

Diffusion in a tube of varying cross section: Numerical study of reduction to effective one-dimensional description

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Brownian dynamics simulations of the particle diffusing in a long conical tube (the length of the tube is much greater than its smallest radius) are used to study reduction of the three-dimensional diffusion in tubes of varying cross section to an effective one-dimensional description. The authors find that the one-dimensional description in the form of the Fick-Jacobs equation with a position-dependent diffusion coefficient, $D(x)$, suggested by Zwanzig [J. Phys. Chem. **96**, 3926 (1992)], with $D(x)$ given by the Reguera-Rubí formula [Phys. Rev. E **64**, 061106 (2001)], $D(x) = D/\sqrt{1+R'(x)^2}$, where D is the particle diffusion coefficient in the absence of constraints, and $R(x)$ is the tube radius at x , is valid when $|R'(x)| \leq 1$. When $|R'(x)| > 1$, higher spatial derivatives of the one-dimensional concentration in the effective diffusion equation cannot be neglected anymore as was indicated by Kalinay and Percus [J. Chem. Phys. **122**, 204701 (2005)]. Thus the reduction to the effective one-dimensional description is a useful tool only when $|R'(x)| \leq 1$ since in this case one can apply the powerful standard methods to analyze the resulting diffusion equation. © 2007 American Institute of Physics. [DOI: 10.1063/1.2719193]

I. INTRODUCTION

The problem of diffusion in a tube of varying cross section arises in different contexts. Examples include diffusion of ions and macromolecular solutes through the channels in biological membranes,¹ transport in zeolites² and nanostructures of complex geometry,³ controlled drug release,⁴ and diffusion in man-made periodic porous materials.⁵ It is intuitively appealing to formulate the problem as one dimensional, i.e., in terms of the effective one-dimensional concentration of diffusing molecules that satisfies a one-dimensional diffusion equation. However, reduction of the three-dimensional diffusion equation with reflecting boundary condition on the wall of the tube to the effective one-dimensional one is a tricky problem, which has been discussed in the literature for a long time.^{6,7} Real progress in understanding this reduction has been made in recent papers by Zwanzig,⁸ Reguera and Rubí,⁹ and Kalinay and Percus.¹⁰⁻¹³

The present paper deals with diffusion in a cylindrical tube of varying cross section. Local concentration of diffusing solute molecules, $C(x, y, z, t)$, satisfies the diffusion equation

$$\frac{\partial C(x, y, z, t)}{\partial t} = D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) C(x, y, z, t), \quad (1.1)$$

where D is the solute diffusion coefficient in space with no constraints, with reflecting boundary condition on the wall of the tube. The description dramatically simplifies if one as-

sumes that the distribution of the solute in any cross section of the tube is uniform as it is at equilibrium. The point is that this assumption allows one to reduce the three-dimensional problem with a complex boundary to the one-dimensional problem of diffusion along the tube axis in the presence of an entropy potential.⁸

Directing the x axis along the centerline of the tube and denoting the cross-section area of the tube at x by $A(x)$ one can introduce the effective one-dimensional concentration of the solute, $c(x, t)$,

$$c(x, t) = \int_{A(x)} C(x, y, z, t) dy dz. \quad (1.2)$$

When distributions in the cross sections are uniform, this concentration satisfies the Fick-Jacobs (FJ) equation⁶

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial}{\partial x} \left\{ A(x) \frac{\partial}{\partial x} \left[\frac{c(x, t)}{A(x)} \right] \right\}, \quad (1.3)$$

which is the Smoluchowski equation for diffusion in the entropy potential $U(x)$ defined as⁸

$$U(x) = -k_B T \ln \frac{A(x)}{A(x_0)}, \quad (1.4)$$

where k_B and T are the Boltzmann constant and the absolute temperature, and $U(x)$ at $x=x_0$ is taken to be zero.

