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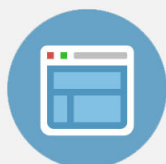J. Chem. Phys. 111, 7272 (1999); 10.1063/1.480052

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Time moment analysis of first passage time, time lag and residence time problems via Taylor expansion of transmission matrix

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Taylor expansion (with respect to the Laplace variable, s) of the transmission matrix, $T(s)$, has been developed for the diffusion transport with position-dependent diffusivity, $D(x)$ and partition coefficient, $K(x)$. First, we find the relation between the expansion coefficients of the matrix elements and the moments of the first passage times by connecting them to $\hat{J}(s)$, the Laplace transform of the escaping flux, $J(t)$. The moments can be formulated by repeated integrals of $K(x)$ and $[D(x)K(x)]^{-1}$ from solving the backward diffusion equation subject to appropriate initial and boundary conditions. In this way, Taylor expansion coefficients of $T_{11}(s)$, $T_{21}(s)$, and $T_{22}(s)$ are expressed in terms of the repeated integrals. Further application of the identity $\det[T(s)]=1$ leads to the Taylor expansion $T_{12}(s)$. With the knowledge of the Taylor expansion of $T(s)$, the formulation of the time moments for diffusion problems with position dependent $D(x)$ and $K(x)$ subject to various initial and boundary conditions is then just a simple, algebraic manipulation. Application of this new method is given to the membrane permeation transport and mean residence time problem. © *2000 American Institute of Physics.* [S0021-9606(00)50810-1]

INTRODUCTION

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 operation,[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 cannot 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 $t_L=\int_0^\infty t[(d/dt)J_d(t)/J_{d,ss}]dt$,[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 $(d/dt)J_d(t)/J_{d,ss}$ 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. Recently, the matrix theoretical analysis in the Laplace domain on the diffusion transport problem has been put forth.[17–22] This analysis allows us to formulate the time lag and mean first passage time in terms of the derivative (with respect to the Laplace variable, s) of the elements of the transmission matrix.[17] We will extend the analysis to the treatment on the higher moments for first passage time and membrane transport problems as well. We shall see that Taylor expansion of the transmission matrix, $T(s)$, plays an important role in the analysis. We found that the coefficients of expansion appear to be in the forms of repeated integrals of $K(x)$ and $[D(x)K(x)]^{-1}$. With this as an instrument, the moment analysis for the afore-mentioned diffusion problems can be reduced to a simple, algebraic manipulation.

TRANSMISSION MATRIX FOR DIFFUSION TRANSPORT

Traditionally the membrane permeation transport, due to whose underlying process is diffusion, described by the Fick's diffusion equation, or Smoluchowski equation if the

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membrane is inhomogeneous and/or is subject to external force. Alternative to this description is through the vehicle of transmission matrix.[17–22] In this approach the membrane permeation system is treated as an electrical network system with two input ports and two output ports. The penetrant activity and flux at the upstream face are then assigned to the input ports as an ordered pair, and those at the downstream face to output ports as another ordered pair. The transmission matrix which links two ordered pairs appears to be characteristic to the properties of the membrane, including its thickness, the diffusivity and partition coefficient of the penetrant in the membrane. The magnitude of the last two entities may be position dependent.

For further uses we shall summarize for diffusion transport three previously derived equations corresponding to different initial conditions.[17,19–22] A one-dimensional linear diffusion transport with zero initial activity within the whole domain, $0 < x < h$, and time-dependent conditions for both boundaries can be described in the Laplace domain in terms of a transmission matrix, $T(s)$, by[17,19]

$$\begin{bmatrix} \hat{a}_d(s) \\ \hat{J}_d(s) \end{bmatrix} = T(s) \begin{bmatrix} \hat{a}_u(s) \\ \hat{J}_u(s) \end{bmatrix} = \begin{bmatrix} T_{11}(s) & T_{12}(s) \\ T_{21}(s) & T_{22}(s) \end{bmatrix} \begin{bmatrix} \hat{a}_u(s) \\ \hat{J}_u(s) \end{bmatrix}, \quad (1)$$

where $\hat{a}_u(s)$ and $\hat{J}_u(s)$ are the Laplace transform of the penetrant activity, $a_u(t)$, and flux $J_u(t)$, respectively, at the face $x = 0$, or at upstream face. Their counterparts at the face $x = h$, or at downstream face, are $\hat{a}_d(s)$ and $\hat{J}_d(s)$, respectively. For convenience, the face at $x = 0$ and the upstream face are used interchangeably, so are the face at $x = h$ and downstream face.

