Diffusion in a two-dimensional channel with curved midline and varying width: Reduction to an effective one-dimensional description

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Diffusion in a narrow two-dimensional channel with a midline that need not be straight and a width that may vary is reduced to an effective one-dimensional equation of motion. This equation takes the form of the Fick-Jacobs equation with a spatially varying effective diffusivity. The effective diffusivity includes a contribution that comes from the slope of the midline as well as the usual term stemming from variations in the channel width along the length of the channel. Our derivation of our equation of motion is completely rigorous and is based on an asymptotic expansion in a small dimensionless parameter that characterizes the channel width. For a channel that has a straight midline or wall, our equation of motion reduces to Zwanzig's equation [R. Zwanzig, J. Phys. Chem. **96**, 3926 (1992)]. Our derivation therefore provides a rigorous proof of the validity of the latter equation. Finally, the equation of motion is solved analytically for channels with curved midline and constant width.

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I. INTRODUCTION

The problem of diffusion in a narrow channel arises in many contexts and is important in biology, chemistry, and nanotechnology. Channels of current interest include pores in zeolites [1], carbon nanotubes [2], serpentine channels in microfluidic devices [3], artificially produced pores in thin solid films [4], and channels in biological membranes [5].

The subject of the present paper is diffusion in a two-dimensional (2D) channel that lies in the $X-Z$ plane and has hard walls. The diffusing particles are confined to the region with $H_-(X)<Z<H_+(X)$ and arbitrary X, where H_+ and H_- are smooth single-valued functions of X but are otherwise arbitrary. We will develop an approximate one-dimensional (1D) equation of motion that is a good approximation for narrow channels and for sufficiently long times T.

This problem has already been studied in depth for channels with $H_-(X)=0$ for all X, and, equivalently, for channels that have $H_-(X)=-H_+(X)$ and so are symmetric under reflection about the X axis [6–17]. For a narrow symmetric channel, the midline is straight and the lowest-order approximation is the Fick-Jacobs (FJ) equation [6]. The number density of particles Φ is taken to have reached equilibrium locally in this approximation, so that Φ is independent of Z. In his classic paper on the topic, Zwanzig developed an effective 1D equation of motion that is an improvement on the FJ equation because it includes the lowest-order deviation from local equilibrium [7]. Unfortunately, Zwanzig made a number of unjustified assumptions in deriving his equation and so was compelled to test its validity by comparing its predictions to two exactly solvable special cases. A more convincing derivation of the Zwanzig equation was given by Kalinay and Percus (KP), who also developed an equation that includes the lowest-order correction to the Zwanzig equation [9]. Although their work was an important step toward placing the Zwanzig equation on a firm theoretical foundation, KP assumed that knowledge of the density averaged over the channel width is all that is needed to determine the density throughout the channel. It is not at all obvious that this assumption is correct and so the validity of the Zwanzig equation could still be called into question, despite its widespread usage. Indeed, tests of the Zwanzig equation for 2D channels and its counterpart for three-dimensional tubes continue to appear in the literature [9,14,15].

The channels that occur in nature as a rule have a curved midline, and frequently artificially produced channels do as well. With this as our motivation, in this paper we will generalize the FJ and Zwanzig equations to narrow asymmetric 2D channels. Our derivation of these equations, which is based on an asymptotic expansion in a small dimensionless parameter ϵ that characterizes the channel width, is completely rigorous and the KP assumption is not needed. The FJ equation is valid to zeroth order in ϵ and is found to take on the same form for both symmetric and asymmetric channels. The generalized Zwanzig equation is valid to first order in ϵ. The effective diffusivity that appears in this equation includes a contribution that comes from variations in the channel midline height $S(X)\equiv[H_+(X)+H_-(X)]/2$ as well as the well-known term stemming from changes in the channel width $W(X)\equiv H_+(X)-H_-(X)$. The special case in which the channel width W is constant is analyzed in some detail, as it is relevant to diffusion within a narrow crack and the effective 1D equation of motion is especially simple. Finally, for symmetric channels, the KP assumption is demonstrated to be valid to order ϵ^2.