Reduction to the one-dimensional description based on the local equilibrium assumption is obviously oversimplified. Zwanzig derived a corrected form of the FJ equation in

which small deviations from local equilibrium are taken into account.⁸ Assuming that the tube radius, $R(x)$, does not change too fast, i.e., $|R'(x)| \ll 1$, he showed that $c(x, t)$ satisfies the conservation probability equation

$$\frac{\partial c(x, t)}{\partial t} = - \frac{\partial j(x, t)}{\partial x}, \quad (1.5)$$

in which the flux, $j(x, t)$, is given by

$$j(x, t) = -A(x)D(x) \frac{\partial}{\partial x} \left[\frac{c(x, t)}{A(x)} \right]. \quad (1.6)$$

The expression for the position-dependent effective diffusion coefficient, $D(x)$, derived by Zwanzig, has the form

$$D_{Zw}(x) = D \left[1 - \frac{1}{2} R'(x)^2 \right] \approx \frac{D}{1 + (1/2)R'(x)^2}. \quad (1.7)$$

Later Reguera and Rubí generalized Zwanzig's result. Based on heuristic arguments they suggested that $D(x)$ entering into Eq. (1.6) is given by⁹

$$D_{R-R}(x) = \frac{D}{\sqrt{1 + R'(x)^2}}. \quad (1.8)$$

The approximate expression for the flux in Eq. (1.6) contains only the first spatial derivative of $c(x, t)$. However, based on general ideas one might expect that the exact expression for the flux obtained by reduction to the one-dimensional description must contain all derivatives, $\partial^k c(x, t) / \partial x^k$, $k=1, 2, \dots$. Such an expression has been obtained by Kalinay and Percus.¹⁰⁻¹³ Based on their analysis we can write the flux as

$$j(x, t) = -A(x) \hat{D} \left(x, \frac{\partial}{\partial x} \right) \frac{\partial}{\partial x} \left[\frac{c(x, t)}{A(x)} \right], \quad (1.9)$$

where we have introduced the operator $\hat{D}(x, \partial/\partial x)$ which we will call the diffusivity operator.

To write an expression for this operator we first assume that diffusion in the tube is highly anisotropic: it occurs much slower along the tube axis than in the normal direction so that corresponding diffusion coefficients, D_x and D_\perp , satisfy $\varepsilon = D_x/D_\perp \ll 1$. Then the diffusivity operator can be written as

$$\hat{D} \left(x, \frac{\partial}{\partial x} \middle| \varepsilon \right) = D_x \left[1 - \sum_{k=0}^{\infty} \varepsilon^{k+1} \zeta_k(x, \varepsilon) \frac{\partial^k}{\partial x^k} \right], \quad (1.10)$$

where functions $\zeta_k(x, \varepsilon)$ are also expressed as Taylor series in ε . The first three terms of the ε expansion of $\hat{D}(x, \partial/\partial x | \varepsilon)$ are¹³

$$\hat{D} \left(x, \frac{\partial}{\partial x} \middle| \varepsilon \right) = D_x \left\{ 1 - \frac{\varepsilon}{2} R'^2 - \frac{\varepsilon^2 R'}{24} \left[R^2 R''' + R R' R'' - 7R'^3 + R(RR'' + R'^2) \frac{\partial}{\partial x} \right] \right\}. \quad (1.11)$$

The diffusivity operator entering into Eq. (1.9) is the operator in Eq. (1.10) with $D_x = D$ and $\varepsilon = 1$. The diffusivity operator reduces to $D_{Zw}(x)$ in Eq. (1.7) if one approximates the infinite sum in Eq. (1.10) by the first two terms. This is

justified when $|R'(x)| \ll 1$ (in spite of the fact that $\varepsilon = 1$) since Zwanzig's result gives the leading correction due to the deviation from local equilibrium in this limiting case.

In Ref. 13 Kalinay and Percus consider the stationary flux through a long tube of varying cross section at fixed concentrations of the molecules at the tube ends. They show that the general relation between the stationary flux j_{st} and the stationary concentration $c_{st}(x)$,

$$j_{st} = -A(x) \hat{D} \left(x, \frac{\partial}{\partial x} \right) \frac{\partial}{\partial x} \left[\frac{c_{st}(x)}{A(x)} \right], \quad (1.12)$$

dramatically simplifies. The infinite sum of the derivatives of $c_{st}(x)/A(x)$ can be summed up and the stationary flux can be written in the conventional form

$$j_{st} = -A(x) D_{st}(x) \frac{\partial}{\partial x} \left[\frac{c_{st}(x)}{A(x)} \right]. \quad (1.13)$$