If the initial condition is of Dirac delta-function type located at x_0, such that $0 < x_0 < h$, the transport equation is given by[17]

$$\begin{bmatrix} \hat{a}_d(s) \\ \hat{J}_d(s) \end{bmatrix} = T(s) \begin{bmatrix} \hat{a}_u(s) \\ \hat{J}_u(s) \end{bmatrix} + T^*(s) \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad (2)$$

where $T^*(s)$ is the transmission matrix for the subdomain from the face x_0 to the face h.

If, on the other hand, the initial condition is of saturated equilibrium with a constant activity a_0, the transport equation then becomes[22]

$$\begin{bmatrix} \hat{a}_d(s) - \dfrac{a_0}{s} \\ \hat{J}_d(s) \end{bmatrix} = \begin{bmatrix} T_{11}(s) & T_{12}(s) \\ T_{21}(s) & T_{22}(s) \end{bmatrix} \begin{bmatrix} \hat{a}_u(s) - \dfrac{a_0}{s} \\ \hat{J}_u(s) \end{bmatrix}. \quad (3)$$

For a simple, homogeneous diffusion, which has constant D and K, $T(s)$ is explicitly expressed by[17,19]

$$T(s) = \begin{bmatrix} \cosh(qh) & -\dfrac{\sinh(qh)}{DqK} \\ -DqK\sinh(qh) & \cosh(qh) \end{bmatrix}, \quad (4)$$

where $q = \sqrt{s/D}$ and h is the thickness of the domain. For diffusion through a heterogeneous domain $T(s)$ takes on the form[17]

$$T(s) = T^{(n)}(s) T^{(n-1)}(s) \cdots T^{(1)}(s). \quad (5)$$

This is a consequence of the fact that the heterogeneous domain is look upon as an assembly of many (say n) thin subdomains, with the first connected to the upstream face at $x = 0$, followed by the second, etc., up to the last (nth) which adjoins the downstream face at $x = h$. Here $T^{(i)}(s)$, the transmission matrix for the ith subdomain, takes the same form of Eq. (4), except that D, K, q, h, are replaced, respectively, by D_i, K_i, q_i, h_i, the corresponding entities for the ith subdomain.

TAYLOR EXPANSION OF TRANSMISSION MATRIX

The coefficients of the s^n terms ($n = 0,1,2,...$) of $T_{11}(s)$ and $T_{22}(s)$ will be derived by the use of the backward diffusion equation[11,12,23]

$$\frac{1}{K} \frac{d}{dx} DK \frac{d}{dx} \mu_n = -n\mu_{n-1},$$

$$n = 1,2,3,..., \quad \text{with} \quad \mu_0 = 1, \quad (6)$$

where μ_{n-1} and μ_n are the $(n-1)$th and nth moments, respectively. We consider a particle initially located at a reflecting face $x = 0$, and the other boundary at $x = h$, from which the particle escapes, is absorbing. The moments are solved in Eqs. (A1)–(A3) in the Appendix. The escaping probability as a function of time is represented by $J_d(t)$,[17] whose Laplace transform is related by

$$\hat{J}_d(s) = \frac{1}{T_{11}(s)}, \quad (7)$$

which is obtained by a substitution of $\hat{a}_d(s) = 0$, $\hat{J}_u(s) = 0$, and $T^*(s) = T(s)$ into Eq. (2). To proceed, we expand $T_{11}(s)$ and $\hat{J}_d(s)$ in terms of Taylor series about $s = 0$

$$T_{11}(s) = T_{11}(0) + \frac{s}{1} \lim_{s \to 0} \frac{dT_{11}(s)}{ds} + \frac{s^2}{2!} \lim_{s \to 0} \frac{d^2 T_{11}(s)}{ds^2} + \cdots$$

$$= \alpha_0 + \alpha_1 s + \alpha_2 s^2 + \cdots, \quad (8)$$

$$\hat{J}_d(s) = \hat{J}_d(0) + \frac{s}{1!} \lim_{s \to 0} \frac{d\hat{J}_d(s)}{ds} + \frac{s^2}{2!} \lim_{s \to 0} \frac{d^2 \hat{J}_d(s)}{ds^2} + \cdots$$

$$= \mu_0^d - \frac{s}{1!} \mu_1^d + \frac{s^2}{2!} \mu_2^d \cdots. \quad (9)$$

The definition of α_n, $n = 0,1,2,3,...$, is self-explanatory as seen from Eq. (8). The use of the superscript d is to specify that the particle exits from the downstream face. The equality in Eq. (9) is due to the fact that

