Diffusion in the presence of cylindrical obstacles arranged in a square lattice analyzed with generalized Fick-Jacobs equation

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The generalized Fick-Jacobs equation is widely used to study diffusion of Brownian particles in three-dimensional tubes and quasi-two-dimensional channels of varying constraint geometry. We show how this equation can be applied to study the slowdown of unconstrained diffusion in the presence of obstacles. Specifically, we study diffusion of a point Brownian particle in the presence of identical cylindrical obstacles arranged in a square lattice. The focus is on the effective diffusion coefficient of the particle in the plane perpendicular to the cylinder axes, as a function of the cylinder radii. As radii vary from zero to one half of the lattice period, the effective diffusion coefficient decreases from its value in the obstacle free space to zero. Using different versions of the generalized Fick-Jacobs equation, we derive simple approximate formulas, which give the effective diffusion coefficient as a function of the cylinder radii, and compare their predictions with the values of the effective diffusion coefficient obtained from Brownian dynamics simulations. We find that both Reguera-Rubi and Kalinay-Percus versions of the generalized Fick-Jacobs equation lead to quite accurate predictions of the effective diffusion coefficient (with maximum relative errors below 4% and 7%, respectively) over the entire range of the cylinder radii from zero to one half of the lattice period.

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I. INTRODUCTION

This paper is devoted to diffusion of a point Brownian particle in the presence of identical parallel cylindrical obstacles arranged in a square lattice. The focus is on the effective diffusion coefficient, D_{eff} , of the particle in the plane perpendicular to the cylinders, which characterizes the particle motion on times when the displacement significantly exceeds the lattice period. To find D_{eff} , we consider an equivalent problem of diffusion on a plane containing impermeable disks arranged in a square lattice (Fig. 1(a)). A distinctive feature of this geometry is that D_{eff} is identical to the effective diffusion coefficient of the particle in a corresponding two-dimensional channel, two examples of which are shown in Figs. 1(b) and 1(c). One can approximately describe diffusion in such channels of varying width as one-dimensional diffusion along the channel axis in the presence of entropy potential using the generalized Fick-Jacobs (FJ) equation.² This one-dimensional description allows one to find D_{eff} by means of the Lifson-Jackson formula.²

This approach is realized in the present paper. As the disk/cylinder radius b increases from zero to its maximum value $b_{\text{max}} = l/2$, where l is the lattice period, D_{eff} decreases from its value D_0 in the obstacle free space to zero. We derive simple formulas giving the ratio D_{eff}/D_0 as a function of $b/b_{\text{max}} = \nu$ over the entire range of ν from zero to unity,

Eqs. (3.1), (3.3) and (3.4), using different versions of the generalized Fick-Jacobs equation. These formulas, together with the general approach, which is based on reformulation of the problem in terms of the Fick-Jacobs equation, are main results of the present paper. To check the accuracy of the formulas, we compare their predictions with the values of D_{eff}/D_0 obtained from Brownian dynamics simulations in Fig. 2 and give the relative errors of the predictions in Table I and in Fig. 3.

The problem of finding D_{eff} considered in the paper belongs to a broad class of problems of transport in composite media. Studies of these problems were pioneered by Maxwell³ and Rayleigh⁴ in the 19th century (see the history in the review article⁵) with the main focus on the effective conductivity of the medium. One of the two major approaches to the problem is the effective medium theory (EMT). Using this theory, one can find that the ratio D_{eff}/D_0 in the case under consideration is given by⁶

$$\frac{D_{\text{eff}}^{\text{EMT}}}{D_0} = \frac{1}{1 + \Phi} = \frac{1}{1 + \pi \nu^2/4}, \quad (1.1)$$

where $\Phi = \pi \nu^2/4$ is the surface fraction occupied by the disks. This formula is asymptotically exact as $\nu \rightarrow 0$. It accurately describes a smooth decrease of the ratio D_{eff}/D_0 from

FIG. 1. Schematic diagram of a square lattice of impermeable circular disks (panel (a)), representing cylindrical obstacles, and equivalent two-dimensional channels (panels (b) and (c)).

unity to 0.6, as ν increases from 0 to 0.8, and fails to predict sharp decrease of D_{eff}/D_0 as ν approaches unity (Fig. 2).