The effective position-dependent diffusion coefficient $D_{st}(x)$ can be found solving the equation

$$A(x) \hat{D} \left(x, \frac{\partial}{\partial x} \right) \left[\frac{1}{A(x) D_{st}(x)} \right] = 1. \quad (1.14)$$

Introducing the inverse diffusivity operator, $\hat{D}(x, \partial/\partial x)^{-1}$, one can write the solution to Eq. (1.14) as

$$\frac{1}{D_{st}(x)} = A(x) \hat{D} \left(x, \frac{\partial}{\partial x} \right)^{-1} \left[\frac{1}{A(x)} \right]. \quad (1.15)$$

Kalinay and Percus show that for a long conical tube with $R(x) = R(x_L) + \lambda(x - x_L)$, where $R(x_L)$ is the tube radius at $x = x_L$ and $\lambda = R'(x)$ is a constant, $D_{st}(x) = \text{const}$, given by the formula suggested by Reguera and Rubí, Eq. (1.8),

$$D_{st}(x) = \frac{D}{\sqrt{1 + \lambda^2}}. \quad (1.16)$$

Note that a conical tube may be considered as long when its length is greater than variation of its radius, i.e., when $\lambda < 1$.

Reduction to the effective one-dimensional diffusion equation is a useful tool to analyze diffusion in a tube of varying cross section only if this equation is not too complicated. In this respect the conventional form of the one-dimensional diffusion equation, Eqs. (1.5) and (1.6), has an important advantage over the generalized form, Eqs. (1.5), (1.9), and (1.10). The point is that powerful techniques have been developed to analyze the conventional diffusion equation, while there are no standard methods of analysis of the generalized version. The purpose of this study is to establish the range of applicability of the reduction to the conventional form of the diffusion equation and to indicate geometrical constraints under which such a reduction is justified. It seems natural to formulate the constraints in terms of $R'(x)$. We will see that although initially Zwanzig⁸ showed that the reduction is justified only when $|R'(x)| \ll 1$, in fact, the range of its applicability is much broader, $|R'(x)| \leq 1$. Understanding these constraints seems important for potential applications of the effective one-dimensional diffusion equation, for example, in studies of diffusion in quasi-one-dimensional periodic porous structures.¹⁴

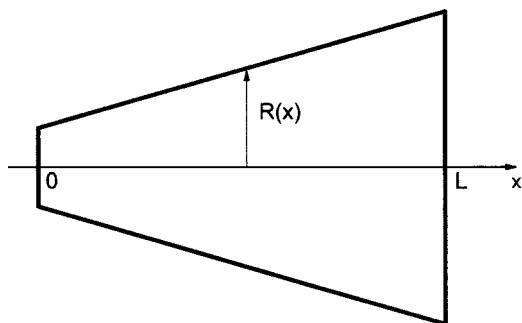


FIG. 1. Conical tube used in our Brownian dynamics simulations. The local radius of the tube, $R(x)$, is given by Eq. (2.1).

In the present paper we report on our numerical study of the reduction to the effective one-dimensional description using Brownian dynamics simulations. Our goal is to understand (i) under which conditions one can neglect higher spatial derivatives of $c(x,t)$ and use conventional expression for the flux given in Eq. (1.6) and (ii) the relation between the effective diffusion coefficient found numerically and those given by the Zwanzig and Reguera-Rubí formulas, Eqs. (1.7) and (1.8). Our main results are as follows. One can use the conventional expression for the flux in Eq. (1.6) with $D(x)$ given in Eq. (1.8) when $|R'(x)| \leq 1$. For larger values of $|R'(x)|$ higher spatial derivatives of $c(x,t)$ cannot be neglected. Note that even when $|R'(x)| = 1$ Eqs. (1.7) and (1.8) lead to close values of $D(x)$: $D_{Zw}(x) \cong 0.66D$, $D_{R-R}(x) \cong 0.71D$, which are not much less than D .

