PHYSICAL REVIEW E **95**, 052804 (2017)

Relation between the porosity and tortuosity of a membrane formed by disconnected irregular pores and the spatial diffusion coefficient of the Fick-Jacobs model

Aldo Ledesma-Durán, S. I. Hernández, and Iván Santamaría-Holek[*]
Unidad Multidiscliplinaria de Docencia e Investigación-Juriquilla, Facultad de Ciencias, Universidad Nacional Autónoma de México, CP 76230, Juriquilla, Querétaro, Mexico

(Received 6 December 2016; revised manuscript received 6 March 2017; published 22 May 2017)

In this work, we provide a theoretical relationship between the spatial-dependent diffusion coefficient derived in the Fick-Jacobs (FJ) approximation and the macroscopic diffusion coefficient of a membrane that depends on the porosity, tortuosity, and the constriction factors. Based on simple mass conservation arguments under equilibrium as well as in nonequilibrium conditions, we generalize previous expressions for the effective diffusion coefficient of an irregular pore, originally obtained by Festa and d'Agliano for horizontal and periodic pores, and then extended by Bradley for tortuous periodic pores, to the case of pores with arbitrary geometry. Through a formal definition of the constrictivity factor in terms of the geometry of the pore, our results provide very clear physical interpretation of experimental measurements since they link the local properties of the flow with macroscopic quantities of experimental relevance in the design and optimization of porous materials. The macroscopic diffusion coefficient as well as the spatiotemporal evolution of the concentration profiles inside a pore have been recently measured by using pulse field gradient NMR techniques. The advantage of using the FJ approach is that the spatiotemporal concentration profile inside a pore of irregular geometry is directly related to the pore's shape and, therefore, that the macroscopic diffusion coefficient can be obtained by comparing the spatiotemporal concentration profiles from such experiments with those of the theoretical model. Hence, the present study is relevant for the understanding of the transport properties of porous materials where the shape and arrangement of pores can be controlled at will.

DOI: 10.1103/PhysRevE.95.052804

I. INTRODUCTION

The effective diffusion coefficient D_m of a given fluid in the presence of a membrane is lower than the corresponding molecular diffusion coefficient D_0 of the same fluid in its absence [1]. Several expressions for the diffusivity of the membrane, defined by the ratio D_m/D_0 [2], have been previously proposed on the basis of empirical correlations, as well as on theoretical models in which the pore geometry was oversimplified [3–5]. In most of these models, it is customary to split the diffusivity upon three factors: the void space inside the porous medium, the average path length that the particle has to travel in order to cross the medium, and the reduction in the effective flow due to the changes on the cross section of the pores [1,6]. From a macroscopic point of view, these three factors are taken into account by using three characteristic parameters of the porous media called the porosity ϕ, the tortuosity τ, and the constrictivity factor δ. The most common representation for the effective diffusion coefficient of a membrane D_m in terms of these parameters is [7]

$$D_m = D_0\frac{\phi}{\tau}\delta. \tag{1}$$

The last sentence emphasizes the lack of consensus with respect to the specific dependence of the diffusivity on ϕ, τ, and δ, since, depending upon the specific pore model used, each parameter depends on the two others in different ways [8,9]. This obstacle has not prevented that such quantities continue to be used in the experimental description of porous media; see for instance Refs. [10–14].

Roughly speaking, two different approaches can be carried out in order to model the effective diffusive flux across a porous media. In the first one, the porous medium is visualized as the interstitial space between solid particles of precise shapes such as spheres, ellipsoids, and cylinders. In this approach, the diffusive and volumetric fluxes across the particle are calculated inside a unit cell whose porosity is taken as representative of the entire material [15–17]. This approach is more convenient for granular porous media. In the second approach, the porous media are described as a bunch of almost cylindrical tubes where the average internal flux can be calculated [18–21]. Then, a specific probability function which establishes the distribution of lengths and radius of the pores is assumed in order to average the internal fluxes [22–24]. These models are more convenient for describing nonstructured or disordered porous media where the local effects of pore junctions on the total flux can be easily averaged [25]. These two traditional schemes for describing diffusion in porous media have been confirmed on several physical and numerical experiments for these types of porous materials [3,25–27]. For a review see Ref. [5].

However, nowadays there is a new kind of experimental technique which allows us to create artificial porous materials, where the arrangement and form of the pores composing the membrane can be produced at will. Some examples are shown in Refs. [28–33]. These membranes allow us to control the amount of material transferred from side to side and, in the case of adsorbing catalytic materials, the amount of material adsorbed and transformed during the process [34–39]. This class of materials is not disordered or granular, like those studied by the previous models and, most importantly, the specific shape of the pores is crucial in their chemical properties. The transport inside this kind of material is the focus of our study.

---

[*] isholek.fc@gmail.com

The approach of this work is to combine both analytical approaches cited before, in order to describe the effective diffusion coefficient of porous media composed of irregular and independent pores. This coefficient is very important not only from a theoretical perspective but, more importantly, because it can be now measured by using experimental techniques such as pulse field gradient NMR or interference microscopy; see examples in Refs. [40–44]. In these experiments, the measured spatiotemporal concentration profile provides curves that can be adjusted using the solution of the diffusion equation and two adjusting parameters: the effective diffusivity of the membrane D_m and the surface permeability [45–47]. Therefore, by linking the microscopic aspects enclosed by the Fick-Jacobs diffusion coefficient with these macroscopic coefficients, our approach provides a very solid theoretical basis for modeling and evaluating the performance of new materials.

We proceed by considering the pore-cell system of the first approach and the averaging process of the internal flux of the second, in order to get the appropriate averages of the microscopic quantities. Thus, our model resembles the strategies used in parallel capillary models [18,20,21]. The difference with these traditional approaches is that in our model the flux inside the pores can be calculated in a very precise way by using the projection scheme of the Fick-Jacobs (FJ) model. This mean-field approximation allows us to establish closed expressions for the porosity, tortuosity, and constriction factor in terms of the width of the pore, its inclination, and its changes on cross section. In using the FJ model we are interested only in the diffusive regime, i.e., in processes where the volumetric velocity of the particles flowing inside the pore is negligible.