The paper is organized as follows: The problem is stated precisely and is then reformulated in dimensionless form in Sec. II. In Sec. III, we carry out the asymptotic expansion in the small parameter ϵ. These results are used in Sec. IV to reduce the full 2D problem to an effective 1D description, yielding the Fick-Jacobs and generalized Zwanzig equations. We also explore some of the consequences of the generalized Zwanzig equation in Sec. IV. The KP assumption is shown to be valid to second order in ϵ in Sec. V. In Sec. VI, we give our conclusions.

II. FORMULATION OF THE PROBLEM

Consider the diffusion of a large number of pointlike identical noninteracting particles in a 2D channel that lies in the $X-Z$ plane and that has hard walls at $Z=H_+(X)$ and $Z=H_-(X)$. We assume that $H_+(X)$ and $H_-(X)$ are smooth single-valued functions of X and that $H_+(X)>H_-(X)$. The number density of particles at the point (X,Z) at time T will be denoted by $\Phi(X,Z,T)$; stated more explicitly, the number of particles in the region $(X,X+dX)\times(Z,Z+dZ)$ at time T is $\Phi(X,Z,T)dXdZ$. The equation of motion is the 2D diffusion equation

$$\Phi_T = D(\Phi_{XX} + \Phi_{ZZ}), \tag{1}$$

where D is the diffusivity and subscripts denote partial derivatives (and so, for example, $\Phi_T=\partial\Phi/\partial T$). Since the channel walls are impenetrable, the diffusive flux thorough the walls must vanish, i.e.,

$$\Phi_Z(X,H_+(X),T) = H_{+X}(X)\Phi_X(X,H_+(X),T) \tag{2}$$

and

$$\Phi_Z(X,H_-(X),T) = H_{-X}(X)\Phi_X(X,H_-(X),T), \tag{3}$$

for arbitrary X and T.

Our goal is to develop an approximate equation of motion for

$$G(X,T) \equiv \int_{H_-(X)}^{H_+(X)} \Phi(X,Z,T)dZ \tag{4}$$

that is valid for narrow channels. [Note that $G(X,T)dX$ is the number of particles between X and $X+dX$ at time T.] We will sometimes find it more convenient to work with the number density averaged over the channel width $\Psi(X,T)\equiv G(X,T)/W(X)$ rather than with G.

We assume that

$$H_\pm(X) = L_Z F_\pm\left(\frac{X}{L_X}\right), \tag{5}$$

where the functions F_+ and F_- do not depend on a length scale. Thus, L_X and L_Z are characteristic lengths in the X and Z directions, respectively. In the case of a periodic channel, L_X is simply the spatial period and L_Z is proportional to the mean channel width.

We introduce the dimensionless variables $x\equiv X/L_X$, $z\equiv Z/L_Z$, $t\equiv DT/L_X^2$, $h_\pm\equiv H_\pm/L_Z$, $w\equiv W/L_Z$, $s\equiv S/L_Z$, $\phi\equiv L_XL_Z\Phi$, and $\psi\equiv L_XL_Z\Psi$. Setting $\epsilon\equiv(L_Z/L_X)^2$, we obtain

$$\epsilon\phi_t = \phi_{zz} + \epsilon\phi_{xx} \tag{6}$$

for $h_-(x)<z<h_+(x)$ and arbitrary x,

$$\phi_z = \epsilon h_{+x}\phi_x \quad \text{for } z=h_+ \tag{7}$$

and

$$\phi_z = \epsilon h_{-x}\phi_x \quad \text{for } z=h_-. \tag{8}$$

III. ASYMPTOTIC EXPANSION

We are interested in narrow channels, or, equivalently, channels with slowly varying H_+ and H_-. Accordingly, we will suppose that $\epsilon=(L_Z/L_X)^2$ is small. For small ϵ, the density ϕ may be expanded in powers of ϵ: we set

$$\phi = \sum_{n=0}^{\infty} \epsilon^n \phi_n(x,z,t), \tag{9}$$

where the ϕ_n's are independent of ϵ. We will seek solutions in which $t=\epsilon DT/L_Z^2$ is of order unity, which means that T must be large compared to the transverse diffusion time L_Z^2/D for these solutions to be valid. From a physical standpoint, these solutions are a good approximation to the full 2D dynamics when local equilibrium has nearly been reached.