II. RESULTS OF NUMERICAL STUDY

To study the reduction to the effective one-dimensional description we run Brownian dynamics simulations in the long conical tube of length L shown in Fig. 1. The tube radius, $R(x)$, is given by

$$R(x) = 1 + \lambda x, \quad 0 < x < L, \quad (2.1)$$

where we have chosen the radius of the narrow end of the tube as a unit length and $\lambda = R'(x)$ is a positive constant, $\lambda \geq 0$. A cylindrical tube of unit radius corresponds to $\lambda = 0$. Particle trajectories start from one end of the tube, which, as well as the wall of the tube, is a perfectly reflecting boundary, and are terminated at their first contact with the opposite end, which is a perfectly absorbing boundary. In simulations we find the mean first passage times from one end of the tube to the other, $\tau_\lambda(n \rightarrow w)$ and $\tau_\lambda(w \rightarrow n)$, where n and w denote the narrow and wide ends of the tube, as functions of λ for $L = 20$. When running simulations we take $D = 1$ and the time step $\Delta t = 2 \times 10^{-4}$, so that $\sqrt{2D\Delta t} = 2 \times 10^{-2} \ll 1$. Each mean first passage time is obtained by averaging the first passage times of 10^4 trajectories whose starting points are uniformly distributed over the reflecting end of the tube. To estimate the accuracy of our numerical results we run 10^5 trajectories in the cylindrical tube ($\lambda = 0$) and in the conical tube with $\lambda = 2$. We divide the entire set of trajectories into the subsets of 10^4 trajectories and determine the mean first passage time for each subset. For the cylindrical tube these times are compared with the exact value, $L^2/(2D)$, while for the conical tube the times are compared with the mean first passage time

found by averaging the times of all 10^5 trajectories. The comparison shows that the relative error of the first passage times found in our simulations is less than 2% in both cases.

The mean first passage times found in simulations are used to determine the effective diffusion coefficients, $D_\lambda(n \rightarrow w)$ and $D_\lambda(w \rightarrow n)$, assuming that the flux entering into Eq. (1.5) is given by the conventional expression in Eq. (1.6). We chose the conical geometry of the tube because for this geometry $R'(x) = \lambda = \text{const}$ and, as a consequence, the effective diffusion coefficient, $D(x)$, in Eq. (1.6) is constant. The fact that the diffusion coefficient is independent of x allows us to use standard simple expressions for the first passage times,

$$\tau_\lambda(n \rightarrow w) = \frac{L^2}{6D_\lambda(n \rightarrow w)} \frac{3 + \lambda L}{1 + \lambda L} \quad (2.2)$$

and

$$\tau_\lambda(w \rightarrow n) = \frac{L^2}{6D_\lambda(w \rightarrow n)} (3 + 2\lambda L). \quad (2.3)$$

Respectively, the diffusion coefficients for transitions in both directions are

$$D_\lambda(n \rightarrow w) = \frac{L^2}{6\tau_\lambda(n \rightarrow w)} \frac{3 + \lambda L}{1 + \lambda L} \quad (2.4)$$

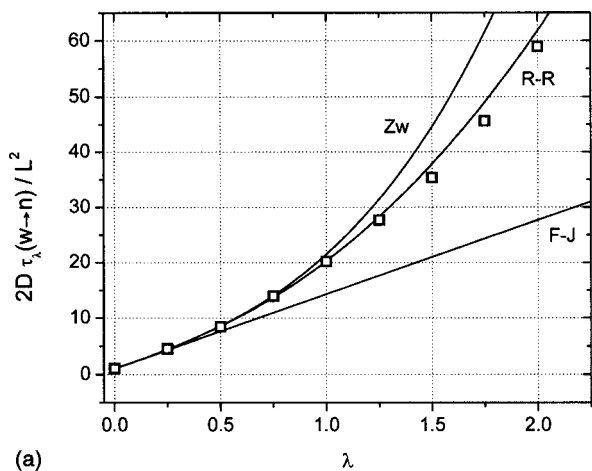
and

$$D_\lambda(w \rightarrow n) = \frac{L^2}{6\tau_\lambda(w \rightarrow n)} (3 + 2\lambda L). \quad (2.5)$$