$$\mu_n^d = \int_0^\infty t^n J_d(t) dt = (-1)^n \lim_{s \to 0} \frac{d^n \hat{J}_d(s)}{ds^n}, \quad (10)$$

since $J_d(t)$ is look upon as the escaping probability density. Inserting Eqs. (8) and (9) into Eq. (7), we obtain the Taylor expansion of $T_{11}(s)$ in terms of repeated integrals over $K(x)$ and $[D(x)K(x)]^{-1}$ as

$$T_{11}(s) = \alpha_0 + \alpha_1 s + \alpha_2 s^2 + \cdots, \quad (11)$$

with

$$\alpha_0 = \mu_0^d = 1, \tag{12}$$

$$\alpha_1 = \mu_1^d = \int_0^h K \int_{x_1}^h \frac{1}{DK} dx_1' \, dx_1, \tag{13}$$

$$\alpha_2 = \frac{1}{2!} (2(\mu_1^d)^2 - \mu_2^d)$$

$$= \int_0^h K \int_{x_2}^h \frac{1}{DK} \int_{x_2'}^h K \int_{x_1}^h \frac{1}{DK} dx_1' \, dx_1 \, dx_2' \, dx_2, \tag{14}$$

where Eqs. (A1)–(A3) in the Appendix with $x_0 = 0$ have been used.

If a particle is initially at a reflecting face at $x = h$, and the exit $x = 0$ is absorbing, also from Eq. (2) we have

$$\hat{J}_u(s) = -\frac{1}{T_{22}(s)}, \tag{15}$$

which is given by substituting $T^*(s) = I$ and $\hat{J}_d(s) = 0$, $\hat{a}_u(s) = 0$. Exactly following the procedure for obtaining the Taylor expansion of $T_{11}(s)$, we arrive at the Taylor expansion $T_{22}(s)$ as

$$T_{22}(s) = \delta_0 + \delta_1 s + \delta_2 s^2 + \cdots, \tag{16}$$

with

$$\delta_0 = \mu_0^\mu = 1, \tag{17}$$

$$\delta_1 = \mu_1^u = \int_0^h \frac{1}{DK} \int_{x_1}^h K \, dx_1' \, dx_1, \tag{18}$$

$$\delta_2 = \frac{1}{2!} (2(\mu_1^u)^2 - \mu_2^u)$$

$$= \int_0^h \frac{1}{DK} \int_{x_2}^h K \int_{x_2'}^h \frac{1}{DK} \int_{x_1}^h K \, dx_1' \, dx_1 \, dx_2' \, dx_2. \tag{19}$$

The definition of $\mu_i^u (i = 0,1,2)$ has been given in the appendix and their integral expression in Eqs. (A4) and (A5) have been used.

With respect to the Taylor series of $T_{21}(s)$, we consider an initial activity of saturated equilibrium at a constant level a_0 throughout the whole diffusion domain. The face at $x = 0$ is reflecting, while the exit face at $x = h$ is absorbing. The Laplace transform of $J_d^e(t)$ becomes

$$\hat{J}_d^e(s) = -\frac{T_{21}(s)}{T_{11}(s)} \frac{a_0}{s}, \tag{20}$$

which is given from Eq. (3) by substitution of $\hat{a}_d(s) = 0$ and $\hat{J}_u(s) = 0$.[22] The superscript e in Eq. (20) is to specify that the initial condition is of saturated equilibrium distribution. The Taylor expansion of $\hat{J}_d^e(s)$ for saturated equilibrium distribution can be expressed by

$$\hat{J}_d^e(s) = \left(\mu_0^e - \mu_1^e s + \frac{\mu_2^e}{2!} s^2 - \cdots \right) \int_0^h a_0 K(x_0) dx_0 \tag{21}$$

whose expansion coefficients $\mu_i^e (i = 0,1,2)$ are taken from Eqs. (A7)–(A9). Putting Eqs. (11) and (21) into Eq. (20), we obtain the Taylor expansion of $T_{21}(s)$ as

$$T_{21}(s) = -\gamma_0 - \gamma_1 s - \gamma_2 s^2 - \cdots, \tag{22}$$

with

$$\gamma_0 = 0, \tag{23}$$

$$\gamma_1 = \mu_0^e \int_0^h K \, dx_1 = \int_0^h K \, dx_1, \tag{24}$$

$$\gamma_2 = (\alpha_1 \mu_0^e - \mu_1^e) \int_0^h K \, dx$$

$$= \int_0^h K \int_{x_2}^h \frac{1}{DK} \int_{x_2'}^h K \, dx_1 \, dx_2' \, dx_2, \tag{25}$$

where Eqs. (13), (A7), and (A8) have been used. The negative sign before $\gamma_i (i = 0,1,2,...)$ is artificially put on to render all γ_i positive.