The second major approach suggested in a classical paper of Rayleigh⁴ allows one to find a formally exact solution for the conductivity of a regular composite media. The solution is an infinite series that should be truncated to find

the conductivity. One can use this solution to find D_{eff}/D_0 by means of the Einstein relation, and the concentration correction discussed by Kalnin *et al.*⁶ As ν approaches unity, more and more terms of the infinite series are required for accurate prediction of the conductivity. Keller⁷ proposed a method of finding the asymptotic behavior of the conductivity of a composite media containing a dense square array of nonconducting cylinders, which allows one to bypass summation of the infinite series. The method is based on two results obtained by Keller: the asymptotic behavior of the conductivity of a composite media containing a dense square array of perfectly conducting cylinders⁷ and the reciprocity theorem.^{7,8} The latter, in particular, establishes the relation between conductivities of composite medium containing identical square arrays of perfectly conducting and nonconducting cylinders. Following this way, we find the asymptotic behavior of the conductivity of the second media. Then using the Einstein relation and the concentration correction,⁶ we obtain

$$\frac{D_{eff}}{D_0} = \frac{\sqrt{2(1-\nu)}}{\pi(1-\pi\nu^2/4)}, \quad \nu \rightarrow 1. \quad (1.2)$$

This result without the concentration correction is given in Eq. (12.22b) of the book by Crank.⁹

In Ref. 10, the authors generalized Keller's result for the asymptotic behavior of the conductivity of a composite media containing a square array of perfectly conducting cylinders. They obtained an approximate formula, which gives the conductivity over the entire range of ν from zero to unity, reduces to Keller's result as $\nu \rightarrow 1$, and correctly predicts the asymptotic behavior of the conductivity in the opposite limit when $\nu = 0$. Using this formula, the reciprocity theorem, the Einstein relation, and the concentration correction⁶ mentioned above, we obtain an expression

$$\frac{D_{eff}}{D_0} = \frac{1}{(1-\pi\nu^2/4) \left(\frac{2}{\sqrt{1-\nu^2}} \arctan \sqrt{\frac{1+\nu}{1-\nu}} - \frac{\pi}{2} + 1-\nu \right)}, \quad (1.3)$$

which gives the ratio D_{eff}/D_0 as a function of ν for the entire range of ν from zero to unity, and reduces to the asymptotic behavior in Eq. (1.2) as $\nu \rightarrow 1$. Interestingly enough, we will see that the formula in Eq. (1.3) can be obtained using the regular Fick-Jacobs equation, which is a special case of the generalized Fick-Jacobs equation. The latter allows one to find more accurate formulas for D_{eff}/D_0 , which predict this ratio closer to the values obtained from the simulations.

"The relation between the variation in the obstacle density and in the effective diffusion coefficient in the high-crowding limit", which in our notations corresponds to ν close to unity is also considered in a recent paper.¹¹ The authors approach to the problem is based on the analysis of the mean first passage time of the particle diffusing on the plane with periodic obstacles to the bottleneck separating neighboring compartments. The asymptotic behavior of the ratio D_{eff}/D_0 obtained in Ref. 10 differs from the one in Eq. (1.2) by the

factor 0.5. Finally, we mention several related papers¹²⁻¹⁵ on directed transport in the presence of periodic arrays of cylindrical obstacles.

The outline of the present paper is as follows. In Sec. II, we briefly discuss the generalized Fick-Jacobs equation and general formulas for the effective diffusion coefficient of a point Brownian particle in a two-dimensional channel of periodically varying width. We use these formulas in Sec. III to find ν -dependences of the ratio D_{eff}/D_0 . To check the accuracy of these formulas, we compare their predictions with values of D_{eff}/D_0 obtained from Brownian dynamics simulations.