We next insert the expansion (9) into Eqs. (6)–(8) and equate like powers of ϵ. For $n\geq 0$, this yields

$$\phi_{nzz} = \phi_{n-1,t} - \phi_{n-1,xx} \quad \text{for } h_- \leq z \leq h_+, \tag{10}$$

$$\phi_{nz} = h_{+x}\phi_{n-1,x} \quad \text{for } z=h_+, \tag{11}$$

and

$$\phi_{nz} = h_{-x}\phi_{n-1,x} \quad \text{for } z=h_-, \tag{12}$$

where $\phi_{-1}\equiv 0$.

For $n=0$, Eq. (10) shows that ϕ_{0z} is independent of z. Equations (11) and (12) imply that in fact $\phi_{0z}=0$ for all x and t. We conclude that ϕ_0 depends only on x and t, and write

$$\phi_0 = \theta_0(x,t). \tag{13}$$

For $n=1$, Eq. (10) gives

$$\phi_{1zz} = \theta_{0t} - \theta_{0xx}, \tag{14}$$

where Eq. (13) has been employed. Integrating this with respect to z, we have

$$\phi_{1z} = (\theta_{0t} - \theta_{0xx})z + f_1, \tag{15}$$

where f_1 depends only on x and t and $h_-\leq z\leq h_+$. The boundary conditions (11) and (12) show that

$$h_{+x}\theta_{0x} = (\theta_{0t} - \theta_{0xx})h_+ + f_1 \tag{16}$$

and

$$h_{-x}\theta_{0x} = (\theta_{0t} - \theta_{0xx})h_- + f_1. \tag{17}$$

Subtraction of the latter equation from the former yields $w_x\theta_{0x}=(\theta_{0t}-\theta_{0xx})w$ or

$$w\theta_{0t} = \partial_x(w\theta_{0x}). \tag{18}$$

As we shall see in the next section, Eq. (18) is the generalization of the FJ equation to asymmetric channels.

Using Eq. (17) to eliminate f_1 from Eq. (15) and setting

$$b_2(x) \equiv (h_+h_{-x} - h_-h_{+x})/w \tag{19}$$

and

$$b_3(x) \equiv w_x/w, \tag{20}$$

we obtain $\phi_{1z}=(b_3z+b_2)\theta_{0x}$. Integrating with respect to z once again, we have

$$\phi_1 = \left(\frac{1}{2}b_3z^2 + b_2z\right)\theta_{0x} + \theta_1, \tag{21}$$

where θ_1 depends only on x and t.

We now move on to the case $n=2$. For convenience, we set

$$c_j \equiv b_j \partial_x \left[\frac{1}{w} \partial_x (w \theta_{0x}) \right] - \partial_x^2 (b_j \theta_{0x}) \tag{22}$$

for $j=2$ and 3; note that c_2 and c_3 depend only on x and t. Using Eqs. (18) and (21) in the $n=2$ version of Eq. (10), we obtain

$$\phi_{2zz} = \theta_{1t} - \theta_{1xx} + c_2 z + \frac{1}{2} c_3 z^2. \tag{23}$$

Integration of Eq. (23) with respect to z yields

$$\phi_{2z} = (\theta_{1t} - \theta_{1xx}) z + \frac{1}{2} c_2 z^2 + \frac{1}{6} c_3 z^3 + f_2, \tag{24}$$

where $f_2 = f_2(x,t)$. We now insert Eqs. (21) and (24) into Eqs. (11) and (12) with $n=2$ and take the difference of the resulting two equations. This gives

$$w\theta_{1t} - \partial_x (w \theta_{1x}) = \sum_{j=2}^{3} \left\{ \partial_x [a_j \partial_x (b_j \theta_{0x})] - a_j b_j \partial_x \left[\frac{1}{w} \partial_x (w \theta_{0x}) \right] \right\}, \tag{25}$$

where

$$a_j \equiv \frac{1}{j!} (h_+^j - h_-^j). \tag{26}$$

For present purposes, we will not need to consider n values greater than 2. However, we can obtain corrections to the FJ equation of any desired degree of accuracy by considering larger values of n. Unfortunately, the calculations grow more complex with each successive increase in n.