As far as the Taylor expansion of $T_{12}(s)$ is concerned, the identity[19]

$$T_{11}(s) T_{22}(s) - T_{12}(s) T_{21}(s) = 1, \tag{26}$$

is employed. Substitution of Eqs. (11), (16), and (22), respectively for $T_{11}(s)$, $T_{22}(s)$, and $T_{21}(s)$ with their coefficients expressed by repeated integrals into Eq. (26), we obtain after some algebra the Taylor expansion of $T_{12}(s)$ as

$$T_{12}(s) = -\beta_0 - \beta_1 s - \beta_2 s^2 - \cdots, \tag{27}$$

with

$$\beta_0 = \int_0^h \frac{1}{DK} dx, \tag{28}$$

$$\beta_1 = \int_0^h \frac{1}{DK} \int_x^h K \int_{x_1}^h \frac{1}{DK} dx_1' \, dx_1 \, dx, \tag{29}$$

$$\beta_2 = \int_0^h \frac{1}{DK} \int_x^h K \int_{x_2}^h \frac{1}{DK} \int_{x_2'}^h K \int_{x_1}^h \frac{1}{DK} dx_1' \, dx_1 \, dx_2' \, dx_2 \, dx. \tag{30}$$

Again the negative sign before $\beta_i (i = 0,1,2,...)$ is to render β_i positive.

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

$$T(s) = \begin{bmatrix} \sum\limits_{n=0}^{\infty} \alpha_n s^n & -\sum\limits_{n=0}^{\infty} \beta_n s^n \\ -\sum\limits_{n=1}^{\infty} \gamma_n s^n & \sum\limits_{n=0}^{\infty} \delta_n s^n \end{bmatrix}, \tag{31}$$

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

$$\tilde{\alpha}_0(x) = 1, \quad \tilde{\alpha}_n(x) = \int_x^h K \int_y^h \frac{1}{DK} \tilde{\alpha}_{n-1}(z) dz \, dy,$$

$$\alpha_n = \tilde{\alpha}_n(0), \quad n \geq 1, \tag{32}$$

$$\tilde{\beta}_0(x) = \int_x^h \frac{1}{DK} dy, \quad \tilde{\beta}_n(x) = \int_x^h \frac{1}{DK} \int_y^h K \tilde{\beta}_{n-1}(z) dz\, dy,$$

$$\beta_n = \tilde{\beta}_n(0), \quad n \geq 1, \tag{33}$$

$$\tilde{\gamma}_1(x) = \int_x^h K\, dy, \quad \tilde{\gamma}_n(x) = \int_x^h K \int_y^h \frac{1}{DK} \tilde{\gamma}_{n-1}(z) dz\, dy,$$

$$\gamma_n = \tilde{\gamma}_n(0), \quad n \geq 2, \tag{34}$$

$$\tilde{\delta}_0(x) = 1, \quad \tilde{\delta}_n(x) = \int_x^h \frac{1}{DK} \int_y^h K \tilde{\delta}_{n-1}(z) dz\, dy,$$

$$\delta_n = \tilde{\delta}_n(0), \quad n \geq 1. \tag{35}$$

It is interesting to note that if the integrands K and $1/DK$ are exchanged in α_n, δ_n is obtained, and vice versa; if they are exchanged in β_n then we obtain γ_{n+1}, and vice versa.

APPLICATION

Equation (31) with coefficients expressed by Eqs. (32)–(35) is the principal result of our derivation. It will be applied to the time moment analysis of the membrane permeation transport and the residence time problem. But before doing this, the classical problem of first passage time for a particle initially located at a point x_0 within a finite diffusion domain will be worked out. We consider quite a general case that both the boundaries at $x=0$ and at $x=h$ are partially absorbing with radiative constant κ_u and κ_d, respectively. Substituting $\hat{J}_u(s) = \kappa_u \hat{a}_u(s)$ and $\hat{J}_d(s) = \kappa_d \hat{a}_d(s)$ into Eq. (2), one obtains

$$\hat{J}_u(s) = \kappa_u \frac{T_{22}^*(s) - \kappa_d T_{12}^*(s)}{(\kappa_d T_{11}(s) - T_{21}(s)) + \kappa_u(\kappa_d T_{12}(s) - T_{22}(s))}, \tag{36}$$

$$\hat{J}_d(s) = \kappa_d \frac{T_{11}(s)T_{22}^*(s) - T_{21}(s)T_{12}^*(s) + \kappa_u(T_{12}(s)T_{22}^*(s) - T_{22}(s)T_{12}^*(s))}{(\kappa_d T_{11}(s) - T_{21}(s)) + \kappa_u(\kappa_d T_{12}(s) - T_{22}(s))}. \tag{37}$$