II. GENERAL RELATIONS

The generalized FJ equation describes diffusion in a symmetric channel of varying width $w(x)$, where the x -coordinate is measured along the centerline of the channel, as one-

dimensional diffusion along the channel axis,¹

$$\frac{\partial G}{\partial t} = \frac{\partial}{\partial x} \left\{ D(x) w(x) \frac{\partial}{\partial x} \left[\frac{G}{w(x)} \right] \right\}. \quad (2.1)$$

Here t is time, $G = G(x, t|x', t')$ is the particle propagator or the Green's function, and $D(x)$ is a position-dependent diffusion coefficient. One can find detailed discussion of the adiabatic elimination of fast variables leading to the generalized Fick-Jacobs equation in Ref. 16. The generalized FJ equation reduces to the ordinary FJ equation¹⁷ when the x -dependence of the position-dependent diffusion coefficient is neglected, $D(x) = D_0$. Introducing entropy potential $U_{ent}(x)$, counted from its value at $x = x_0$,

$$U_{ent}(x) - U_{ent}(x_0) = -k_B T \ln \left(\frac{w(x)}{w(x_0)} \right), \quad (2.2)$$

where k_B is the Boltzmann constant and T is the absolute temperature, one can write the generalized FJ equation as the Smoluchowski equation,

$$\frac{\partial G}{\partial t} = \frac{\partial}{\partial x} \left\{ D(x) e^{-\beta U_{ent}(x)} \frac{\partial}{\partial x} [e^{\beta U_{ent}(x)} G] \right\}, \quad (2.3)$$

where $\beta = 1/(k_B T)$.

When both $U_{ent}(x)$ and $D(x)$ are periodic functions with period l , one can find the effective diffusion coefficient of the particle using the Lifson-Jackson formula²

$$D_{eff} = \frac{1}{\langle e^{-\beta U(x)} \rangle \langle e^{\beta U(x)} / D(x) \rangle}, \quad (2.4)$$

where the angular brackets denote averaging over the period,

$$\langle f(x) \rangle = \frac{1}{l} \int_{-l/2}^{l/2} f(x) dx. \quad (2.5)$$

Using the definition of the entropy potential, Eq. (2.2), one can write D_{eff} in Eq. (2.4) as

$$D_{eff} = \frac{1}{\langle w(x) \rangle \langle 1/[D(x)w(x)] \rangle}. \quad (2.6)$$

We consider three expressions for the position dependent diffusion coefficient:

$$D(x) \approx D_{Zw}(x) = \frac{D_0}{1 + w'(x)^2/12}, \quad (2.7)$$

$$D(x) \approx D_{RR}(x) = \frac{D_0}{[1 + w'(x)^2/4]^{1/3}}, \quad (2.8)$$

$$D(x) \approx D_{KP}(x) = \frac{\arctan(w'(x)/2)}{w'(x)/2} D_0, \quad (2.9)$$

where $w'(x) = dw(x)/dx$, obtained by Zwanzig (Zw),¹ Reguera and Rubi (RR),¹⁸ and Kalinay and Percus (KP),¹⁹ respectively. Martens *et al.*²⁰ recently gave a new derivation of the Kalinay-Percus expression for $D(x)$, Eq. (2.9).