IV. REDUCTION TO AN EFFECTIVE ONE-DIMENSIONAL DESCRIPTION

In this section, we will develop an approximate equation of motion for $G=G(X,T)$ that is valid for narrow channels and sufficiently long times T. As a preliminary observation, note that Eq. (9) implies that

$$\psi = \sum_{n=0}^{\infty} \epsilon^n \psi_n(x,t), \tag{27}$$

where

$$\psi_n(x,t) = \frac{1}{w(x)} \int_{h_-(x)}^{h_+(x)} \phi_n(x,z,t) dz. \tag{28}$$

We will first derive a 1D equation of motion that is valid to zeroth order in ϵ. Using Eq. (13), we see that

$$\psi_0 = \theta_0. \tag{29}$$

Equation (18) shows that

$$w\psi_{0t} = \partial_x (w \psi_{0x}). \tag{30}$$

To zeroth order in ϵ, $\psi = \psi_0$ and Eq. (30) may be written

$$w\psi_t = \partial_x (w \psi_x). \tag{31}$$

In terms of the original, dimensional variables, Eq. (31) is

$$W\Psi_T = D \partial_X (W \Psi_X) \tag{32}$$

or

$$\frac{\partial G}{\partial T} = D \frac{\partial}{\partial X} \left[W \frac{\partial}{\partial X} \left(\frac{G}{W} \right) \right]. \tag{33}$$

Equation (33) is the FJ equation [6]. It is valid to zeroth order in ϵ, and applies to both symmetric and asymmetric channels. To zeroth order in ϵ, $\phi(x,z,t) = \psi(x,t)$, and so the density of diffusing particles is independent of z to this order. Thus, in this approximation, local equilibrium has been reached.

We now turn to developing an equation of motion that is valid to first order in ϵ. Equation (21) gives

$$\psi_1 = \theta_1 + (a_2 b_2 + a_3 b_3) \theta_{0x} / w. \tag{34}$$

Differentiating this with respect to time and using Eqs. (18) and (25), we find that

$$w\psi_{1t} = \partial_x (w \theta_{1x}) + \sum_{j=2}^{3} \partial_x [a_j \partial_x (b_j \theta_{0x})]. \tag{35}$$

In this paragraph, we will work to first order in ϵ. Utilizing Eqs. (30) and (35), we have

$$w\psi_t = \partial_x [w(\theta_{0x} + \epsilon \theta_{1x})] + \epsilon \sum_{j=2}^{3} \partial_x [a_j \partial_x (b_j \psi_x)]. \tag{36}$$

On the other hand,

$$\psi = \psi_0 + \epsilon \psi_1 = \theta_0 + \epsilon \theta_1 + \epsilon (a_2 b_2 + a_3 b_3) \theta_{0x} / w \tag{37}$$

and so

$$\partial_x (w \psi_x) = \partial_x [w(\theta_{0x} + \epsilon \theta_{1x})] + \epsilon \partial_x \{ w \partial_x [(a_2 b_2 + a_3 b_3) \psi_x / w] \}. \tag{38}$$

Subtraction of Eq. (38) from Eq. (36) yields

$$w\psi_t - \partial_x (w \psi_x) = -\epsilon \sum_{j=2}^{3} \partial_x \left[w \partial_x \left(\frac{a_j}{w} \right) b_j \psi_x \right]. \tag{39}$$

Equation (39) is the desired equation of motion. It takes on a more illuminating form when h_+ and h_- are eliminated in favor of the dimensionless channel width $w(x) = h_+(x) - h_-(x)$ and the dimensionless channel midline height $s(x) = [h_+(x) + h_-(x)]/2$. This gives

$$w\psi_t = \partial_x \left\{ w \left[1 - \epsilon \left(s_x^2 + \frac{1}{12} w_x^2 \right) \right] \psi_x \right\}. \tag{40}$$

Equation (40) is phrased in terms of the dimensionless variables. In terms of the original, dimensional variables, it becomes

$$W\Psi_T = D \partial_X \left[W \left(1 - S_X^2 - \frac{1}{12} W_X^2 \right) \Psi_X \right] \tag{41}$$

or

$$\frac{\partial G}{\partial T} = D \frac{\partial}{\partial X} \left[W \left(1 - S_X^2 - \frac{1}{12} W_X^2 \right) \frac{\partial}{\partial X} \left(\frac{G}{W} \right) \right]. \tag{42}$$

Equation (42) is valid to first order in ϵ. For a symmetric channel, $S(X)=0$ for all X and Eq. (42) reduces to the Zwanzig equation [7]. Thus, the Zwanzig equation has been rigorously shown to be valid to first order in ϵ. Equation (42)—which generalizes the Zwanzig equation to asymmetric channels—takes the form of the FJ equation with a spatially varying diffusivity

$$D_{\text{eff}}(X) \equiv D\left(1 - S_X^2 - \frac{1}{12}W_X^2\right). \tag{43}$$

