20}$$

Similar expressions are easily derived for other common boundary conditions (e.g., reflecting or radiation). The only effect of changing the boundary conditions is to change the form of $\varphi_n^{(0)}(\xi)$ to some other form of sinusoid, as exemplified by Eqs. (8) and (9).

Corrections to the lowest-order approximations can be found by iterating the integral equations given in ref. 2, but this seems not to have been implemented, possibly because the subsequent calculations become quite complicated. However, there is some motivation to carrying out such an analysis because it might provide information about the range of time over which an expansion such as that in Eq. (18) might be expected to be accurate. It is presumably possible to extend our analysis to Smoluchowski equations in higher dimensions, but the results would necessarily be restricted to shapes for which the eigenfunctions are of a reasonably simple form.

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Communicated by J. L. Lebowitz