Extended Fick-Jacobs equation: Variational approach

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We derive an extended Fick-Jacobs equation for the diffusion of noninteracting particles in a two- and symmetric three-dimensional channels of varying cross section $A(x)$, using a variational approach. The result is a diffusion differential equation of second order in only one space (longitudinal) coordinate. This equation is tested on the task of calculating the stationary flux through a hyperboloidal tube, and its solution is compared with that of other methods.

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I. INTRODUCTION

Constructions by nature, and by man, proceed in a time-ordered fashion, so that spatially ordered conceptually one-dimensional structures are typical dominant units, e.g., linear polymers. Even when strict one-dimensionality is not observed, it is often discernible at low resolution, as in pores and channels of high aspect ratio. Successful empirical descriptions typically deal with quantities at low resolution, the implicit assumption being that any further information decays quickly in time. We then deal in essence with the question of dimensional reduction: when can dynamics be fashioned—and be valid—at this level alone?

A first step in the understanding process involves examining systems of only a few degrees of freedom, one of which can be identified as one-dimensional location, say x, and seeing to what extent the dynamics of the latter is self-maintained. This question has been addressed by many workers, the result of Jacobs [1] (and reputedly of Fick, well prior) on diffusion of a simple particle in a pore of varying cross-sectional area $A(x)$ now being classical. It asserts that if a particle diffuses in a region of longitudinal coordinate x, transverse vector $\vec{y}$, where the transverse area $A(x)$ at fixed x is "small," then the equation for the full probability density

$$\frac{\partial\rho(x,\vec{y},t)}{\partial t} = D\left(\frac{\partial^2}{\partial x^2} + \nabla_{\vec{y}}^2\right)\rho(x,\vec{y},t) \tag{1.1}$$

with reflecting boundary conditions, can be replaced by

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left(A(x)\frac{\partial}{\partial x}\frac{1}{A(x)}P(x,t)\right), \tag{1.2}$$

where

$$P(x,t) = \int_{area\ A(x)} \rho(x,\vec{y},t)d\vec{y}. \tag{1.3}$$

It reflects the distortion of the flow by the varying boundary, whose effect cannot be neglected. In fact, it represents the simplest form of equation of continuity for one-dimensional density $P(x,t)$.

Zwanzig [2] has examined the same situation from the point of view of a thermodynamically equivalent Kolmogorov equation, and concluded that (1.2) should be modified to read

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}D(x)A(x)\frac{\partial}{\partial x}\frac{1}{A(x)}P(x,t), \tag{1.4}$$

where the effective diffusion coefficient is $D(x) = D(1-\frac{1}{3}A'^2(x))$ in 2D cylindrical geometry, or $D(x) = D(1-A'^2(x)/8\pi A(x))$ in 3D. As was shown in the example of stationary flux through a hyperboloidal tube, this is only a slight improvement over the Fick-Jacobs equation (1.2) and further corrections are necessary.

Better results are achieved in case of specific geometries of the tube, if its boundaries can be easily transformed to a rectangle under some (conformal [3]) transformation, and also for quasi stationary processes in periodic channels [4], where the wavelength can serve as a good small parameter. But in general, flattening the boundaries by a simple coordinate transformation [5] and treating the problem using standard perturbative technique, may lead to a complicated expansion, recovering in essence the Zwanzig correction term.

The essential question here is the choice of small parameter, in which one could do an expansion, yielding next corrections to the Fick-Jacobs equation. Recently [6], we revisited this problem and adopted the strategy of introducing a distinct transverse diffusion constant D_y and expanding in the parameter $\lambda = D/D_y$. Small λ (high transverse diffusion constant) makes the transverse relaxation more speedy; rapid transverse sojourns quickly relax the transverse profile to a steady-state form. In other words, $\lambda \to 0$ helps to separate two time scales, the slow longitudinal processes from the rapid transverse relaxation. Mathematically, λ appeared to be a good small parameter, enabling us to carry out the expansion of the spatial operator of the one-dimensional differential equation for $P(x,t)$ (1.3). Supposing that the time necessary to form the steady-state transverse profile of density $\rho(x,\vec{y},t)$ after variations of $P(x,t)$ is negligible with respect to the typical times of these variations (steady-state approximation), we arrived at the equation [6]

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[A - \frac{\lambda}{3}AA'^2 - \frac{\lambda^2}{45}AA'\left(2A(AA''+A'^2)\frac{\partial}{\partial x} + AA'A'' + A^2A^{(3)} - 7A'^3\right) + \cdots\right]\frac{\partial}{\partial x}\frac{P(x,t)}{A(x)}. \tag{1.5}$$

Notice, that the leading term corresponds exactly to the Fick-Jacobs equation and the next term (of the order λ^1) recovers the Zwanzig correction [2].