The effective diffusivity $D_{\text{eff}}(X)$ includes a term coming from the variation of the channel width W with X, as well as a contribution that stems from the X dependence of the channel midline height S. As first noted by Zwanzig [7], a change in the channel width produces a reduction in the effective diffusivity $D_{\text{eff}}(X)$ whether the change is an increase or a decrease in W. A variation in the channel midline height S with X also leads to a reduced $D_{\text{eff}}(X)$. To gain a physical understanding of this, consider a channel with constant width. If the midline height S varies with X, a diffusing particle must travel a greater distance in moving from one X value to another than it would if S were simply a constant. In the equivalent 1D description, this is manifested in a reduced $D_{\text{eff}}(X)$ for the case in which S varies with X.

In general, it is not possible to solve the generalized Zwanzig equation (42) analytically. The special case in which the channel width W is a constant independent of position is especially simple, however, and the generalized Zwanzig equation can be solved for arbitrary initial conditions. This special case is also of physical interest because a channel with a width that is very nearly constant can be formed simply by making a crack in a solid. Suppose that initially $\psi=f(x)$. If w is a constant, Eq. (40) reduces to

$$\psi_t = \partial_x[(1-\epsilon s_x^2)\psi_x], \tag{44}$$

which takes the form of the 1D diffusion equation with spatially varying diffusivity $1-\epsilon s_x^2$. Setting $\psi=\psi_0+\epsilon\psi_1$ in Eq. (44) and equating terms of the same order in ϵ, we obtain

$$\psi_{0t} - \psi_{0xx} = 0 \tag{45}$$

and

$$\psi_{1t} - \psi_{1xx} = -\partial_x(s_x^2\psi_{0x}). \tag{46}$$

These equations must be solved subject to the initial conditions $\psi_0(x,0)=f(x)$ and $\psi_1(x,0)=0$. Equation (45) is just the homogeneous 1D diffusion equation and is of course exactly solvable for arbitrary initial conditions. Explicitly, for $t>0$ we have

$$\psi_0(x,t) = \int_{-\infty}^{\infty} G(x-x',t)\psi_0(x',0)dx', \tag{47}$$

where

$$G(x,t) = \frac{1}{2\sqrt{\pi t}}\exp\left(-\frac{x^2}{4t}\right)H(t) \tag{48}$$

is the Green's function for the 1D diffusion equation and $H(t)$ is the Heaviside function. Equation (46) is the inhomogeneous 1D diffusion equation with an inhomogeneous term $q\equiv -\partial_x(s_x^2\psi_{0x})$ that is known exactly by virtue of Eq. (47). Applying the initial condition $\psi_1(x,0)=0$, we obtain

$$\psi_1(x,t) = \int_0^t dt' \int_{-\infty}^{\infty} dx' G(x-x',t-t')q(x',t). \tag{49}$$

Together, Eqs. (47) and (49) give the solution to the initial value problem $\psi=\psi_0+\epsilon\psi_1$ to first order in ϵ.

The generalized Zwanzig equation has a number of interesting applications, two of which we will consider here. First, suppose a single particle is present in a periodic channel. For short times T, the mean-square displacement of the particle $\overline{[X(T)-X(0)]^2}$ is $2DT$. At long times, on the other hand, the mean-square displacement tends to $2D^*T$, where the constant D^* will be referred to as the asymptotic diffusivity. To find D^*, we set $W(X)=\exp[-\beta V(X)]$ in the generalized Zwanzig equation (42) and so obtain

$$G_T = \partial_X[D_{\text{eff}}(X)(G_X + \beta V_X G)]. \tag{50}$$

Equation (50) is formally identical to the Smoluchowski equation for a particle with spatially varying diffusivity $D_{\text{eff}}(X)$ moving in 1D in the presence of the periodic external potential $V(X)$ if the ambient temperature is $(k_B\beta)^{-1}$. The asymptotic diffusivity for this problem is given by

$$\frac{1}{D^*} = \langle \exp(\beta V) D_{\text{eff}}^{-1}(X)\rangle\langle\exp(-\beta V)\rangle, \tag{51}$$

where the angular brackets denote an average over one spatial period [18,19]. As a consequence, for a particle in a periodic channel,

$$\frac{1}{D^*} = \frac{1}{D}\left\langle\left[W\left(1 - S_X^2 - \frac{1}{12}W_X^2\right)\right]^{-1}\right\rangle\langle W\rangle. \tag{52}$$

Equation (52) generalizes Zwanzig's result for symmetric channels [7] to asymmetric channels and shows that spatial variations in the midline height result in a reduced asymptotic diffusivity D^*.

