行政院國家科學委員會專題研究計畫成果報告

透過傳輸矩陣對擴散過程進行時矩研究
Time Moment Analysis of Diffusion Processes via Transmission Matrix

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一、中文摘要

本研究利用傳輸矩陣在各種不同的條件之下計算擴散流速並與反向擴散方程式所得結果比較，再利用傳輸矩陣的行列式為1的特殊性質進而求出矩陣各元素對s的泰勒級數展開。此級數可以應用在各種擴散問題的時矩分析。

關鍵詞：傳輸矩陣，泰勒級數，時矩分析

Abstract

Combination of solving the flux by transmission matrix T(s) and backward diffusion equation, respectively, with the help of det[T(s)] = 1 enables us to develop the elements of transmission matrix in Taylor series in s. This series is useful in evaluation of the time moments of residence time, first passage time and time lag.

Keywords: transmission matrix, Taylor series, time moments analysis

二、緣由與目的

Diffusion is a ubiquitous process in the physical world. It is of great theoretical importance with a multiplicity of applications in such diverse fields as chemical reaction,[1,2] electrochemistry,[3] colloidal science,[4] solid state physics,[5] semiconductor-device fabrication and operations,[6] physical ceramics,[7] biophysics,[8] drug delivery,[9] and environmental science.[10] One way to characterize a diffusion system in which a particle initially located at $x = x_0$, within a finite domain is by means of the probability density of the time required for the particle escaping from this domain for the first time, i.e., the distribution of the first passage time.[11,12] Complete information of the probability distribution can be obtained only for some particular cases. Thus, one is usually forced to resort to the time moments. Of the most important among them is the first moment, i.e., the mean first passage time. The latter is often related to the reciprocal of a (first-order) rate constant if a chemical reaction is modeled by diffusion over a potential.[12] In order to have more information about the distribution, higher moments are required. For example, without the second moment the dispersion of the distribution can not be estimated.[13]

For a diffusion with initial condition of Dirac delta-function type, the first and higher moments are obtainable from solving the backward diffusion equation with appropriate boundary conditions.[12] Another approach proposed by Deutch[14] is the use of repeated integration over the original diffusion equation. He obtained the mean first passage time for a heterogeneous domain with initial distributions of either Dirac delta-function type or of saturated equilibrium. However, the results for the second moment is not given.

Now turn our attention to membrane diffusion transport. Of them the absorptive permeation is the commonest practice. The experiment is set up under a zero initial activity within the whole membrane, and a constant and a zero activity at the upstream and downstream faces, respectively. Permeability, P, and time lag, t_L, are crucial parameters to estimate the total release Q(t) as a function of time through the asymptotic linear equation $Q(t) = P(t - t_L)$.[15,16] t_L can be expressed by $t_L = \int_0^\infty t \frac{\frac{d}{dt}J_d(t)}{J_{d,ss}} dt$,[17] with $J_d(t)$ the time dependent flux at the downstream face and $J_{d,ss}$ the steady-state flux. Mathematically t_L is the first moment of the $\frac{\frac{d}{dt}J_d(t)}{J_{d,ss}}$ distribution. Various mathematical techniques have been employed to formulate the first moment, i.e., the time lag, for diffusion with position-dependent partition coefficient and diffusivity. However, up to date, we have not found the formulation for the higher moments.

三、結果與討論

（一）結果

Extended calculation to higher terms enables us to generalize the Taylor expansion of the transmission matrix, T(s), to

$$T(s) = \begin{bmatrix} \sum_{n=0}^{\infty} \alpha_n s^n & -\sum_{n=0}^{\infty} \beta_n s^n \\ -\sum_{n=1}^{\infty} \gamma_n s^n & \sum_{n=0}^{\infty} \delta_n s^n \end{bmatrix} \quad (1)$$

with α_n, β_n, γ_n, δ_n, following the iterative schemes:

$$\tilde{\alpha}_n(x) = \int_x^h K \int_y^h \frac{1}{DK} \tilde{\alpha}_{n-1}(z) dz dy,$$

$$\tilde{\alpha}_0(x) = 1, \alpha_n = \tilde{\alpha}_n(0), n \ge 1 \quad (2)$$

$$\tilde{\beta}_n(x) = \int_x^h \frac{1}{DK} \int_y^h K \tilde{\beta}_{n-1}(z) dz dy$$

$$\tilde{\beta}_0(x) = \int_x^h \frac{1}{DK} dy, \; \beta_n = \tilde{\beta}_n(0), n \geq 1 \quad (3)$$

$$\tilde{\gamma}_n(x) = \int_x^h K \int_y^h \frac{1}{DK} \tilde{\gamma}_{n-1}(z) dz dy$$

$$\tilde{\gamma}_1(x) = \int_x^h K dy, \; \gamma_n = \tilde{\gamma}_n(0), n \geq 2 \quad (4)$$

$$\tilde{\delta}_n(x) = \int_x^h \frac{1}{DK} \int_y^h K \tilde{\delta}_{n-1}(z) dz dy$$

$$\tilde{\delta}_0(x) = 1, \; \delta_n = \tilde{\delta}_n(0), n \geq 1 \quad (5)$$

（二）討論

Recently Zwanzig[18] has elucidated the effect of potential roughness on the effective diffusivity of a particle under the influence of the potential $U_0(x) + U_1(x)$, where $U_0(x)$ is the spatially varying part and $U_1(x)$ is the fluctuating part. The latter is responsible for the potential roughness. It is found that the effective diffusivity D^* is related to the original diffusivity D by

$$D^* = \frac{D}{< \exp[(U_1(x)/kT)] >< \exp[-(U_1(x)/kT)] >} \quad (6)$$

where k is the Boltzmann constant and < > denotes the spatial average. As a first example, if the roughness is simply $U_1(x) = \varepsilon \cos(qx)$, then[18]

$$D^* = \frac{D}{[I_0(\varepsilon / kT)]^2} \quad (7)$$

where I_0 is the modified Bessel function of the zeroth kind and ε / kT is its argument. If the amplitude of the roughness is a Gaussian distribution, with a probability proportional to $\exp(-U^2/2\varepsilon^2)$ in which $\varepsilon^2 = < U_1^2 >$, then

$$D^* = D\exp[-(\varepsilon / kT)^2] \quad (8)$$

In the above examples, it is interesting to note that the parameters α_n, β_n, γ_n, and δ_n are modified by being multiplied by a factor $[I_0(\varepsilon / kT)]^{2n}$ for the first example and by $\{\exp[-(\varepsilon / kT)^2]\}^n$ for the second. Since both $I_0(\varepsilon / kT) > 1$ and $\exp(-\varepsilon / kT) < 1$ for $\varepsilon > 0$, we assert that the effect of potential roughness in this two cases is to increase the magnitude of and hence the time moments of orders ≥ 1.

In conclusion, we have given an alternative approach to the time moment analysis for diffusion problems.

（三）計畫結果自評

As compared to the traditional iterative Green function,[11] solving the backward diffusion equation[11,12,18] and repeated interation,[14] our method gains some advantage in the sense that it can be accomplished in a simple, straightforward way, involving only algebraic operation.

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