$T_{ij}^*(s)$ in Eqs. (36) and (37) is the matrix element of $T^*(s)$, which is the transmission matrix for the subdomain from $x=x_0$ to $x=h$. The coefficients of $T_{ij}^*(s)$ are identical to those of $T_{ij}(s)$, except that 0 for the lower limit of the last integration in Eqs. (32)–(35) is replaced by x_0, for example, $\alpha_2^* = \int_{x_0}^h K \int_{x_2}^h (1/DK) \int_{x_2'}^h K \int_{x_1}^h (1/DK) dx_1' dx_1 dx_2' dx_2$ and $\gamma_2^* = \int_{x_0}^h K \int_{x_2}^h (1/DK) \int_{x_2'}^h K dx_1 dx_2' dx_2$.

To proceed, the Taylor expansion of $\hat{J}_d(s) - \hat{J}_u(s)$ is calculated by Eqs. (36) and (37) to be

$$\hat{J}_d(s) - \hat{J}_u(s) = \frac{A_0}{B_0} + \frac{A_1 - B_1}{B_0} s$$
$$+ \frac{A_2 B_0 - B_0 B_2 - A_1 B_1 + B_1^2}{B_0^2} s^2 + \cdots, \tag{38}$$

where

$$A_0 = B_0 = \kappa_d - \kappa_u - \kappa_u \kappa_d \beta_0, \tag{39}$$

$$A_1 = -\kappa_u \delta_1^* + \kappa_d(\alpha_1 + \delta_1^* - \gamma_1 \beta_0^*)$$
$$- \kappa_u \kappa_d(\beta_1 + \beta_0 \delta_1^* - \delta_1 \beta_0^*), \tag{40}$$

$$A_2 = -\kappa_u \delta_2^* + \kappa_d(\alpha_2 + \delta_2^* + \alpha_1 \delta_1^* - \gamma_1 \beta_1^* - \gamma_2 \beta_0^*)$$
$$- \kappa_u \kappa_d(\beta_0 \delta_2^* + \beta_1 \delta_1^* - \delta_1 \beta_1^* + \beta_2 - \delta_2 \beta_0^*), \tag{41}$$

$$B_1 = \kappa_d \alpha_1 - \kappa_u \delta_1 - \kappa_u \kappa_d \beta_1 + \gamma_1, \tag{42}$$

$$B_2 = \kappa_d \alpha_2 - \kappa_u \delta_2 - \kappa_u \kappa_d \beta_2 + \gamma_2. \tag{43}$$

Since the moments correspond to the expansion coefficients in Eq. (38), it readily follows that

$$\mu_0 = 1, \tag{44}$$

$$\mu_1 = \frac{B_1 - A_1}{B_0}, \tag{45}$$

$$\mu_2 = 2 \frac{A_2 B_0 - B_0 B_2 - A_1 B_1 + B_1^2}{B_0^2}. \tag{46}$$

In the case that the face $x=0$ is radiative, and the face $x=h$ is reflecting, i.e., $\kappa_d = 0$, we have from Eq. (45) the first moment

$$\mu_1 = \lim_{\kappa_d \to 0} \frac{B_1 - A_1}{B_0}$$

$$= \delta_1 - \delta_1^* - \frac{\gamma_1}{\kappa_u}$$

$$= \int_0^{x_0} \frac{1}{DK} \int_x^h K\, dy\, dx - \frac{\int_0^h K\, dx}{\kappa_u}, \tag{47}$$

and from Eq. (46) the second moment

$$\mu_2 = \lim_{\kappa_d \to 0} 2 \frac{A_2 B_0 - B_0 B_2 - A_1 B_1 + B_1^2}{B_0^2} = 2 \frac{\kappa_u(-\kappa_u \delta_2 + \gamma_2 + \kappa_u \delta_2^*) + (\gamma_1 - \kappa_u \delta_1)(\gamma_1 + \kappa_u \delta_1^* - \kappa_u \delta_1)}{\kappa_u^2}, \tag{48}$$

whose explicit expression in terms of integrals is a little bit complicated and will not be given here. Equation (47) after some algebraic manipulation is in agreement with the result [Eq. (8) in Ref. 14] derived by Deutch by means of the method of repeated integration.