In the FJ approach, the diffusion equation is averaged along the transverse direction of the channel giving as a result an equation for the transport along the longitudinal coordinate x [48]. This integration supposes that the sinuosity and corrugation of the pores are not so marked and, therefore, the flow direction does not deviate too much from the transport direction [49–51]. Under these restrictions, the following equation holds for the averaged concentration $C_{FJ}(x,t) = (1/w)\int C(x,y,t)dy$ [52,53]:

$$\frac{\partial C_{FJ}}{\partial t} = \frac{1}{w(x)}\frac{\partial}{\partial x}\left[D_{FJ}(x)w(x)\frac{\partial C_{FJ}}{\partial x}\right], \tag{2}$$

where $w(x)$ represents the transverse area of the pore and $D_{FJ}(x)$ is an effective diffusion coefficient which considers the effect of the walls [49,54,55]. Several methodologies for obtaining this local coefficient have been provided depending on the geometry and dimensionality of the system. Those models range from semiempirical arguments [48,49] to complex projection mechanisms [54,56–58], where the local dependence of this coefficient with the geometric parameters has been estimated to various orders of approximation. For a bidimensional system, most of these coefficients can be reduced in some approximation [55] to the expression we will use in this paper, which is based on that of Bradley's work Ref. [56]:

$$D_{FJ}(x) = \frac{D_0}{1 + h_x^2(x) + \frac{1}{12}w_x^2(x)}, \tag{3}$$

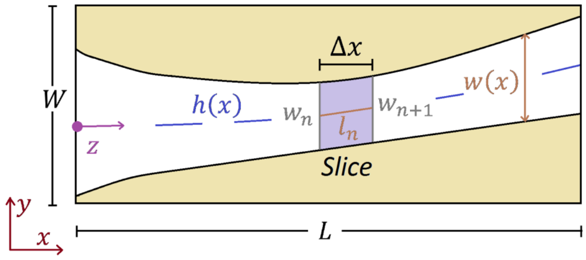


FIG. 1. Geometry of the pore-cell system. The void space (in white) has local width $w(x)$ and actual length L_Z. A slice of length l_n is shown between two adjacent areas w_n and w_{n+1}. The cell has length L and width W. The coordinate axes are shown with x being the direction of transport. The z axis is measured along the middle line of the pore starting from the left.

where $h(x)$ represents the middle line of the channel and the subscript x denotes derivative respect x; see Fig. 1. The particular election of Eq. (3) simplifies the algebraic manipulation of the formulas. However, as already mentioned, other more complete relations like that of Ref. [55] can also be used [in fact Eq. (43) in Ref. [56] is the Taylor approximation of Eq. (3) in the limit of $h_x^2, w_x^2 \ll 1$]. In the last expression, the tortuousness and constriction of the pore cause a local diminution of the flux [48]. Therefore, unlike the traditional jointed-tube models [18,20,21], the FJ approach explicitly considers the divergence-convergence of the flow near necks and funnels through the use of appropriate boundary conditions [50,51,59].

In its current state, the application of the FJ scheme for obtaining an effective diffusion coefficient is restricted to periodic pores, where this coefficient D^* is

$$\frac{1}{D^*} = \left\langle \frac{1}{D_{FJ}(x)w(x)} \right\rangle_X \langle w(x)\rangle_X. \tag{4}$$

The brackets represent a spatial average over a period of the pore [56,60]. We emphasize the spatial average by using the subscript X. This expression is also restricted to horizontal pores, i.e., pores whose middle line coincides with the direction of transport. In periodic pores, this theoretical expression has been confirmed by comparing the FJ diffusion coefficient with Brownian dynamics [61] and macrotransport theory [62].

The objective of this work is to use the FJ approach, essentially Eq. (3), in order to deduce the effective diffusion coefficient of a membrane, empirically defined by Eq. (1). In doing this deduction, we will give microscopic expressions for the macroscopic quantities, in particular for the constrictivity factor δ_c which strongly depends on the shape of the pore. In this form, we will study the porous medium in three different levels: (1) considering only the pore, (2) considering the pore inside a rectangular cell, and (3) considering a cell system composed of several pores.

Let us emphasize that the objective and the relevance of our study is that it constitutes a bridge between the microscopic arrangement and geometry of the pores and the effective diffusion coefficient given by Eq. (1), which contains important measurable quantities such as porosity, tortuosity, constriction, mass transfer coefficient, and internal effectiveness factors [4,63,64].

This work is organized as follows. In Sec. II A we will establish the effective resistance of a pore with basis only on conservation arguments. In Sec. II B we compare the flux of the pore-cell system in order to obtain a generalization of Eq. (4) for pores whose only geometric restriction is that the FJ equation is valid for them. In Sec. II C we generalize this method for a cell of multiple pores in order to relate the spatial diffusion coefficient $D_{FJ}(x)$ with D_m in Eq. (1). In Sec. III we illustrate how to compare the results of the FJ approach with those of the effective medium theory. Finally, in Sec. IV we discuss the scope and perspective of our work.

II. EFFECTIVE DIFFUSION COEFFICIENT OF A MEMBRANE OF NON-INTERCONNECTED PORES

In this section, first we will use the FJ scheme in order to calculate the resistance to diffusion that a single pore exerts over the flux of material. In this treatment, each section of the pore is seen as an individual resistance and, therefore, the total resistance is that of a series circuit. Then we will study the pore-cell system, where each individual pore is enclosed in a rectangular cell in such a way that the diminution of effective volume available is taken into account. This pore-cell system is specially convenient for artificial porous media where the geometry and the arrangement of multiple pores can be easily controlled [65–69]. Finally, we will extend these ideas to more general systems where the effect of diverse pore geometries in the same material can be considered simultaneously.

Let us consider a porous media of the parallel-capillary type. In these systems, the following conditions hold: (1) the material can be seen as a collection of non-interconnected pores, (2) all the pores are open to both extremes of the membrane and they do not connect with themselves, (3) the internal walls of the pores have geometries which can be approximated by continuous and differentiable functions, and (4) the characteristic width of the pore is much smaller than the longitudinal length of the pore. The first two hypotheses allow us to calculate averages over the material in a simple way. The last two hypotheses allow us to establish the validity of the reduction Fick-Jacobs system in every pore.

A. Internal resistance to the diffusive flux of a single pore

Let us consider a simple pore of longitudinal size L and width $w(x)$; see Fig. 1. We will assume that the pore is filled due to a difference of concentration at both sides of the membrane $\Delta C = C_N - C_0$. This concentration C corresponds approximately to the concentration C_{FJ} in Eq. (2) when the pore is long enough compared with its width. In this limit $w/L \ll 1/2$, the Fick-Jacobs approach holds [53] and, therefore, the effective diffusion coefficient derived from it can be used in order to estimate the local flux. The number of particles crossing a section of the pore can be measured by the flux H given by

$$H = \int_w \mathbf{J} \cdot \mathbf{dw}, \tag{5}$$

where $\mathbf{J}$ is the flow per unit of area. It should be noted that the concentrations $C \approx C_{FJ}$ have the same units of mol by unit of internal volume, and they should not be confused with the reduced concentration or density of probability $c = w(x)\, C_{FJ}$ used in the standard form of the Fick-Jacobs equation [48]. The advantages of using the average concentration are that it allows us to relate more easily the diffusion process with the external conditions at the pore and with possible chemical interactions since its physical interpretation is more direct; see Refs. [53,63].