Although the steady-state approximation was used, the next analysis [7] showed that the full expansion in λ represents an exact map of (1.1) on a reduced space of eigenstates of its spatial operator. The recurrent procedure in [6] does this mapping without needing to know the spectrum.

The problem is that this mapping ends up with a differential equation, whose spatial operator has very complicated structure. The nth order term in λ contains all derivatives in x up to ∂_x^{n+1}, so even the second-order correction cannot be expressed in the convenient Zwanzig form (1.4), involving only some next correction of the effective diffusion coefficient $D(x)$. An intermediate approach that maintains the simplicity of (1.4) but greatly improves its accuracy would be welcome.

In this paper, we offer such a simplification. It comes from the idea that the complicated structure of the mapped spatial operator could be caused by unsuitable choice of the coordinate system. Having been inspired by the solvable geometries mentioned above, we suppose that some kind of curvilinear coordinates instead of Cartesian ones would be more appropriate. The longitudinal curvilinear variable $z = z(x,\vec{y})$ should be related to (or coincide with) x on the reference longitudinal axis, but the surfaces defined by $z(x,\vec{y})=\text{const}$ should better reflect the structure of the 2D (3D) local fluxes, given by the curved walls of the channel. Aspiring to find another representation of mapping onto the longitudinal dimension, we then suppose that the 2D (3D) density depends only on z; $\rho(x,\vec{y},t)=\rho(z(x,\vec{y}),t)=\rho(z,t)$.

The question is how to find the proper curvilinear coordinate system. If ρ depends only on the variable $z=z(x,\vec{y})$, the surfaces $z(x,\vec{y})=\text{const}$ are normal to the local flux. But this condition cannot be used backward for defining the relation $z=z(x,\vec{y})$; the normal surfaces to the flux change in time and depend also on the initial condition in general. To fix the coordinate transformation, we use a softer condition, requiring that the Neumann b.c. for $\rho(z)$ are satisfied exactly.

However, the density depending only on one variable $\rho(z,t)$ can be just an approximation, it represents in fact some kind of ansatz for the exact density $\rho(x,\vec{y},t)$. This encourages us to adopt a variational technique for finding the optimal mapped equation for it. We arrive at an equation having the form of the corrected Fick-Jacobs equation (1.4); it is a second order differential equation in z in any order of λ. This is the content of the following section.

In Sec. III, we compare this extended Fick-Jacobs equation with the steady state approximation (1.5), showing that after returning to the x coordinate, they coincide up to the second order in λ. Finally, in Sec. IV, we test this approximation on exactly solvable models: in 2D for $A(x)=x$ and in 3D for diffusion in a rotationally symmetric hyperboloid, and compare it with other approximative methods.

II. VARIATIONAL FORMULATION

Variational methods are widely used in quantum mechanics, but not for the description of the diffusion, so we pay more attention to this point in this section.

A variational technique is based upon construction of a functional of the function to be found that is stationary under arbitrary infinitesimal changes in this function when it actually is a solution to the system of equations. Under the best of circumstances, it will be an absolute minimum (or maximum) and the functional will itself represent a physical quantity of interest. But even if these properties are not satisfied, such a formulation still gives a reproducible recipe for selecting optimal parameters in simple parametrized models of the solution, and this is the aspect that we will use to advantage. The equation to be solved is (1.1), generalized to transverse diffusion constant $D_y=D/\lambda$, and its associated reflection boundary conditions, over a time interval, say t_0 to t_1. For simplicity, let us first concentrate on the two-dimensional case—one longitudinal coordinate x and one transverse coordinate y.