An approximate expression for the asymptotic diffusivity has already been found for particular type of periodic 2D channel with a curved midline—a so-called serpentine channel [3]. For a periodic serpentine channel, the height of the midline S is a periodic function of X with period L_X. The walls of the channel are by definition the loci of points situated at a fixed distance δ from the midline. Let

$$l \equiv \int_0^{L_X} \sqrt{1+S_X^2}\,dX \tag{53}$$

be the arclength of one period of the midline. Yariv *et al.* [3] showed that for small δ/l (i.e., for a narrow channel), the asymptotic diffusivity of the channel is to leading order

$$D^* = D\left(\frac{L_X}{l}\right)^2. \tag{54}$$

Let us apply our result [Eq. (52)] to a serpentine channel and compare with Eq. (54). In terms of the dimensionless variables, Eq. (52) is

$$\frac{D}{D^*} = \int_0^1 \frac{dx}{w\left[1-\epsilon\left(s_x^2+\frac{1}{12}w_x^2\right)\right]}\int_0^1 w dx. \tag{55}$$

The dimensionless width of a serpentine channel is

$$w = \frac{2\delta}{L_Z}\left(1+\frac{1}{2}\epsilon s_x^2\right) \tag{56}$$

to first order in ϵ. Inserting this into Eq. (55), we find that to order ϵ

$$\frac{D}{D^*} = \left(\int_0^1 \sqrt{1+\epsilon s_x^2}dx\right)^2 = \left(\frac{1}{L_X}\int_0^{L_X} \sqrt{1+S_X^2}dx\right)^2. \tag{57}$$

Using Eq. (53), we recover Eq. (54), which shows that our result agrees with that of Yariv *et al.* to first order in ϵ.

Yariv *et al.* also found the lowest order correction to Eq. (54), yielding an approximate expression for D^* that is considerably more accurate than ours [3]. The result of Yariv *et al.*, though, only applies to serpentine channels and so is much less general than our result [Eq. (52)].

As a second application of the generalized Zwanzig equation, consider a narrow channel of length L_X that joins reservoirs of fixed number density in the regions $X\leq 0$ and $X\geq L_X$. Equation (42) shows that the current of particles through the channel is

$$J = -DW\left(1-S_X^2-\frac{1}{12}W_X^2\right)\Psi_X. \tag{58}$$

Let us suppose that the steady state has been reached, so that J is independent of X. Solving Eq. (58) for Ψ_X and integrating over X, we find that

$$\Delta\Psi = -RJ, \tag{59}$$

where $\Delta\Psi \equiv \Psi(L_X)-\Psi(0)$ and

$$R = \frac{1}{D}\int_0^{L_X} \frac{dX}{W\left(1-S_X^2-\frac{1}{12}W_X^2\right)} \tag{60}$$

is the resistance of the channel to the flow of particles through it. Equation (60) is valid to first order in ϵ. If only terms of zeroth order in ϵ are retained, Eq. (60) is replaced by

$$R = \frac{1}{D}\int_0^{L_X} \frac{dX}{W}. \tag{61}$$

Comparing Eqs. (60) and (61), we see that the corrections coming from spatial variations of the midline height and channel width both increase the channel resistance R.

As we have already noted, to zeroth order in ϵ, the density $\phi(x,z,t)$ is independent of z and $\phi(x,z,t)=\psi(x,t)$. Let us find the first order correction to the density for small but nonzero ϵ. Using Eqs. (13), (21), and (29), we find that to first order in ϵ,

$$\phi = \phi_0 + \epsilon\phi_1 = \theta_0 + \epsilon\theta_1 + \epsilon\left(b_2 z + \frac{1}{2}b_3 z^2\right)\psi_x. \tag{62}$$

We next employ Eq. (37) to eliminate $\theta_0+\epsilon\theta_1$ from Eq. (62) and then replace h_+ and h_- by $s+w/2$ and $s-w/2$, respectively. This yields

$$\phi = \psi + \epsilon\left[(ws_x - w_x s)(z-s) + \frac{1}{2}w_x\left(z^2 - s^2 - \frac{1}{12}w^2\right)\right]\frac{\psi_x}{w}. \tag{63}$$

Equation (63) gives the first order deviation of the density from local equilibrium. Once Eq. (40) has been solved for a given channel geometry and initial distribution $\psi(x,0)$, this result yields the density throughout the channel.