Now, we subdivide the pore in N slices along the horizontal direction; see Fig. 1. The idea is that each slice represents an individual resistance to the flow that it is simple to calculate. The width of this subdivision is taken short enough in order to consider that the transversal area $w_n = w(x_n)$ of each slice is roughly constant at the point x_n. In the stationary state, we can consider that in each one of the N transverse areas the number of particles flowing per second is approximately constant. This is mass conservation. This means that H in Eq. (5) is constant for any transversal area w_n. Therefore

$$H = \int_{w_n} \mathbf{J}_n \cdot \mathbf{dw_n}. \tag{6}$$

If the FJ model is valid in the particular pore then we can assume that the flux per unit of transverse area along each slice obeys a reduced Fickean law of diffusion. This means that the effective flux along the pore can be calculated as

$$J = -D_{FJ}(x)\frac{\partial C}{\partial x}. \tag{7}$$

In terms of the discretization, the flow per unit of area in the nth slice is $J_n \approx -D_n(C_{n+1} - C_n)/\Delta x$ where $D_n = D_{FJ}(x_n)$ is the local value of the effective diffusion coefficient D_{FJ} near the nth slice; see Eq. (3). This is the major hypothesis of our work, since it establishes that the validity of the FJ scheme for an entire pore (which comprises the aspect relation of pore's wide and length) can be extended locally to small sections of the pore. Different forms of establishing the validity of the FJ approach are stated in Refs. [54–57]. We will use the criterion founded numerically in Ref. [53], $w/L \ll 1/2$. This hypothesis will be corroborated in Sec. III for some illustrative examples, in which we include a comparison with the numerical solution of the complete diffusion equation.

Now we will assume that the local deviations of flux along the transverse coordinates are not comparable with the total change of concentration along the longitudinal direction of the pore. This hypothesis is also required in the FJ approach [48,49]. In this case, the integral in Eq. (6) is

$$H = -\left[\frac{D_n\, w_n}{\Delta x}\right](C_{n+1} - C_n), \quad n = 1, \ldots, N. \tag{8}$$

In analogy with the language of electrical circuits, the quantity in square brackets can be seen as the inverse of the local resistance to the flux of each slice. This is

$$\rho_n = \frac{\Delta x}{D_n\, w_n}. \tag{9}$$

Therefore, ρ_n depends upon the local width of the pore, its length measured along the x coordinate, and the effective diffusion coefficient in a neighborhood of the slice. The *effective resistance of the pore* ρ_s can be defined through the equation

$$H = -\frac{1}{\rho_s}(C_N - C_0). \tag{10}$$

In order to obtain an expression for this total resistance ρ_s in terms of the individual resistances ρ_n, we may apply mathematical induction over the N slices accomplishing Eq. (8). The result is the same that for a circuit of resistances connected in series and, therefore, the total resistance of a pore is the sum of the individual resistances of each slice. This is

$$\rho_s \simeq \sum_{n=1}^{N} \rho_n. \tag{11}$$

In this expression, the symbol of approximation stands for the fact that the discrete result depends on the number of slices in which we divide the pore. Substituting Eq. (9) for individual resistances in the last equation and the fact that $\Delta x \to dx$ in the limit $N \to \infty$ (see Fig. 1), then ρ_s can be calculated in the limit of infinite slices. In this case, the sum over the N slices becomes an integral along the spatial coordinate x, and we have

$$\rho_s = \int_0^L \frac{1}{D_{FJ}(x)\, w(x)} dx. \tag{12}$$

In this expression, the longitudinal length of the pore L, i.e., its length measured along the direction of transport x, is not necessarily the same as the actual length of the pore L_z; see Fig. 1. According to these two characteristic lengths of the pore, the last equation can be written in two different ways. The first one is in terms of an average along the longitudinal coordinate x. If we define the spatial average along x as $\langle f(x)\rangle_X = \frac{1}{L}\int_0^L f(x)\, dx$, the last equation can be written as

$$\frac{\rho_s}{L} = \left\langle \frac{1}{D_{FJ}(x)\, w(x)} \right\rangle_X. \tag{13}$$

This expression remarks that the average in the brackets has the meaning of a *resistance per unit of longitudinal length* and was deduced by following similar arguments as in Ref. [56].

For our purpose about relating the effective macroscopic diffusion coefficient of a membrane with the local results provided by the FJ approximation, it is more convenient to introduce the auxiliary coordinate

$$z(x) = \int_0^x \sqrt{1 + h_x^2(x')}dx', \tag{14}$$

in order to express Eq. (12). This auxiliary coordinate $z(x)$ is measured along the middle line of the pore; see Fig. 1. Its value at $x = 0$ is zero and its value at $x = L$ is the actual length of the pore $z(L) = L_z$. Using Eq. (14), the ratio between both lengths can be written as

$$\frac{L_z}{L} = \langle\sqrt{1 + h_x^2(x)}\rangle_X. \tag{15}$$

In terms of the variable z, we can define the average along the middle line as $\langle f(z)\rangle_Z = \frac{1}{L_Z}\int_0^{L_z} f(z)\, dz$. In this variable, it is easy to prove that $1 + h_x^2 = (1 - h_z^2)^{-1}$ and $0 \leqslant h_z^2 \leqslant 1$. In these terms, Eq. (12) can be written as

$$\frac{\rho_s}{L_z} = \left\langle \frac{\sqrt{1 - h_z^2(z)}}{D_{FJ}(z)\, w(z)} \right\rangle_Z. \tag{16}$$

In this case, the average in brackets is taken along the middle line of the pore and therefore has the meaning of *resistance per unit of internal length*.

The relevance of Eqs. (13) and (16) for the purposes of the macroscopic description of mass diffusion in porous media emerges from two facts. The first is that they connect the microscopic geometric aspects of pore geometry with a macroscopic parameter, the resistance of the pore, which can be measured in uptake experiments consistent with Eq. (10). The second and more important is that they allow one to discern the physical meaning underlying the parameters introduced when it is assumed that the effective diffusion of a membrane obeys the empirically formulated Eq. (1). This is the central point, because it follows that the physical interpretation of Eqs. (13) and (16) should be crucial when comparing theory with experiments. For instance, although both equations give equivalent quantitative results when assessing the concentration distribution along a pore, as we do in Sec. III, the unique way to deduce a relation for the effective diffusion coefficient of a membrane consistent with Eq. (1), in particular after introducing the definition of the tortuosity τ parameter, is by choosing Eq. (16) as we will show in Sec. II B. The main consequence of this fact is that the constrictivity factor δ that is measured in experiments is related with the real resistance of the pores since it corresponds with the *resistance per unit of internal length* given in Eq. (16).