Although our method provides another instrument in dealing with the classical problem of first passage time. We would not like to claim that it is superior over the established methods such as solving backward diffusion equation or repeated integration on the original diffusion equation. However, up to date, we found the corresponding backward diffusion equation for the time moments of membrane permeation and for the residence time problem is of not avail, and the method of repeated integration appears to be applicable with the limitation to first moment (time lag) analysis. In what follows we will demonstrate that the time moment analysis of these problems can be solved by our new method.

For a absorptive permeation experiment, the system is stipulated with a zero initial activity throughout the whole membrane and the boundary conditions at the downstream face $\hat{a}_d(s)=0$, and at the upstream face $\hat{a}_u(s)=\rho_0/K_u s$ where K_u is the partition coefficient, ρ_0 is a constant penetrant concentration at the upstream face. Solution for $\hat{J}_d(s)$ from Eq. (1) is found to be

$$\hat{J}_d(s)=-\frac{1}{T_{12}(s)}\hat{a}_u(s)=-\frac{1}{T_{12}(s)}\frac{\rho_0}{K_u s}$$

$$=\left\{\frac{1}{\beta_0}-\frac{\beta_1}{\beta_0^2}s+\left(\frac{\beta_1^2}{\beta_0^3}-\frac{\beta_2}{\beta_0^2}\right)s^2+\cdots\right\}$$

$$\times\left(\frac{\rho_0}{K_u s}\right). \tag{49}$$

The first moment (time lag) then is given by

$$t_L=\int_0^\infty \frac{t\,d/dt\,J_d(t)}{J_{d,ss}}dt$$

$$=\lim_{s\to 0}\frac{-(d/ds)s\hat{J}_d(s)}{J_{d,ss}}$$

$$=\frac{\beta_1}{\beta_0}$$

$$=\frac{\int_0^h(1/DK)\int_x^h K\int_{x_1}^h(1/DK)dx'_1\,dx_1\,dx}{\int_0^h(1/DK)dx}$$

$$=\frac{\int_0^h K\int_0^x(dy/DK)\int_x^h(dy/DK)dx}{\int_0^h(1/DK)dx}. \tag{50}$$

The last equality is due to the Dirichlet formula.[24] Equation (50) is also derived by repeated integration.[25,26]

For the second moment, $t_L^{(2)}$, we have

$$t_L^{(2)}=\int_0^\infty t^2\frac{d}{dt}J_d(t)dt/J_{d,ss}$$

$$=\lim_{s\to 0}\frac{(d^2/ds^2)s\hat{J}_d(s)}{s\hat{J}_d(s)}$$

$$=\frac{2((\beta_1^2/\beta_0^3)-(\beta_2/\beta_0^2))}{(1/\beta_0)}$$

$$=2\left(\frac{\beta_1^2}{\beta_0^2}-\frac{\beta_2}{\beta_0}\right)=2\left(t_L^2-\frac{\beta_2}{\beta_0}\right), \tag{51}$$

where the explicit expressions for t_L, β_0, and β_2 and shown in Eqs. (50), (28), and (30), respectively.

Another important membrane transport is desorptive permeation, which is stipulated with the same boundary conditions as absorptive permeation except for a constant initial activity a_0 throughout the whole membrane. Solving for $\hat{J}_d(s)$ using Eq. (3), we obtain

$$\hat{J}_d(s)=-\frac{T_{22}(s)}{T_{12}(s)}\frac{a_0}{s}$$

$$=\left[\frac{1}{\beta_0}+\frac{\delta_1\beta_0-\beta_1}{\beta_0^2}s\right.$$

$$\left.+\frac{\beta_0^2\delta_2-\beta_0\beta_2-\beta_1\delta_1\beta_0+\beta_1^2}{\beta_0^3}s^2+\cdots\right]\frac{a_0}{s}. \tag{52}$$

Again we have the first moment, i.e., the time lead, t_+

$$t_+=\lim_{s\to 0}\frac{-(d/ds)s\hat{J}_d(s)}{J_{d,ss}}=\frac{\beta_1-\delta_1\beta_0}{\beta_0}. \tag{53}$$

Substituting the Taylor expansion coefficients in the form of repeated integers followed by using Dirichlet formula, we have

$$t_+=-\frac{\int_0^h K\int_0^x(dy/DK)\int_0^x(dy/DK)dx}{\int_0^h(1/DK)dx}. \tag{54}$$

The second moment ($t_+^{(2)}$) expression in terms of repeated integrals appears to be a little bit cumbersome, and only that in terms of expansion coefficients is given

$$t_+^{(2)}=2\left[\delta_2-\frac{\beta_2}{\beta_0}+\frac{\beta_1}{\beta_0}t_+\right]=2\left[\delta_2-\frac{\beta_2}{\beta_0}+t_L t_+\right], \tag{55}$$

where Eq. (50) for t_L has been used.