For a symmetric channel, $s=0$ and Eq. (63) reduces to

$$\phi = \psi + \frac{1}{2}\epsilon\left(z^2 - \frac{1}{12}w^2\right)\frac{w_x}{w}\psi_x, \tag{64}$$

which shows that to first order in ϵ, the density ϕ varies quadratically with z. For a channel of constant width w, on the other hand,

$$\phi = \psi + \epsilon s_x(z-s)\psi_x, \tag{65}$$

and so ϕ is a linear function of the vertical displacement from the centerline $z-s$ to first order in ϵ.

V. VALIDITY OF THE KALINAY AND PERCUS ASSUMPTION FOR SYMMETRIC CHANNELS

In their reduction of two-dimensional diffusion in a narrow symmetric channel to an effective one-dimensional description, Kalinay and Percus [9] make the assumption that there is a linear operator $\mathcal{L}$ that acts on $\psi(x,t)$ to give $\phi(x,z,t)$, i.e.,

$$\phi(x,z,t) = \mathcal{L}\psi(x,t). \tag{66}$$

Further, KP assume that

$$\mathcal{L} = 1 + L(x,z,\partial_x,\epsilon)\partial_x \tag{67}$$

and that the linear operator L may be expanded in powers of ϵ: specifically, they write

$$L(x,z,\partial_x,\epsilon) = \sum_{n=1}^{\infty}\epsilon^n L_n(x,z,\partial_x), \tag{68}$$

where the operators L_n are taken to be independent of ϵ. We will refer to Eqs. (66)–(68) as the KP assumption. If true, this assumption would mean that knowledge of the density averaged over the channel width $\psi(x,t)$ is all that is needed to determine the density $\phi(x,z,t)$ throughout the channel.

The validity of the KP assumption is far from self evident. In this section, we will show rigorously that the KP assumption is valid to second order in ϵ. To do so, we must establish that

$$\phi_0 = \psi_0, \tag{69}$$

and that there are linear operators $L_1=L_1(x,z,\partial_x)$ and $L_2=L_2(x,z,\partial_x)$ that satisfy the relations

$$\phi_1 = \psi_1 + L_1\psi_{0x} \tag{70}$$

and

$$\phi_2 = \psi_2 + L_1\psi_{1x} + L_2\psi_{0x}. \tag{71}$$

Thus, we will need ϕ_i and ψ_i for a symmetric channel for $i=0,1,2$.

ϕ_0 and ψ_0 are given by Eqs. (13) and (29), respectively. For a symmetric channel, ϕ is an even function of z and hence ϕ_z is an odd function of z. Equation (21) therefore reduces to

$$\phi_1 = \theta_1 + \frac{1}{2}b_3\theta_{0x}z^2 \tag{72}$$

and Eq. (24) simplifies to become

$$\phi_{2z} = (\theta_{1t} - \theta_{1xx})z + \frac{1}{6}c_3z^3. \tag{73}$$

Integrating the latter with respect to z, we find that

$$\phi_2 = \frac{1}{2}(\theta_{1t} - \theta_{1xx})z^2 + \frac{1}{24}c_3z^4 + \theta_2, \tag{74}$$

where $\theta_2=\theta_2(x,t)$. Furthermore, setting $h\equiv w/2$ for convenience and using Eqs. (28), (72), and (74), we find that

$$\psi_1 = \theta_1 + \frac{1}{6}b_3\theta_{0x}h^2 \tag{75}$$

and

$$\psi_2 = \theta_2 + \frac{1}{6}(\theta_{1t} - \theta_{1xx})h^2 + \frac{1}{120}c_3h^4. \tag{76}$$

Equation (69) follows immediately from Eqs. (13) and (29). Inserting Eqs. (72) and (75) into Eq. (70), we see that Eq. (70) is satisfied if we set

$$L_1 = \frac{h_x}{2h}\left(z^2 - \frac{1}{3}h^2\right). \tag{77}$$

$L_1=L_1(x,z)$ is a linear operator, as required by the KP assumption. In addition, note that our expression for L_1 is in agreement with Eq. (64).