It is readily seen that a suitable functional is then given by

$$F = \int_{t_0}^{t_1} dt \int_{x_L}^{x_R} dx \int_0^{A(x)} dy \left(\frac{1}{2}(\dot{\rho}\bar{\rho} - \dot{\bar{\rho}}\rho) + \partial_x\bar{\rho}\partial_x\rho + \frac{1}{\lambda}\partial_y\bar{\rho}\partial_y\rho\right). \tag{2.1}$$

The stationary condition $\delta F=0$ is satisfied if the function $\rho(x,y,t)$ and its complementary $\bar{\rho}(x,y,t)$ satisfy the equations

$$\dot{\rho} = \partial_x^2\rho + \frac{1}{\lambda}\partial_y^2\rho \quad \text{and} \quad -\dot{\bar{\rho}} = \partial_x^2\bar{\rho} + \frac{1}{\lambda}\partial_y^2\bar{\rho} \tag{2.2}$$

as well as the Neumann boundary conditions, expressing the reflection condition that the boundary fluxes $\mathbf{j}=(-\partial_x\rho, -(1/\lambda)\partial_y\rho)$ and $\bar{\mathbf{j}}=(-\partial_x\bar{\rho}, -(1/\lambda)\partial_y\bar{\rho})$ have vanishing normal component:

$$\partial_y\rho = 0|_{y=0}, \quad \partial_y\bar{\rho} = 0|_{y=0} \tag{2.3}$$

$$\frac{1}{\lambda}\partial_y\rho = A'(x)\partial_x\rho|_{y=A(x)}, \quad \frac{1}{\lambda}\partial_y\bar{\rho} = A'(x)\partial_x\bar{\rho}|_{y=A(x)} \tag{2.4}$$

and $\partial_x\rho=\partial_x\bar{\rho}=0|_{x=x_L,x_R}$.

The first equation (2.2) is just the diffusion equation for the 2D density $\rho(x,y,t)$ in an anisotropic environment. We have introduced the diffusion constant D_y in the transverse direction, supposed greater than the longitudinal diffusion constant D; $\lambda=D/D_y$ and time is rescaled by D.

The second equation represents diffusion running backwards in time, from t_1 to t_0, completely meaningful in light of the finite time interval. Note that, at stationarity, the functional F is readily evaluated and has precisely the value 0. But what we will take advantage of is that, nonetheless, the stationary condition does imply the diffusion equation, with

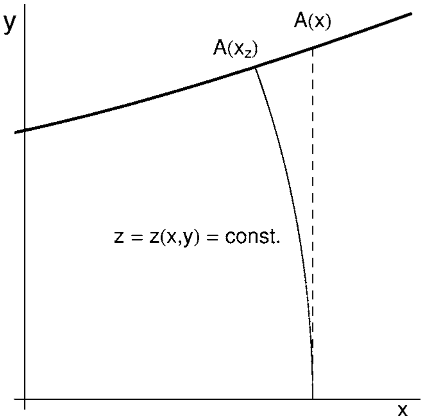

FIG. 1. Integration over y is carried out from 0 up to $A(x_z)$ after transformation to the coordinates (z,y).

its boundary conditions, and approximations in the evaluation of the stationary functional will then produce approximations to the diffusion. Note too that the Neumann conditions (2.3) and (2.4) do not *have* to be inserted by hand-they are a consequence of the variational principle.

The advantage of the variational form is that it is formally easy to do approximations. Having chosen an ansatz for the varied functions, it finds the best possible solution within the allowed freedom. Here we are going to suppose that ρ and $\bar{\rho}$ are functions of only one spatial variable z, depending on x and y: $\rho=\rho(z(x,y),t)$ and $\bar{\rho}=\bar{\rho}(z(x,y),t)$. Next, our plan is to rewrite the original diffusion functional F (2.1) in this variable and find the corresponding differential equation from the condition of its stationarity.

After substituting for ρ and $\bar{\rho}$ in F (2.1) according to this supposition and transforming from the coordinates (x,y) to (z,y), we have

$$F=\int_{t_0}^{t_1}dt\int_{z_L}^{z_R}dz\int_0^{A(x_z)}dy\frac{\partial x}{\partial z}\left[\frac{1}{2}(\dot{\rho}\bar{\rho}-\dot{\bar{\rho}}\rho)+\left(\left(\frac{\partial z}{\partial x}\right)^2+\frac{1}{\lambda}\left(\frac{\partial z}{\partial y}\right)^2\right)\partial_z\bar{\rho}\partial_z\rho\right], \tag{2.5}$$