B. Effective diffusion of a pore-cell system

In this section we will focus on the importance of the solid material around the pore and how it affects the diffusive transport on a membrane. In order to do this, in this section we will consider a pore-cell system as the one depicted in Fig. 1. This system can be representative of a membrane only if the ratio between the void volume of the pore and cell is equivalent to the same ratio measured in the entire material. Let us consider the pore studied before inside a cell of length L and width W_c. Ignoring the particular shape of the pore, the effective diffusion coefficient of this cell D_c can be defined through the relation

$$H = -\frac{D_c W_c}{L}(C_N - C_0). \tag{17}$$

By proposing this equation, we are assuming that the longitudinal length L of the pore is the same that the length of the cell in order to fulfill the hypothesis that the pore is open to both ends. Furthermore, we are using the fact that the internal concentration at the extremes of the pore should be the same as the external concentration at both sides of the membrane. Now, we will use that the total flux of particles H must be the same as the flux in Eq. (10) since the particles cross the membrane only through the void space of the pore [6]. In this case, comparison between Eqs. (10) and (17) results in a relation between the effective diffusion coefficient of the cell and the resistance associated with the pore:

$$D_c = \frac{L}{W_c}\frac{1}{\rho_{s,c}}. \tag{18}$$

This equation identifies two types of dependencies in the effective diffusion coefficient. The first has to do with the internal structure of the pore in the cell through the term $\rho_{s,c}$. In this resistance we have added a subscript c in order to emphasize its relation with a specific cell. The second aspect is the relation between the relative sizes of the pore and the cell. In order to see this, let us define the *geometric porosity* of the cell ϕ_c in the usual way, i.e., as the ratio between the void volume and the volume of the cell [1,2,6]. This is

$$\phi_c = \frac{\int_0^L w(x)\,dx}{L\,W_c}. \tag{19}$$

This relation can be written in terms of the variables x and z as

$$\phi_c = \frac{1}{W_c}\langle w(x)\rangle_X = \frac{1}{W_c}\frac{L_Z}{L}\big\langle w(z)\sqrt{1-h_z^2(z)}\big\rangle_Z. \tag{20}$$

Now, let us define a *geometric tortuousness* of the pore as usual, i.e., as the square ratio between the actual length of the pore and the length along the longitudinal coordinate [70]. Using Eq. (15), this is

$$\tau_c = \left(\frac{L_z}{L}\right)^2 = \left[\big\langle\sqrt{1+h_x^2(x)}\big\rangle_X\right]^2. \tag{21}$$

It should be noted that by construction $\phi_c \leqslant 1$ and $\tau_q \geqslant 1$. In these terms, by using these definitions in Eq. (18), the effective diffusion coefficient of a cell can be written in two equivalent ways.

(a) *First form of the effective diffusion coefficient of a cell.* The first one is by using ρ_s as in Eq. (13). In this case, Eq. (18) is

$$\frac{\phi_c}{D_c} = \left\langle\frac{1}{D_{FJ}(x)\,w(x)}\right\rangle_X \langle w(x)\rangle_X. \tag{22}$$

From the comparison between Eqs. (4) and (22) it follows that D^* in Eq. (4) is a particular case of Eq. (22) when only the internal resistance of the pore is considered, since $D_c = \phi D^*$. As we will show later, this implies that the physical meaning of D^*/D_0 in Eq. (4) is closer to the concept of constriction factor than to the concept of effective diffusion coefficient. It is convenient to emphasize also that our Eq. (22) is valid for periodic and nonperiodic pores, as well as for horizontal and inclined pores as long as the FJ scheme is valid in the chosen geometry. This is a very important issue because most of the porous media do not function with restrictions such as being horizontal and periodic. This means that our generalization of the expression originally found by Festa and d'Agliano in Ref. [60] allows one to study more general membrane systems.

(b) *Second form of the effective diffusion coefficient of a cell.* The second way of writing Eq. (18) is by using ρ_s given by Eq. (16). In this case, both dependencies of Eqs. (19) and (21) enter in natural way into Eq. (18). Thus, we have

$$D_c = \frac{\phi_c}{\tau_c}\left[\left\langle\frac{\sqrt{1-h_z^2(z)}}{D_{FJ}(z)\,w(z)}\right\rangle_Z \big\langle w(z)\sqrt{1-h_z^2(z)}\big\rangle_Z\right]^{-1}. \tag{23}$$

This equation also relates the measured diffusion coefficient of a cell D_c and the local diffusion coefficient D_{FJ} obtained from the Fick-Jacobs scheme. However, the key point here is the physical meaning of the term in the parentheses. It that can be understood by substituting Eq. (3) in the last equation in terms of the variable z, that is, $D_{FJ}(z) = D_0(1+\frac{1}{12}w_z^2)/(1-h_z^2)$. In this case, as long as the constriction factor of the individual cell is

$$\frac{1}{\delta_c} = \left\langle\frac{[1-h_z^2(z)]^{3/2}}{[1+\frac{1}{12}w_z^2(z)]\,w(z)}\right\rangle_Z \big\langle w(z)\sqrt{1-h_z^2(z)}\big\rangle_Z, \tag{24}$$

then it is possible to write the effective diffusion coefficient of a cell exactly in the same form as it is given Eq. (1), that is, in the empirical form $D_c = D_0(\phi_c/\tau_c)\,\delta_c$.

The constriction factor (24) measures the change on cross section along the middle line of the pore. In order to clarify its meaning, let us consider the particular case of a horizontal pore, $h_x = h_z = 0$. In this case, using Eq. (3) we have $D_{FJ}/D_0 = 1 + w_x^2/12$, and the constriction factor δ_c is given by

$$\frac{1}{D_0\,\delta_c} = \left\langle\frac{1}{D_{FJ}(x)\,w(x)}\right\rangle_X \langle w(x)\rangle_X. \tag{25}$$

From this equation is clear that the constriction term considers the existence of funnels or throats through the factor w_x^2 in the local diffusion coefficient $D_{FJ}(x)$. When the last equation is compared with Eq. (4), we can conclude that the ratio $D^*/D_0 = \delta_c$ can be interpreted as a constriction factor in the context of diffusion in porous media. Therefore, D^* is related to the *resistance per unit of internal length* of the pore to flow due to the local changes in its width, and not to the *resistance per unit of longitudinal length.*

From the functional form of Eq. (24), it is expected that the effects of the constriction factor in the effective diffusion coefficient are strong only when the pore has significative tortuousness or inclination (measured mainly through h_x^2) or has large caves and throats (measured mainly by w_x^2).

Finally, Eq. (24) shows that splitting in three different aspects the diminution on the effective diffusion coefficient in Eq. (1) constitutes an artificial separation, because the aspects related with the width of the pore cannot be separated from the aspects related with the inclination or the constriction, at least for the kind of pores we are considering. In summary, the present study unravels these tacit dependencies, otherwise hidden in Eq. (1), and allows us to relate with precision the internal aspects of the pore geometry with the experimental characterization of membranes through the use of the porosity, the tortuosity, and the constriction factors, which have been largely used in the experimental study of porous materials and can be determined from uptake experiments.