As the last example of application, we consider the mean residence time at position x for a particle initially located at x_0, $0<x$, $x_0<h$. Both end boundaries are absorbing. The mean residence time is the average of the total time that the particle has resided at position x if the observation time is taken up to a time t.[27–29] Mathematically it can be defined in terms of the integration of Green's function $\rho(x,t'|x_0)$ with respect to t' from 0 to t. The Green's function is a solution of the diffusion equation under the same boundary conditions

with the initial condition $\delta(x-x_0)$. The Green's functionlike penetrant activity has been solved in terms of the transmission matrix element elsewhere[17] to be

$$\hat{a}(x,s) = \begin{cases} -\dfrac{T_{12}^{(3)}(s)T_{12}^{(1)}(s)}{T_{12}(s)} & x<x_0 \\[3mm] -\dfrac{T_{12}^{(32)}(s)T_{12}^{(21)}(s)}{T_{12}(s)} + T_{12}^{(2)}(s) & x>x_0 \end{cases}, \qquad (56)$$

where $T^{(1)}(s)$, $T^{(2)}(s)$, $T^{(3)}(s)$, $T^{(21)}(s)$, and $T^{(32)}(s)$ are the transmission matrix for the subregions from 0 to x, x to x_0, x_0 to h, 0 to x_0, and x to h, respectively, if $x_0>x$. If $x_0<x$, then the coordinates x_0 and x are interchanged. Thus the mean residence time at x for infinite observation time, corresponding to $t\to\infty$, is found to be

$$\tau(x|x_0) = \int_0^\infty \rho(x,t'|x_0)dt' = \lim_{s\to 0}\hat{\rho}(x,s|x_0)$$

$$= \lim_{s\to 0}\hat{a}(x,s)K(x), \qquad (57)$$

where the last equality is due to the definition[17] of activity $a(x,t)=\rho(x,t)/K(x)$. Substitution Eq. (56) into Eq. (57), we find

$$\tau(x|x_0)$$

$$= \begin{cases} \displaystyle\lim_{s\to 0}\dfrac{-T_{12}^{(3)}(s)T_{12}^{(1)}(s)}{T_{12}(s)}K(x) & x<x_0 \\[4mm] \displaystyle\lim_{s\to 0}\left[\dfrac{-T_{12}^{(32)}(s)T_{12}^{(21)}(s)}{T_{12}(s)} + T_{12}^{(2)}(s)\right]K(x) & x>x_0 \end{cases}.$$

$$(58)$$

In terms of repeated integrals it becomes

$$\tau(x|x_0) = \begin{cases} K(x)\displaystyle\int_0^x \dfrac{1}{D(x')K(x')}dx'\int_{x_0}^h \dfrac{1}{D(x)K(x)}dx\left\{\int_0^h \dfrac{1}{D(x)K(x)}dx\right\}^{-1} & x<x_0 \\[4mm] K(x)\displaystyle\int_0^{x_0} \dfrac{1}{D(x)K(x)}dx\int_x^h \dfrac{1}{D(x')K(x')}dx'\left\{\int_0^h \dfrac{1}{D(x)K(x)}dx\right\}^{-1} & x>x_0 \end{cases}. \qquad (59)$$

DISCUSSION AND CONCLUSION

Frisch et al. also studied the time moment problems for membrane absorptive permeation, desorptive permeation and sorption transports.[30] They theoretically investigated the time moments of the amount of penetrant in an absorbing (or desorbing) membrane composed of a linear laminated medium. They have shown that these time moments can be obtained via a precursor $B_n(x)$ by $\mu_n = \int_0^h K(x)B_n(x)dx$, where $B_n(x)$ itself can be obtained from an integral with $B_{n-1}(x)$ as a part of integrand. Thus, with $B_0(x)$ known, other $B_n(x)$ can be recursively calculated. Similar scheme is also applied to the calculation of the time moments for the difference between the instantaneous and asymptotic flows up to a given time through a membrane. As a comparison, our new method appears to be simple and straightforward.