$\partial x/\partial z$ is the Jacobian of the transformation; $x=x(z,y)$ is the relation inverse to $z=z(x,y)$. The integration over y is now carried out at constant z (see Fig. 1), so its upper limit is changed to $A(x_z)$, defined by the equation

$$x_z=x(z,A(x_z)). \tag{2.6}$$

Having completed the integration over y, we get a functional F_{1D}:

$$F_{1D}[\rho(z,t),\bar{\rho}(z,t)]=\int_{t_0}^{t_1}dt\int_{z_L}^{z_R}dz\left[\frac{1}{2}\alpha(z)(\dot{\rho}\bar{\rho}-\dot{\bar{\rho}}\rho)+\kappa(z)\partial_z\bar{\rho}\partial_z\rho\right], \tag{2.7}$$

where the coefficients $\alpha(z)$ and $\kappa(z)$ are defined as follows:

$$\alpha(z)=\int_0^{A(x_z)}dy\frac{\partial x}{\partial z}, \tag{2.8}$$

$$\kappa(z)=\int_0^{A(x_z)}dy\frac{\partial x}{\partial z}\left(\left(\frac{\partial z}{\partial x}\right)^2+\frac{1}{\lambda}\left(\frac{\partial z}{\partial y}\right)^2\right)=\int_0^{A(x_z)}dy\left(\frac{\partial x}{\partial z}\right)^{-1}\left(1+\frac{1}{\lambda}\left(\frac{\partial x}{\partial y}\right)^2\right). \tag{2.9}$$

F_{1D} is also a diffusion functional, but working on a restricted space of the functions ρ, $\bar{\rho}$ of only one spatial variable z. For this functional, we find a new stationary condition $\delta F_{1D}=0$:

$$0=\left[\int_{z_L}^{z_R}dz\frac{\alpha(z)}{2}(\bar{\rho}\delta\rho-\rho\delta\bar{\rho})\right]_{t_0}^{t_1}+\int_{t_0}^{t_1}dt[\kappa(z)(\delta\bar{\rho}\partial_z\rho+\delta\rho\partial_z\bar{\rho})]_{z_L}^{z_R}+\int_{t_0}^{t_1}dt\int_{z_L}^{z_R}dz[\delta\bar{\rho}(\alpha(z)\dot{\rho}-\partial_z\kappa(z)\partial_z\rho)-\delta\rho(\alpha(z)\dot{\bar{\rho}}+\partial_z\kappa(z)\partial_z\bar{\rho})] \tag{2.10}$$

which is satisfied for any variation $\delta\bar{\rho}(z,t)$ and $\delta\rho(z,t)$, if the functions ρ and $\bar{\rho}$ satisfy the equations:

$$\frac{\partial\rho}{\partial t}=\frac{1}{\alpha(z)}\frac{\partial}{\partial z}\kappa(z)\frac{\partial}{\partial z}\rho,\qquad -\frac{\partial\bar{\rho}}{\partial t}=\frac{1}{\alpha(z)}\frac{\partial}{\partial z}\kappa(z)\frac{\partial}{\partial z}\bar{\rho}. \tag{2.11}$$

The first equation, governing $\rho(z,t)$ is the mapped 1D diffusion equation we have been looking for. The only question that must be resolved now is how to find the proper transformation relation $z=z(x,y)$.

First, let us stress that the proposed procedure finds the mapped 1D diffusion equation (2.11) for any chosen relation $z=z(x,y)$. The equation will have the same form but with different functions $\alpha(z)$ and $\kappa(z)$, according to (2.8) and (2.9), for different $z=z(x,y)$. To fix the optimal transformation directly from the functional F_{1D}, one might want to vary the functional F (2.5) before integration over y not only with respect to $\delta\rho$ and $\delta\bar{\rho}$, but also $\delta z(x,y)$. The result is a set of complicated equations, where $z=z(x,y)$ depends on ρ and $\bar{\rho}$—it reflects the fact mentioned in the Introduction, that the normal surfaces to the flux density depend on time and initial density. In other words, using this approach does not lead to a simple 1D diffusion equation for $\rho(z,t)$ of the Fick-Jacobs type.

The easiest way to find an appropriate transformation is to fix $z=z(x,y)$ so that the boundary conditions (2.3) and (2.4) are satisfied for any $\rho(z,t)$. The function $\rho(z(x,y),t)$ must obey

$$\frac{\partial\rho}{\partial z}\frac{\partial z}{\partial y}=0\bigg|_{y=0},\quad \frac{1}{\lambda}\frac{\partial\rho}{\partial z}\frac{\partial z}{\partial y}=A'(x)\frac{\partial\rho}{\partial z}\frac{\partial z}{\partial x}\bigg|_{y=A(x)} \tag{2.12}$$

and the same for $\bar{\rho}(z(x,y),t)$. These conditions will be satisfied for general ρ, $\bar{\rho}$, if $z(x,y)$ has the form of an expansion in λ

$$z=\sum_{j=0}^{\infty}\lambda^j y^{2j} z_j(x). \tag{2.13}$$

This is again an ansatz, having its justification in the following consideration: if $\lambda\to 0$, the transverse relaxation is instant and the density $\rho(x,y,t)$ is immediately smeared to a constant in y direction. In this limit, flux density is parallel to x-axis and so the unity transformation $z=z(x,y)=x$ is sufficient. We have only introduced a more general transformation $z=z_0(x)$ for this limit $\lambda\to 0$. If $\lambda>0$, the transverse relaxation is slower, the steady-state profiles of $\rho(x,y,t)$ are no more constant and the surfaces normal to the flux density become curved, especially near the curved boundaries.