Substituting different expressions for $D(x)$, Eqs. (2.7)–(2.9), as well as $D(x) = D_0$, into Eq. (2.6), we arrive at different expressions for the effective diffusion coefficient

$$D_{eff}^{FJ} = \frac{D_0}{\langle w(x) \rangle \langle 1/w(x) \rangle}, \quad (2.10)$$

$$D_{eff}^{Zw} = \frac{D_0}{\langle w(x) \rangle \langle (1 + w'(x)^2/12)/w(x) \rangle}, \quad (2.11)$$

$$D_{eff}^{RR} = \frac{D_0}{\langle w(x) \rangle \langle (1 + w'(x)^2/4)^{1/3}/w(x) \rangle}, \quad (2.12)$$

$$D_{eff}^{KP} = \frac{D_0}{\langle w(x) \rangle \langle w'(x)/[2w(x) \arctan(w'(x)/2)] \rangle}. \quad (2.13)$$

In Sec. III, we study the v -dependences of the ratio D_{eff}/D_0 predicted by different approximate expressions given in Eqs. (2.10)–(2.13) for the geometry shown in Fig. 1(b), i.e., for $w(x)$ given by

$$w(x) = l - 2\sqrt{b^2 - x^2} H(b - |x|), \quad 0 \leq |x| \leq l/2, \quad (2.14)$$

where the x -coordinate is counted from the center of one of the disks and $H(z)$ is the Heaviside step function.

III. RESULTS

Performing the integrations required to find the averages entering into Eqs. (2.10)–(2.13) we obtain

$$\frac{D_{eff}^{FJ}}{D_0} = \frac{1}{\left(1 - \frac{\pi}{4} v^2\right) \left(\frac{2}{\sqrt{1-v^2}} \arctan \sqrt{\frac{1+v}{1-v}} - \frac{\pi}{2} + 1 - v \right)}, \quad (3.1)$$

$$\frac{D_{eff}^{Zw}}{D_0} = 0, \quad v \neq 0, \quad (3.2)$$

$$\frac{D_{eff}^{RR}}{D_0} = \frac{1}{\left(1 - \frac{\pi}{4} v^2\right) \left[v \int_0^{\pi/2} \frac{(\cos \varphi)^{1/3} d\varphi}{(1 - v \cos \varphi)} + 1 - v \right]}, \quad (3.3)$$

$$\frac{D_{eff}^{KP}}{D_0} = \frac{1}{\left(1 - \frac{\pi}{4} v^2\right) \left[v \int_0^{\pi/2} \frac{\sin \varphi d\varphi}{\varphi(1 - v \cos \varphi)} + 1 - v \right]}. \quad (3.4)$$

FIG. 2. Comparison of the approximate formulas in Eqs. (1.1), (3.1), (3.3), and (3.4) (curves) with the values of the effective diffusion coefficient obtained from Brownian dynamics simulations (symbols).

One can see that D_{eff}^{FJ}/D_0 in Eq. (3.1) is identical to D_{eff}/D_0 in Eq. (1.3) obtained using the expression for the conductivity reported in Ref. 9. This result can be improved using the Reguera-Rubi and Kalinay-Percus formulas for the position-dependent diffusion coefficient, Eqs. (2.8) and (2.9), while Zwanzig's formula for $D(x)$, Eq. (2.7), leads to $D_{eff}^{Zw} = 0$ since the integral, giving the average $\langle w'(x)^2/w(x) \rangle$, diverges when $\nu \neq 0$.

As $\nu \rightarrow 1$, the expressions in Eqs. (3.1), (3.3), and (3.4) take the asymptotic form given in Eq. (1.2). However, the small- ν asymptotic behaviors of these expressions are different. Keeping the first two terms in the Taylor expansion of the effective diffusion coefficient in ν , we find

$$\frac{D_{eff}^{FJ}}{D_0} \approx 1 - \frac{2}{3}\nu^3, \quad \nu \rightarrow 0, \quad (3.5)$$

$$\frac{D_{eff}^{RR}}{D_0} \approx 1 - \left[\int_0^{\pi/2} \frac{d\varphi}{(\cos \varphi)^{1/3}} - 1 \right] \nu, \quad \nu \rightarrow 0, \quad (3.6)$$

$$\frac{D_{eff}^{KP}}{D_0} \approx 1 - \left[\int_0^{\pi/2} \frac{\sin \varphi}{\varphi} d\varphi - 1 \right] \nu, \quad \nu \rightarrow 0, \quad (3.7)$$

while the exact asymptotic behavior of the effective diffusion coefficient in this limit is given by

$$\frac{D_{eff}}{D_0} \approx 1 - \Phi = 1 - \frac{\pi}{4}\nu^2, \quad \nu \rightarrow 0. \quad (3.8)$$