C. Membrane composed of multiple pores

The results obtained in the previous section for a simple pore-cell system can be extended to membranes with multiple pores, as long as they are open to both extremes and do not connect with other pores. Assuming that each cell contains only one pore, the total flux across the membrane composed of M cells is just the sum of all the individual fluxes, i.e., $H_t = \sum_{c=1}^{M} H^{(c)}$, where the superscript c stands for the flux in each cell indexed by c. In this case, the total conductivity of the membrane $1/\rho_M$ is the sum of the individual conductivities as in a parallel circuit:

$$\frac{1}{\rho_M} = \sum_{c=1}^{M} \frac{1}{\rho_s^{(c)}}, \tag{26}$$

where each $\rho_s^{(c)}$ is given, according to Eq. (12), by

$$\rho_s^{(c)} = \int_0^L \frac{1}{D_{FJ}^{(c)}(x)\, w^{(c)}(x)} dx. \tag{27}$$

Since the membrane has width $W = MW_c$ and length L, the total flux is given by an equation similar to Eq. (17) but with the effective diffusion coefficient D_m of the membrane [6]. Therefore, we can deduce an expression equivalent to Eq. (18), where the total conductivity is the sum over the conductivities of all the pores. In this case,

$$D_m = \frac{L}{W} \sum_{c=1}^{M} \frac{1}{\rho_s^{(c)}}. \tag{28}$$

For a membrane composed by M cells, each one containing one pore, the porosity is defined as the sum of all internal volumes divided by the total volume. Using Eq. (19), we have

$$\phi_m = \frac{1}{L\, W} \sum_{c=1}^{M} \int_0^L w^{(c)}(x)\, dx, \tag{29}$$

where $w^{(c)}$ is the width of each pore. This equation can be written in terms of the discrete average over the pores $\overline{f_c}^M = \frac{1}{M} \sum_{c=1}^{M} f_c$, as the average over the total number of cells

$$\phi_m = \frac{\overline{\langle w^{(c)} \rangle_X}^M}{W/M}. \tag{30}$$

In this case, by using the last equation and Eq. (13) in Eq. (28), we have

$$D_m = \frac{\phi_m}{\overline{\langle w^{(c)}(x) \rangle_x}^M} \overline{\left\langle \frac{1}{D_{FJ}^{(c)}(x) w^{(c)}(x)} \right\rangle_X^{-1}}^M. \tag{31}$$

This equation proves that the diffusivity of a membrane depends on the average of the diffusivities of the pores. In the case of a membrane of infinite pores, the discrete average over the pores can be changed by a continuous average over the vertical direction as long as the probability distribution function of the internal geometry is known as a function of y. It is expected that the averages along the coordinates x and y cannot be interchanged, at least that some simplifications are carried out. This means that for this kind of material, a probability distribution function of the internal geometry given only in terms of lengths and cross sections of the pores in an element of volume does not seem an appropriate tool in the description of the effective flux [18–21]. However, in artificial materials where the pore shape and arrangement can be controlled [65–69] this is not a problem, since the model we have studied here provides the tools for studying with detail the membrane when the geometry and number of pores are known.

The deduction given in this section for the diffusion coefficient of a membrane composed of multiple pores may be very relevant in the context of diffusion in porous media because D_m, in Eq. (31), establishes the link of the internal diffusion measured by D_{FJ} inside each pore of a membrane with the key macroscopic quantities of interest in the engineering of reactors, such as the mass transfer coefficient and the effectiveness internal factor [63]. Nonetheless, in the next section we will concentrate our attention only on the relation between the microscopic and macroscopic flux in a single pore-cell system, leaving the numerical study of composite materials for a subsequent work.

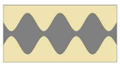
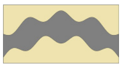
III. COMPARISON BETWEEN THE FLUXES IN PORE-CELL SYSTEMS

In order to illustrate the use of the effective diffusion coefficient given by Eq. (23) and its relation with the local diffusion coefficient of the FJ scheme, we will make a quantitative comparison of the total fluxes predicted by the FJ reduction scheme and the effective medium theory we have developed in this work with the numerical results arising from the two-dimensional diffusion equation. We will focus on the pore-cell systems depicted in Table I for two types of boundary conditions of great relevance in reactor engineering.

A. Net flux boundary conditions

We consider that the cell separates two regions of different concentration and, therefore, the boundary conditions at the pore ends are $C(x=0) = C_0$ and $C(x=L) = C_N = 0$ which

TABLE I. Pore-cell systems studied in Fig. 2. The three pores correspond to the wall functions $w_1(x) = \alpha_1 \sin(\alpha_3 \pi x/5) + \alpha_2 \sin(7\pi x/5)$ and $w_2(x) = 1 + \alpha_1 \sin(\alpha_3 \pi x/5) - \alpha_2 \sin(7\pi x/5)$. The values of α_i are given here for each pore. The local width is $w(x) = w_2(x) - w_1(x)$ and the middle line is $h(x) = (1/2)[w_1(x) + w_2(x)]$. The width of the cell is $W_c = 2.5$, and the length is $L = 5$ in all cases.

Pore	Cell	Geometry			Transport Parameters					Stat. Flux	
No.	$L = 5, W = 2.5$	α_1	α_2	α_3	ρ_s	ϕ_c	τ_c	D_c/D_0	δ_c	H_{FJ}	H_{cell}
1		0	0.4	1	12.4	0.386	1.0	0.167	0.433	0.082	0.083
2		0.8	0.2	1	7.09	0.401	1.12	0.293	0.822	0.142	0.141
3		0.6	0	2	6.42	0.416	1.27	0.324	0.99	0.158	0.156

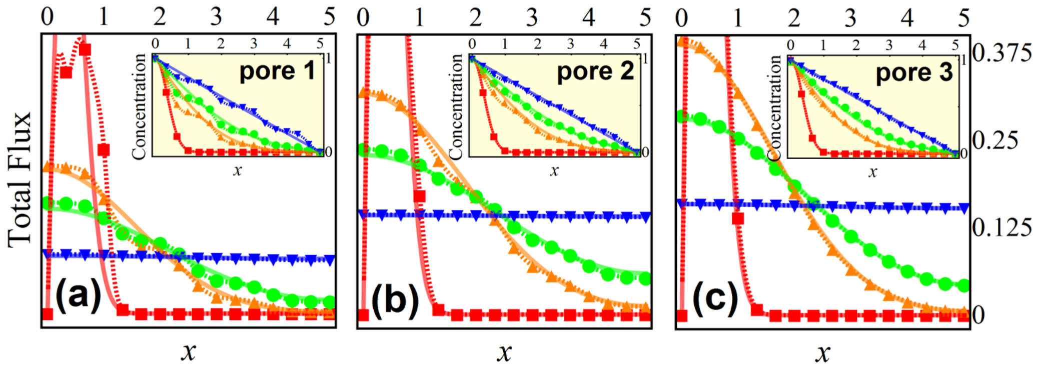


FIG. 2. Concentration (inset) and total fluxes as functions of position and time for net flux boundary conditions. The time is represented by different colors, red being the initial condition ($t = 0$) and blue the stationary state ($t_{\max}$). Intermediate values are $t_{\max}/10$ and $t_{\max}/5$ for orange and green, respectively. Each column corresponds to one pore depicted in Table I. The stationary time (blue color) was $t_{\max} = 25, 25$, and 15, respectively. The diffusion coefficient in the nonconfined situation was fixed at $D_0 = 1$.

correspond to nonequilibrium boundary conditions. For this study, we have chosen sinusoidal geometries due to their resemblance with zeolites.