Recently Zwanzig[23] 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

$$D^* = \frac{D}{\langle\exp[(U_1(x)/kT)]\rangle\langle\exp[-(U_1(x)/kT)]\rangle}, \qquad (60)$$

where k is the Boltzmann constant and $\langle\ \rangle$ denotes the spatial average. As a first example, if the roughness is simply $U_1(x)=\epsilon\cos(qx)$, then[23]

$$D^* = \frac{D}{[I_0(\epsilon/kT)]^2}, \qquad (61)$$

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 $\exp(-U^2/2\epsilon^2)$ in which $\epsilon^2=\langle U_1^2\rangle$, then[23]

$$D^* = D\exp[-(\epsilon/kT)^2]. \qquad (62)$$

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 $[I_0(\epsilon/kT)]^{2n}$ for the first example and by $\{\exp[-(\epsilon/kT)^2]\}^n$ for the second. Since both $I_0(\epsilon/kT)>1$ and $\exp(-\epsilon/kT)<1$ for $\epsilon>0$, we assert that the effect of potential roughness in this two cases is to increase the magnitude of D^*, and hence the time moments of orders ≥ 1.

In conclusion, we have given an alternative approach to the time moment analysis for diffusion problems. First we calculate in the Laplace domain the escaping flux with appropriate boundary conditions using one of the transport equations [Eqs. (1)–(3)]. Expand the flux into a power series of s, we found the coefficients of expansion, which correspond to the time moments, is a combination of the coefficients of the Taylor series of the matrix elements. With the latter expressed by repeated integrals as shown in Eqs. (32)–(35), the time moments can be also represented by the repeated integrals as well. As compared to the traditional iterative Green's function,[11] solving the backward diffusion equations[11,12,23] and repeated integration,[14] our method gains

some advantage in the sense that it can be accomplished in a simple, straightforward way, involving only algebraic operation.

APPENDIX

The boundary conditions for a reflecting boundary at $x=0$ and an absorbing boundary at $x=h$ are $\mu_n^d(h)=0$, $(d\mu_n^d/dx)|_{x=0}=0$, where the superscript d is used to specify the escaping flux is from the downstream face. With the initial position at $x=x_0$ the time moments for escaping probability are

$$\mu_0^d=1, \tag{A1}$$

$$\mu_1^d=\int_{x_0}^h \frac{1}{DK}\int_0^{x_1} K\,dx_1'\,dx_1, \tag{A2}$$

$$\mu_2^d=(2!)\int_{x_0}^h \frac{1}{DK}\int_0^{x_2} K\int_{x_2'}^h \frac{1}{DK}\int_0^{x_1} K\,dx_1'\,dx_1\,x_2'\,dx_2, \tag{A3}$$

where Eq. (A1) is directly from Eq. (6), and Eqs. (A2) and (A3) are obtained by direct integration on Eq. (6) with the help of boundary conditions. If initial position is at $x=0$, the lower integrating limit x_0 is replaced by 0.

The boundary conditions for an absorbing face at $x=0$ and a reflecting face at $x=h$ are $\mu_n^u(0)=0$, $(d\mu_n^u/dx)|_{x=h}=0$. The superscript u is to specify that the flux exits from the upstream face. With the initial position at $x=h$ the time moments for escaping probability are

$$\mu_0^u=1, \tag{A4}$$

$$\mu_1^u=\int_0^h \frac{1}{DK}\int_{x_1}^h K\,dx_1'\,dx_1, \tag{A5}$$

$$\mu_2^u=(2!)\int_0^h \frac{1}{DK}\int_{x_2}^h K\int_0^{x_2'} \frac{1}{DK}\int_{x_1}^h K\,dx_1'\,dx_1\,x_2'\,dx_2, \tag{A6}$$

where Eq. (A4) is directly from Eq. (6), and Eqs. (A5) and (A6) are obtained by direct integration.

The time moments for a reflecting boundary at $x=0$ and an absorbing boundary at $x=h$ with initial position at $x=x_0$ has been given in Eqs. (A1)–(A3). The nth moment for the initial condition of saturated equilibrium distribution is the average over the initial distribution, i.e., it is weighted by a Boltzmann factor $K(x_0)[\int_0^h K(x_0)dx_0]^{-1}$. With this in mind we have

$$\mu_0^e=1, \tag{A7}$$

$$\mu_1^e=\frac{\int_0^h K\int_x^h (1/DK)\int_0^{x_1} K\,dx_1'\,dx_1\,dx}{\int_0^h K\,dx}, \tag{A8}$$

$$\mu_2^e=2!\,\frac{\int_0^h K\int_x^h (1/DK)\int_0^{x_2} K\int_{x_2'}^h (1/DK)\int_0^{x_1} K\,dx_1'\,dx_1\,dx_2'\,dx_2\,dx}{\int_0^h K\,dx}, \tag{A9}$$

where the superscript e is to specify the initial saturated equilibrium condition throughout the whole domain.

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