Notice that the parameter λ is a scaling parameter of the transverse space; it disappears from (2.2) under rescaling $y\to y/\sqrt{\lambda}$ and the diffusion becomes isotropic. To be consistent with this scaling, we must expand $z(x,y)$ in λy^2 instead of only λ. The odd powers of y in (2.13) are not present because of BC at $y=0$. Finally, putting the ansatz (2.13) into the boundary condition (2.12) results indeed in a consistent recurrence relation for the coefficients $z_j(x)$

$$z_j(x)=\frac{1}{2j}\frac{A'(x)}{A(x)}z'_{j-1}(x). \tag{2.14}$$

The zeroth coefficient $z_0(x)$ is not fixed; we can choose it to find the transformation relation in the most convenient way. The "natural" choice is $z_0(x)=x$, when the points on the x axis ($y=0$) have the same x and z coordinate, but the summation of the corresponding expansion

$$z=x+\frac{1}{2}\frac{A'(x)}{A(x)}\lambda y^2+\frac{1}{8}\frac{A'(x)}{A(x)}\left(\frac{A'(x)}{A(x)}\right)'\lambda^2y^4+\cdots \tag{2.15}$$

may be too complicated. Instead, one can choose $z_0(x)$ such that the next coefficient $z_1(x)=\text{const}$ and the following terms according to the recurrence scheme (2.14) are zero.

Finally notice, if one takes the simplest transformation relation, $z=x$, which is proper in the limit $\lambda\to 0$, our variational procedure recovers the standard Fick-Jacobs equation; $\alpha(x)=\kappa(x)=A(x)$ according to (2.8) and (2.9). In this case, our calculation reproduces the variational derivation of the Fick-Jacobs equation in [8].

In the case of $\lambda=0$, the scaling of the transverse space $y\to y/\sqrt{\lambda}$, removing the anisotropy of the diffusion, shrinks the channel into the line, so the Fick-Jacobs equation, coming from the most calculations as an essential approximation, represents then the exact mapping. Considering a finite rate of transverse diffusion ($\lambda>0$) requires to look for the corrections. We suppose that our λ-expansion is valid up to $\lambda=1$ (isotropic diffusion), which we are obviously interested in. The error is hard to estimate even having taken the full expansion of $z=z(x,t)$ in λ; it strongly depends on the shape of channel, e.g., the function $A(x)$. We will be content to compare this result with other methods applied to two solvable geometries in Sec. IV.

A. Variational mapping for 3D channel of cylindrical symmetry

The above variational method can be easily extended to the mapping of diffusion in a 3D channel with cylindrical symmetry. We suppose that the 3D density $\rho(x,y_1,y_2,t)=\rho(x,r,t)$ depends only on the radius $r=\sqrt{y_1^2+y_2^2}$ in the transverse directions and not on the angle $\phi=\arctan(y_2/y_1)$. Likewise, the channel is defined by a function $R(x)$, not depending on ϕ: $0<r<R(x)$. The corresponding diffusion functional is then

$$F=2\pi\int_{t_0}^{t_1}dt\int_{x_L}^{x_R}dx\int_0^{R(x)}rdr\left(\frac{1}{2}(\dot{\rho}\bar{\rho}-\dot{\bar{\rho}}\rho)+\partial_x\bar{\rho}\partial_x\rho+\frac{1}{\lambda}\partial_r\bar{\rho}\partial_r\rho\right) \tag{2.16}$$

and ρ, $\bar{\rho}$ must obey the boundary conditions

$$\frac{1}{\lambda}\partial_r\rho=R'\ (x)\partial_x\rho|_{r=R(x)},\quad \frac{1}{\lambda}\partial_r\bar{\rho}=R'\ (x)\partial_x\bar{\rho}|_{y=R(x)}, \tag{2.17}$$

$\partial_x\rho=\partial_x\bar{\rho}=0|_{x=x_L,x_R}$. We also require the functions ρ and $\bar{\rho}$ to be smooth at the rotational axis in Cartesian (x,y_1,y_2) space, which requires that they depend only on even powers of r; $\rho=\rho(x,r^2,t)$, $\bar{\rho}=\bar{\rho}(x,r^2,t)$. This condition is equivalent to (2.3) if y is replaced by r.