First we have to check the validity of the FJ scheme in the three chosen geometries. In order to do so, we compare the solution of the Fick-Jacobs reduction model with the direct solution of the two-dimensional diffusion equation $\frac{\partial C_{2D}}{\partial t} = D_0 \nabla^2 C_{2D}$ [53]. In the insets of Fig. 2, we compare the average concentration given in Eq. (2) (dashed lines) with the average concentration obtained of the direct solution $C_{2Da}(x,t) = \frac{1}{\omega} \int C_{2D}(x,y,t)dy$ (markers) for four different times represented by colors; see Ref. [53] for details. Since the average concentration is almost the same in both cases $C_{FJ} \approx C_{2Da}$, we can conclude that the FJ model is valid for these three geometries, even for transient times and nonequilibrium conditions [53].

Once we have checked the validity of the FJ scheme in the pores, we compare the total fluxes given by the FJ model and the effective medium theory. The flux of particles inside the pore is just

$$H_{FJ}(x,t) = -D_{FJ}(x)\, w(x) \frac{dC_{FJ}}{dx}. \tag{32}$$

In this equation one can also use directly C_{2Da}; see Fig. 2. In both cases, this H_{FJ} represents the actual flux of particles inside the pore and it is based on the *microscopic* scale.

In order to use the effective medium theory for a cell, we have to find the auxiliary concentration of particles in the void volume of the pore C_{cell}. This concentration is related to the concentration measured over the entire volume of the cell C_V, through the relation $\phi C_{\text{cell}} = C_V$. This emphasizes the fact that C_V has a lower value since the number of particles is counted through the integration over the entire volume. Therefore, in order to compare these macroscopic results with C_{FJ} or C_{2Da}, one has to solve the effective one-dimensional diffusion equation:

$$\frac{\partial C_{\text{cell}}}{\partial t} = D^* \frac{\partial^2 C_{\text{cell}}}{\partial x^2}, \tag{33}$$

where the null effect of the solid space in counting the internal number of particles can be considered by removing the porosity from $D_c = \phi D^*$. In Fig. 2 we plot in solid lines the result of the macroscopic model for the expected internal concentration. Furthermore, the flux in the effective medium theory is just

$$H_{\text{cell}}(x,t) = -D_c W \frac{dC_{\text{cell}}}{dx}. \tag{34}$$

Here, D_c can be calculated using Eqs. (22) or (23) since at this level they provide equivalent information. This *macroscopic* flux is based on measurements of the porosity, tortuosity, and constrictivity of the pore. In order to calculate these parameters, in this theoretical work we have used Eqs. (19), (21), and (24), respectively. However, in real porous systems, the importance of this comparison is that these parameters can be measured independently by uptake experiments providing some information on the internal geometry of the system [3,4].

In Fig. 2 we compare the results for the flux and concentrations obtained by direct solution of the bidimensional equation (markers), by the Fick-Jacobs model (dashed lines), and by the macroscopic scheme we have presented in this work (solid lines). As can be seen, for the pores considered in this work, the microscopic Fick-Jacobs model and the macroscopic diffusion coefficient that we have derived from it give very good results in the approximate description of the transport inside this kind of porous structure. We have to emphasize that these results are applicable to periodic and nonperiodic pores as well as to horizontal structures, or those presenting some tortuousness. As we have shown, the only limitation of our results is dictated by the validity of the FJ scheme. As this validity is practically guaranteed for very long pores, this model constitutes a very precise tool able to describe and model the transport in very general porous materials.

The macroscopic diffusion coefficient we have deduced, D_m, provides remarkable good results not only for the stationary concentration profiles but, more importantly, it also gives very good approximations of the transient profiles. This fact is very relevant because, as we have mentioned, the transient profiles of concentration in experimental devices are used to adjust an effective diffusion coefficient [7]. Finally, our simple and intuitive approximation allows us to relate the microscopic structure of the pores with macroscopic quantities

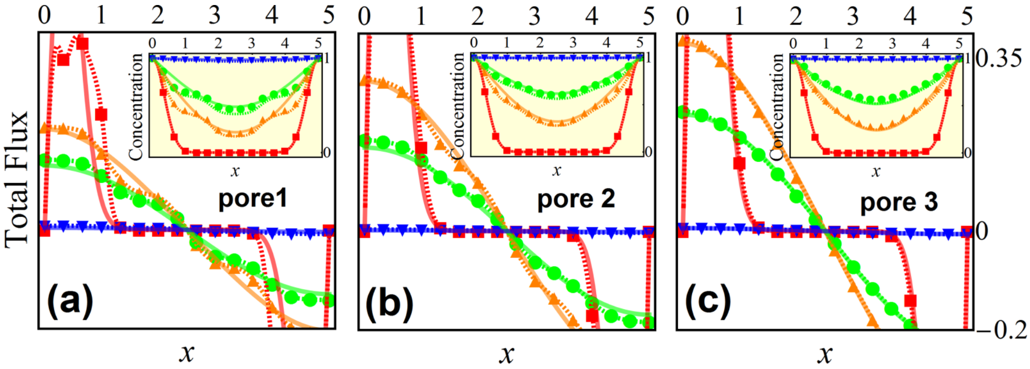


FIG. 3. Concentration (inset) and total fluxes as functions of position and time with the same parameters as in Fig. 2, but using saturation boundary conditions.

such as the porosity, tortuosity, and constriction factor in membranes. For the three examples of pore-cell systems considered, the internal resistance, porosity, tortuosity, diffusivity, and constriction factor found in Eqs. (13), (19), (21), (22), and (24), are respectively shown in Table I.

B. External conditions of saturation

In our deduction of the effective diffusion coefficient of a membrane D_m, Eq. (1), we have used a derivation based on mass conservation through a membrane whose ends are under a net flux due to a concentration difference. However, it is to be expected that, under certain restrictions, the validity of the previous arguments for an entire membrane hold also for small sections of the pore where the concentration difference becomes gradually closer to zero. Hence, one may expect that Eq. (22) could be also valid for a pore under saturation conditions. In this subsection we will show that this hypothesis is reasonable by using some numerical examples. It is important to note that these comparisons can be carried out also with analytical and not only numerical solutions for some particular pores as those obtained in Ref. [71].