We now insert Eqs. (74)–(77) into Eq. (71), employ Eq. (25) and recall the definitions of the a_j's, b_j's, and c_j's. This yields

$$L_2\theta_{0x} = \frac{1}{12}\left(z^2 - \frac{1}{3}h^2\right)\left\{\frac{1}{h}\frac{\partial}{\partial x}\left[h^3\frac{\partial}{\partial x}\left(\frac{h_x}{h}\theta_{0x}\right)\right] - hh_x\frac{\partial}{\partial x}\left[\frac{1}{h}\frac{\partial}{\partial x}(h\theta_{0x})\right] - \frac{h_x}{h}\frac{\partial}{\partial x}(hh_x\theta_{0x})\right\} + \frac{1}{24}\left(z^4 - \frac{1}{5}h^4\right)\left\{\frac{h_x}{h}\frac{\partial}{\partial x}\left[\frac{1}{h}\frac{\partial}{\partial x}(h\theta_{0x})\right] - \frac{\partial^2}{\partial x^2}\left(\frac{h_x}{h}\theta_{0x}\right)\right\}. \tag{78}$$

We conclude that Eq. (71) is satisfied if we put

$$L_2 = \frac{1}{12}\left(z^2 - \frac{1}{3}h^2\right)\left[hh_{xxx} - \frac{h_x^3}{h} - 2h_xh_{xx} + (2hh_{xx} - h_x^2)\partial_x\right] + \frac{1}{24h^2}\left(z^4 - \frac{1}{5}h^4\right)\left[4h_xh_{xx} - 3\frac{h_x^3}{h} - hh_{xxx} + (3h_x^2 - 2hh_{xx})\partial_x\right]. \tag{79}$$

Since L_2 is a linear operator that depends only on x, z, and ∂_x, we have verified that the KP assumption is valid to order ϵ^2, as we set out to do. Our expressions for L_1 and L_2 also agree with the findings of KP [9], and so provide additional corroboration for their work.

VI. CONCLUSIONS

In this paper, diffusion in a narrow two-dimensional channel with a curved midline and varying width was reduced to an effective one-dimensional equation of motion which we dubbed the generalized Zwanzig equation. This equation takes the form of the Fick-Jacobs equation with a spatially varying effective diffusivity. The effective diffusivity includes a contribution that comes from the slope of the channel midline dS/dX as well as the standard term stemming from variations in the channel width.

Our derivation of the generalized Zwanzig equation was completely rigorous and was based on an asymptotic expansion in the small dimensionless parameter ϵ that characterizes the channel width. For a channel that has a straight midline or wall, our equation of motion reduces to Zwanzig's equation [7]. Our derivation therefore provides a rigorous proof of the validity of the latter equation.

Using the generalized Zwanzig equation, we found the long time or asymptotic diffusivity for a narrow periodic channel, generalizing Zwanzig's result for symmetric channels to asymmetric channels. We also determined the resistance of a narrow channel to the passage of diffusing particles. For the special case of a channel with a curved midline and constant width W, we obtained a solution to the generalized Zwanzig equation for arbitrary initial conditions that is correct to order ϵ.

In their reduction of diffusion in a symmetric channel to an effective 1D description, Kalinay and Percus assumed that knowledge of the density averaged over the channel width $\Psi(X,T)$ is all that is needed to determine the density $\Phi(X,Z,T)$ throughout the channel [9]. In this paper, we demonstrated that their assumption is valid to second order in ϵ. Thus, we have proven the validity of the key assumption that Kalinay and Percus make in deriving the Zwanzig equation and the lowest order correction to this equation.

Diffusion in a narrow three-dimensional tube with a straight axis and varying radius can also be reduced to an effective one-dimensional description [7]. This reduction may be put on a firm footing using precisely the same methods as we employed in this paper. We find that the Fick-Jacobs equation for a three-dimensional tube is valid to zeroth order in ϵ and that the Zwanzig equation is correct to first order in ϵ, in complete analogy with our results for symmetric 2D channels [20].

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