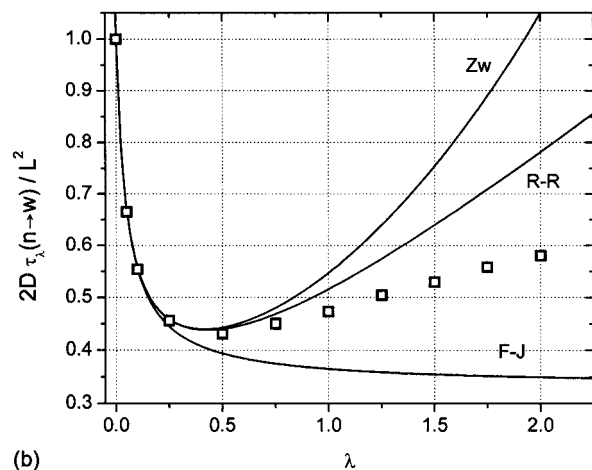
The ratio $D_\lambda(w \rightarrow n)/D_\lambda(n \rightarrow w)$, determined from our simulations of the first passage times according to Eqs. (2.4) and (2.5), may be considered as an indicator whether the conventional expression for the flux is applicable or not. When the expression is applicable the two diffusion coefficients are equal and their ratio must be unity. Deviation of the ratio from unity indicates that the conventional expression for the flux is inapplicable, and higher spatial derivatives of $c(x,t)$ cannot be neglected.

The results of our simulations are presented in Fig. 2 which shows the ratio of $\tau_\lambda(n \rightarrow w)$ and $\tau_\lambda(w \rightarrow n)$ to the corresponding mean first passage time in the cylindrical tube of uniform cross section given by $L^2/(2D)$. The squares represent our numerical results while solid curves show the dependences obtained on the basis of the Fick-Jacobs equation, Eq. (1.3), and its modified version, Eqs. (1.5) and (1.6), with $D(x)$ given in Eqs. (1.7) and (1.8), as indicated by letters near the curves. As might be expected $\tau_\lambda(w \rightarrow n)$ monotonously increases with λ [see Fig. 2(a)]. This happens because both the entropic repulsion and slowdown of diffusion lead to the increase of $\tau_\lambda(w \rightarrow n)$ with λ . Figure 2(a) shows that applying the Reguera-Rubí formula in Eq. (1.8) one can predict variation of $\tau_\lambda(w \rightarrow n)$ over a broad range of times.

In contrast to the monotonic growth of $\tau_\lambda(w \rightarrow n)$ with λ , the λ dependence of $\tau_\lambda(n \rightarrow w)$ is nonmonotonic. This can be understood if one considers the effect of the entropy potential which pulls the particle towards the wider end that leads to the decrease of $\tau_\lambda(n \rightarrow w)$ at small λ . In the opposite limiting case, $\lambda \rightarrow \infty$, the problem reduces to that of one-dimensional diffusion. For this reason, $\tau_\lambda(n \rightarrow w)$ returns to



(a)



(b)

FIG. 2. The ratios of the mean first passage times between the two ends of the conical tube, $\tau_\lambda(w \rightarrow n)$ and $\tau_\lambda(n \rightarrow w)$, to the mean first passage time in a tube of uniform cross section, $L^2/(2D)$, as functions of λ [panels (a) and (b), respectively; see the details in the text].

its value for the cylindrical tube of uniform cross section that corresponds to $\lambda=0$. Equation (2.2) shows that the estimation based on the Fick-Jacobs equation, which neglects slowdown of diffusion with λ , leads to the monotonic decrease of the ratio $2D\tau_\lambda(n \rightarrow w)/L^2$ from unity at $\lambda=0$ to $1/3$ as $\lambda \rightarrow \infty$ [Fig. 2(b)]. The slowdown of diffusion leads to the increase of $\tau_\lambda(n \rightarrow w)$. Competition between the decrease of this time with λ due to the entropy potential and its increase with λ due to the slowdown of diffusion determines the non-monotonic behavior of the ratio $2D\tau_\lambda(n \rightarrow w)/L^2$ shown in Fig. 2(b).

From this figure one can see that the prediction based on the conventional expression for the flux with $D(x)$ given by the Reguera-Rubí formula is in better agreement with the numerical results than the two other predictions shown in the figure. One can also see that even the best of the three predictions fails at $\lambda > 1$. The point is that Eq. (2.2) with $D(x)$ given in Eq. (1.8) leads to incorrect asymptotic behavior of $\tau_\lambda(n \rightarrow w)$ as $\lambda \rightarrow \infty$. As we discussed earlier, in this limiting case $\tau_\lambda(n \rightarrow w)$ tends to its value in the tube of uniform cross section, $L^2/(2D)$, that corresponds to $\lambda=0$, while Eq. (2.2) predicts the linear growth of $\tau_\lambda(n \rightarrow w)$ with λ at large λ , $\tau_\lambda(n \rightarrow w) \approx \lambda L^2/(6D)$ as $\lambda \rightarrow \infty$.