In Fig. 2 we show the ν -dependences predicted by Eqs. (3.1), (3.3), and (3.4) as well as the dependence given in Eq. (1.1), which is obtained using the effective medium theory in Ref. 6. Symbols in the figure show the values of the ratio D_{eff}/D_0 obtained from Brownian dynamics simulations. One can see that both D_{eff}^{RR}/D_0 and D_{eff}^{KP}/D_0 are in good agreement with the simulation results over the entire range of ν from zero to unity. The relative errors of different approximate formulas for the effective diffusion coefficient, Eqs. (1.1), (3.1), (3.3), and (3.4), are given in Table I and

TABLE I. Relative errors of different approximate formulas, Eqs. (3.1), (3.3), (3.4), and (1.1), in percents, given by $100 \times |D_{eff}^{th} - D_{eff}^{sim}|/D_{eff}^{th}$ where D_{eff}^{th} and D_{eff}^{sim} are theoretical and numerical values of the effective diffusion coefficient.

ν	FJ	RR	KP	EMT
0.1	<1.0	2.3	3.0	<1.0
0.2	2.7	3.3	4.7	<1.0
0.3	4.9	4.0	5.9	<1.0
0.4	8.2	3.4	5.8	<1.0
0.5	10.1	3.6	6.3	<1.0
0.6	11.2	3.7	6.4	<1.0
0.7	11.8	3.4	6.0	<1.0
0.8	11.1	3.0	5.2	2.7
0.9	7.6	3.4	5.0	12.5
0.95	4.8	3.3	4.5	34.4
0.98	2.8	2.6	3.3	90.5

in Fig. 3. For the formulas in Eqs. (3.3) and (3.4), the maximum errors do not exceed 4% and 7%, respectively. Thus, in the case under consideration the Reguera-Rubi formula for $D(x)$, Eq. (2.8), leads to a better approximation for D_{eff} than the Kalinay-Percus formula, Eq. (2.9), does. This is in contrast to the case of diffusion in a two-dimensional channel formed by periodic overlapping circles,²¹ where the Kalinay-Percus formula for $D(x)$ leads to the best approximation for the effective diffusion coefficient.

In conclusion, when a point Brownian particle diffuses in the presence of constraints, one can use the generalized Fick-Jacobs equation to describe the effect of varying constraint geometry on the particle motion. In the present paper, we show how this equation can be used to analyze the slowdown of unconstrained diffusion of the particle due to its “collisions” with the obstacles. In this way, we have been able to obtain approximate formulas which describe the effective diffusion coefficient over the entire range of the obstacle size with high accuracy.

FIG. 3. The relative error given in Table I as a function of $\nu = b/b_{max} = 2b/l$.

At the same time, it is well known^{1,16,18,19} that the reduction to the effective one-dimensional description is formally justifiable only when the channel width is a slowly varying function of x , $|w'(x)| \ll 1$. Using $w(x)$ in Eq. (2.14), one can see that $|w'(x)|$ diverges as $|x|$ tends to b , $|x| < b$. This means that the reduction is inapplicable near the edges of the obstacles. The question naturally arises: why do D_{eff}^{RR} and D_{eff}^{KP} , which are obtained on the basis of the one-dimensional description accurately describe D_{eff} ? We believe that this is a consequence of the compensation of errors. Therefore, our analysis should not be considered as an approximate theory; rather, it is as an attempt to construct formulas for D_{eff} and to check their accuracy by comparison with numerical results.

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