Therefore, as in the previous section we will compare the results of the microscopic flux derived from the solution of Eqs. (2) and (32), and the macroscopic results derived from solving Eq. (33) and the flux Eq. (34). The difference with the last section is that now the concentration is the same at both sides of the pore, i.e., $C(x=0)=C(x=L)=C_0$. In Fig. 3 we show that the approximate scheme can be used also as a good approximation for the net fluxes of particles as a function of time in the case of saturation conditions. This is very important because the concentration profiles shown in the insets of Fig. 3 are the kind of spatiotemporal profiles that are recorded in pulse field gradient NMR and interference microscopy experiments [40,43].

In this work, the comparison between microscopic and macroscopic models in Eqs. (2) and (33) is made indirectly through the comparison of their fluxes [in Eqs. (32) and (34)] and also numerically in Figs. 2 and 3 for two different boundary conditions. However, a mathematical derivation of the identity between both schemes that allows us to establish the validity criteria on any of the two descriptions is still needed and constitutes a very interesting open problem in the description of porous media.

IV. DISCUSSION AND CONCLUSIONS

In this work we have found the relation between the spatial-dependent diffusion coefficient $D_{FJ}(x)$ of the Fick-Jacobs model and the effective diffusion coefficient of a membrane composed of parallel pores of irregular shape. In order to do so, we have used simple conservation arguments where each section of the pore is treated as an electric resistance. This has allowed us to generalize the well known expression found by Festa and d'Agliano [60] (whose validity was restricted to periodic and horizontal pores) to a new range of systems with geometries more similar to real porous materials. Besides, our approach has allowed us to give a closed expression for the constriction factor which, together with the porosity and tortuosity, is usually employed in the characterization of porous materials.

We have proved that the effective diffusion coefficient provides good results in estimating the concentration profiles and the stationary flux of particles. This success is based on the fact that we have related the internal geometry of the pore with macroscopic quantities related to the flux diminution. Although we have considered only a few illustrative examples in this work, the conclusions we have developed here let us to think that our expressions for the effective diffusion coefficient of a membrane in terms of the Fick-Jacobs coefficient can be used for any pore, as long as its length is much greater than its width. These achievements open a bridge between the Fick-Jacobs model and significant quantities in reactor design, and therefore constitute a powerful application of this theoretical formalism.

It is important to note that the fluxes established by the approximate reduced model in one dimension assess not only the stationary profile in equilibrium and nonequilibrium conditions but, with some negligible differences, it also can be used in estimating the concentration profiles in transient times. This means that for long pores where the Fick-Jacobs equation is valid, the information of the spatiotemporal profiles can be used in order to obtain the macroscopic diffusion coefficient measured in experimental methods of pulse field gradient NMR and interference microscopy. In these methods, the concentration inside a crystalline porous material can be tracked, and an effective diffusion coefficient is measured by adjusting to these profiles the solutions of an equation similar to Eq. (33) for the concentration. Notwithstanding that in these experiments the adsorption process takes a predominant role, in a future work we will generalize the results achieved here in order to include the presence of an adsorbed phase. However, the type of reasoning that we will use in that case is exactly the same as that which we use here when only the bulk diffusion is present.

Finally, an interesting aspect to study in the future is the relation between Eq. (31) and a possible distribution of pores over the entire volume. That is, we would like to know whether the two averages in Eq. (31), first along the longitudinal direction of transport (along x), and then along the vertical distribution of pores (along y), can be carried out independently. In other words, we want to know whether under some reasonable assumptions it is possible to use a volumetric distribution of the pore geometry as in the traditional parallel capillary models [19,20]. These models use hypotheses about the directionality of the pores and the flux at the junctions that are not necessarily fulfilled in systems like ours. However, in order to study this possibility, a study about the interconnection of pores using the FJ model should be carried out first.

ACKNOWLEDGMENTS

A.L.D. acknowledges CONACyT for financial support under Fellowship No. 221505. I.S.H. and S.I.H. acknowledge UNAM-DGAPA for financial support under Grant No. IN-116617. S.I.H. is grateful for DGTIC-UNAM Project No. LANCAD-UNAM-DGTIC-276.