To evaluate the range of applicability of the conventional

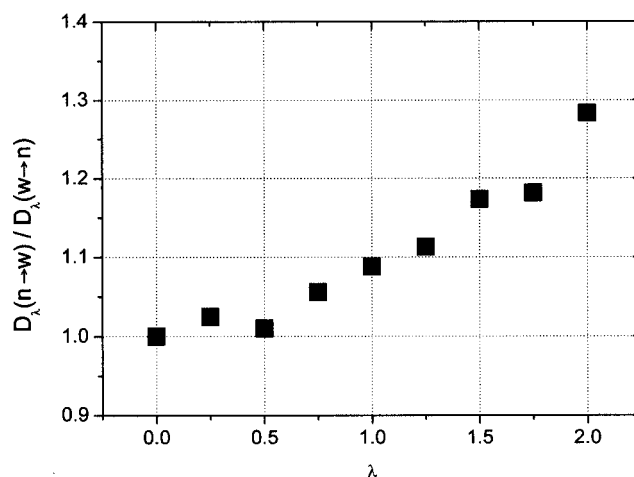


FIG. 3. The ratio of the diffusion coefficients, $D_\lambda(n \rightarrow w)/D_\lambda(w \rightarrow n)$, as a function of λ .

expression for the flux, in Fig. 3 we show the ratio of the diffusion coefficients obtained by means of Eqs. (2.4) and (2.5) using the mean first passage times found in simulation. One can see that the ratio monotonically increases with λ . For $\lambda=1$ the ratio is approximately 1.09. We consider $\lambda=1$ as the upper boundary for the range of applicability of the conventional expression for the flux with the Reguera-Rubí formula for the diffusion coefficient. In Fig. 4 we show the ratios of the two diffusion coefficients to D_{R-R} . This figure shows that $D_\lambda(n \rightarrow w)$ deviates from D_{R-R} much stronger than $D_\lambda(w \rightarrow n)$. Nevertheless, the relative deviation does not exceed 10% for $\lambda \leq 1$.

In summary, our numerical study of diffusion in a long conical tube (the length of the tube is much greater than its smallest radius) of varying cross section has shown that the reduction to the effective one-dimensional description is justified when $|R'(x)| \leq 1$, where $R(x)$ is the tube radius at x . When this condition is fulfilled, one can use the conventional expression for the flux, Eq. (1.6), with $D(x)$ given in Eq. (1.8). Such a reduction provides significant simplification of the analysis of diffusion in periodic porous structures dis-

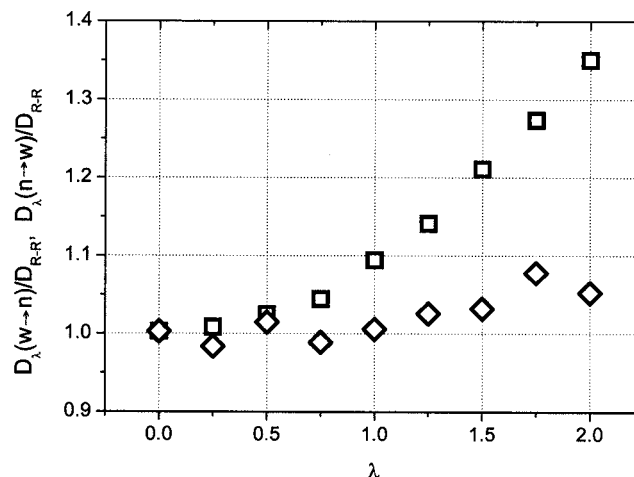


FIG. 4. The ratios of the diffusion coefficients, $D_\lambda(n \rightarrow w)$ and $D_\lambda(w \rightarrow n)$ to $D_{R-R} = D/\sqrt{1+\lambda^2}$, as functions of λ . Squares and diamonds represent $D_\lambda(n \rightarrow w)/D_{R-R}$ and $D_\lambda(w \rightarrow n)/D_{R-R}$, respectively.

cussed recently¹⁴ on the basis of the modified Fick-Jacobs equation. When this approach fails, diffusion in periodic porous structures can be analyzed using an alternative approach,¹⁵ which in a sense is complementary to the first one.

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