[1] J. Van Brakel and P. Heertjes, Int. J. Heat Mass Transf. **17**, 1093 (1974).
[2] J. Hoogschagen, J. Ind. Eng. Chem. **47**, 906 (1955).
[3] C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis* (MIT Press, Massachusetts, 1970).
[4] H. S. Fogler, *Elements of Chemical Reaction Engineering* (Prentice-Hall International, London, 1999).
[5] F. A. Coutelieris and J. M. Delgado, *Transport Processes in Porous Media* (Springer Science & Business Media, Heidelberg, 2012).
[6] N. Epstein, Chem. Eng. Sci. **44**, 777 (1989).
[7] J. Kärger, D. M. Ruthven, and D. N. Theodorou, *Diffusion in Nanoporous Materials* (John Wiley & Sons, Weinheim, 2012).
[8] L. Shen and Z. Chen, Chem. Eng. Sci. **62**, 3748 (2007).
[9] C. F. Berg, Transp. Porous Media **103**, 381 (2014).
[10] L. Holzer, B. Iwanschitz, Th. Hocker, L. Keller, O. Pecho, G. Sartoris, P. Gasser, and B. Muench, J. Power Sources **242**, 179 (2013).
[11] D. Wiedenmann, L. Keller, L. Holzer, J. Stojadinović, B. Münch, L. Suarez, B. Fumey, H. Hagendorfer, R. Brönnimann, P. Modregger *et al.*, AIChE J. **59**, 1446 (2013).
[12] L. Holzer, D. Wiedenmann, B. Münch, L. Keller, M. Prestat, P. Gasser, I. Robertson, and B. Grobéty, J. Mater. Sci. **48**, 2934 (2013).
[13] M. Letellier, V. Fierro, A. Pizzi, and A. Celzard, Carbon **80**, 193 (2014).
[14] S. S. Manickam, J. Gelb, and J. R. McCutcheon, J. Membr. Sci. **454**, 549 (2014).
[15] A. C. Payatakes, C. Tien, and R. M. Turian, AIChE J. **19**, 58 (1973).
[16] A. Payatakes and M. A. Neira, AIChE J. **23**, 922 (1977).
[17] J. M. Zalc, S. C. Reyes, and E. Iglesia, Chem. Eng. Sci. **59**, 2947 (2004).
[18] A. S. Michaels, AIChE J. **5**, 270 (1959).
[19] D. Nicholson and J. Petropoulos, J. Phys. D: Appl. Phys. **1**, 1379 (1968).
[20] V. Burganos and S. V. Sotirchos, AIChE J. **33**, 1678 (1987).
[21] J. I. Freijer, Soil Sci. Soc. Am. J. **58**, 1067 (1994).
[22] D. Nicholson and J. Petropoulos, J. Phys. D: Appl. Phys. **6**, 1737 (1973).
[23] C. Tien, R. M. Turian, and H. Pendse, AIChE J. **25**, 385 (1979).
[24] C. Paraskeva, V. Burganos, and A. Payatakes, Chem. Eng. Commun. **108**, 23 (1991).
[25] F. A. Dullien, *Porous Media: Fluid Transport and Pore Structure* (Academic Press, San Diego, 2012).
[26] P. Adler, *Porous Media: Geometry and Transport* (Heinemann, Boston, 1992).
[27] J. Bear, *Dynamics of Fluids in Porous Media* (Dover Publications, New York, 1988).
[28] L.-F. Huang, M. Saito, M. Miyagi, and K. Wada, Appl. Opt. **32**, 2039 (1993).
[29] Z. Siwy, P. Apel, D. Dobrev, R. Neumann, R. Spohr, C. Trautmann, and K. Voss, Nucl. Instrum. Methods Phys. Res. **208**, 143 (2003).
[30] C. Ho, R. Qiao, J. B. Heng, A. Chatterjee, R. J. Timp, N. R. Aluru, and G. Timp, Proc. Natl. Acad. Sci. USA **102**, 10445 (2005).
[31] Y. Yamauchi, T. Nagaura, A. Ishikawa, T. Chikyow, and S. Inoue, J. Am. Chem. Soc. **130**, 10165 (2008).
[32] Y. Yang, J. Rosalie, L. Bourgeois, and P. A. Webley, Mater. Res. Bull. **43**, 2368 (2008).
[33] G. Mistura, A. Pozzato, G. Grenci, L. Bruschi, and M. Tormen, Nat. Commun. **4**, 2966 (2013).
[34] L. Juszczak, T. Fortuna, and K. Wodnicka, J. Food Eng. **54**, 103 (2002).
[35] Z. Siwy, E. Heins, C. C. Harrell, P. Kohli, and C. R. Martin, J. Am. Chem. Soc. **126**, 10850 (2004).
[36] Z. Siwy, L. Trofin, P. Kohli, L. A. Baker, C. Trautmann, and C. R. Martin, J. Am. Chem. Soc. **127**, 5000 (2005).
[37] M. Ali, B. Yameen, R. Neumann, W. Ensinger, W. Knoll, and O. Azzaroni, J. Am. Chem. Soc. **130**, 16351 (2008).
[38] B. Yameen, M. Ali, R. Neumann, W. Ensinger, W. Knoll, and O. Azzaroni, J. Am. Chem. Soc. **131**, 2070 (2009).
[39] L. Liu, J. Zhao, C.-Y. Yin, P. J. Culligan, and X. Chen, Phys. Chem. Chem. Phys. **11**, 6520 (2009).
[40] J. Kärger, T. Binder, C. Chmelik, F. Hibbe, H. Krautscheid, R. Krishna, and J. Weitkamp, Nat. Mater. **13**, 333 (2014).
[41] J. Kärger and R. Valiullin, Chem. Soc. Rev. **42**, 4172 (2013).
[42] L. Heinke and J. Kärger, New J. Phys. **10**, 023035 (2008).
[43] J. Kärger, P. Kortunov, S. Vasenkov, L. Heinke, D. B. Shah, R. A. Rakoczy, Y. Traa, and J. Weitkamp, Angew. Chem., Int. Ed. Engl. **45**, 7846 (2006).

[44] P. Kortunov, L. Heinke, S. Vasenkov, C. Chmelik, D. B. Shah, J. Kärger, R. A. Rakoczy, Y. Traa, and J. Weitkamp, J. Phys. Chem. B **110**, 23821 (2006).

[45] U. Schemmert, J. Kärger, C. Krause, R. Rakoczy, and J. Weitkamp, Europhys. Lett. **46**, 204 (1999).

[46] U. Schemmert, J. Kärger, and J. Weitkamp, Microporous Mesoporous Mater. **32**, 101 (1999).

[47] F. Stallmach and J. Kärger, Adsorpt.-J. Int. Adsorpt. Soc. **5**, 117 (1999).

[48] R. Zwanzig, J. Phys. Chem. **96**, 3926 (1992).

[49] D. Reguera and J. M. Rubi, Phys. Rev. E **64**, 061106 (2001).

[50] P. S. Burada, G. Schmid, D. Reguera, J. M. Rubi, and P. Hänggi, Phys. Rev. E **75**, 051111 (2007).

[51] A. M. Berezhkovskii, L. Dagdug, and S. M. Bezrukov, J. Phys. Chem. **143**, 164102 (2015).

[52] S. Martens, J. Löber, and H. Engel, Phys. Rev. E **91**, 022902 (2015).

[53] A. Ledesma-Durán, S. I. Hernández-Hernández, and I. Santamaría-Holek, J. Phys. Chem. C **120**, 7810 (2016).

[54] P. Kalinay and J. Percus, J. Phys. Chem. **122**, 204701 (2005).

[55] L. Dagdug and I. Pineda, J. Phys. Chem. **137**, 024107 (2012).

[56] R. M. Bradley, Phys. Rev. E **80**, 061142 (2009).

[57] S. Martens, G. Schmid, L. Schimansky-Geier, and P. Hänggi, Phys. Rev. E **83**, 051135 (2011).

[58] N. Ogawa, Phys. Lett. A **377**, 2465 (2013).

[59] A. Berezhkovskii, M. Pustovoit, and S. Bezrukov, J. Phys. Chem. **126**, 134706 (2007).

[60] R. Festa and E. G. d'Agliano, Physica A (Amsterdam) **90**, 229 (1978).

[61] L. Bosi, P. K. Ghosh, and F. Marchesoni, J. Phys. Chem. **137**, 174110 (2012).

[62] K. D. Dorfman and E. Yariv, J. Phys. Chem. **141**, 044118 (2014).

[63] A. Ledesma-Durán, S. I. Hernández-Hernández, and I. Santamaría-Holek, J. Phys. Chem. C **120**, 29153 (2016).

[64] E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems* (Cambridge University Press, New York, 2009).

[65] D.-H. Choi, G.-W. Yoon, J. W. Park, C. Ihm, D.-S. Lee, and J.-B. Yoon, J. Micromech. Microeng. **25**, 105007 (2015).

[66] S. Ranjan, S. T. Selvan, and Y. Zhang, Adv. Healthc. Mater. **1**, 354 (2012).

[67] P. Y. Apel, I. V. Blonskaya, S. N. Dmitriev, O. L. Orelovitch, A. Presz, and B. A. Sartowska, Nanotechnology **18**, 305302 (2007).

[68] C. C. Harrell, Z. S. Siwy, and C. R. Martin, Small **2**, 194 (2006).

[69] F. Sun, W. Cai, Y. Li, B. Cao, Y. Lei, and L. Zhang, Adv. Funct. Mater. **14**, 283 (2004).

[70] P. C. Carman, Trans. Instn. Chem. Engrs. **15**, 150 (1937).

[71] J. M. Romero, O. González-Gaxiola, and G. Chacón-Acosta, Int. J. Pure Appl. Math. **82**, 41 (2013).