Formally, we have the same picture as in the 2D case, so having applied the same steps, we can immediately write the resultant 1D equation. Supposing that ρ and $\bar{\rho}$ are again functions of only the curvilinear variable $z=z(x,r)$, doing the transformation of coordinates from (x,r) to (z,r), and integrating the transformed functional F (2.16) over r, we get a functional F_{1D} of the same form as (2.7), with slightly different definitions of α and κ:

$$\alpha(z)=2\pi\int_0^{R(x_z)}rdr\frac{\partial x}{\partial z}, \tag{2.18}$$

$$\kappa(z)=2\pi\int_0^{R(x_z)}rdr\left(\frac{\partial x}{\partial z}\right)^{-1}\left[1+\frac{1}{\lambda}\left(\frac{\partial x}{\partial r}\right)^2\right], \tag{2.19}$$

where $x=x(z,r)$ is the relation inverse to $z=z(x,r)$ and $\partial x/\partial z$ is the Jacobian of the transformation. The integration over r is carried out at a constant z, so the new upper limit $R(x_z)$ is defined exactly as in 2D: $x_z=x(z,R(x_z))$.

The stationary condition $\delta F_{1D}=0$ leads to the 1D diffusion equation of the same form as (2.11):

$$\frac{\partial\rho(z,t)}{\partial t} = \frac{1}{\alpha(z)}\frac{\partial}{\partial z}\kappa(z)\frac{\partial}{\partial z}\rho(z,t). \tag{2.20}$$

The transformation relation is again fixed to satisfy the boundary conditions (2.17); if the function $z(x,r)$ is expressed in the form of a λ-expansion

$$z = \sum_{j=0}^{\infty}\lambda^j r^{2j} z_j(x), \tag{2.21}$$

the boundary condition (2.17) results in the same recurrence scheme for the coefficients $z_j(x)$ as in the 2D case:

$$z_j(x) = \frac{1}{2j}\frac{R'(x)}{R(x)}z'_{j-1}(x). \tag{2.22}$$

B. Variational mapping in "natural" coordinates

A special class is formed by channels which can be transformed to rectangles in some orthogonal curvilinear coordinate system; then the points inside the channel described by coordinates $\xi=\xi(x,y)$ and $\eta=\eta(x,y)$ are bounded by simple rectangular relations $\xi_L<\xi<\xi_R$ and $\eta_0<\eta<\eta_1$. Many such systems are exactly solvable in certain circumstances, in particular when their properties under stationary conditions are calculated. So it will be useful to obtain the extended Fick-Jacobs equation for such cases.

First, the functional F (2.1) is rewritten in curvilinear coordinates (ξ,η):

$$F = \int_{t_0}^{t_1}dt\int_{\xi_L}^{\xi_R}d\xi\int_{\eta_0}^{\eta_1}d\eta\frac{\partial(x,y)}{\partial(\xi,\eta)}\left[\frac{1}{2}(\dot\rho\bar\rho-\dot{\bar\rho}\rho)+\left(\left(\frac{\partial\xi}{\partial x}\right)^2 + \left(\frac{\partial\xi}{\partial y}\right)^2\right)\partial_\xi\bar\rho\partial_\xi\rho + \left(\left(\frac{\partial\eta}{\partial x}\right)^2+\left(\frac{\partial\eta}{\partial y}\right)^2\right)\partial_\eta\bar\rho\partial_\eta\rho\right]. \tag{2.23}$$

$\partial(x,y)/\partial(\xi,\eta)$ stands for Jacobian of the transformation.

Let us imagine now that ξ describes position in the longitudinal direction, while η represents the transverse coordinate. As we suppose the transients in the transverse direction to be quickly quenched, the 2D densities ρ and $\bar\rho$, if expressed as functions of only one spatial variable, have to be functions of ξ. If applied to (2.23) and the integration over η carried out, we get again the functional F_{1D} (2.7) in the variable ξ with

$$\alpha(\xi) = \int_{\eta_0}^{\eta_1}d\eta\frac{\partial(x,y)}{\partial(\xi,\eta)}, \tag{2.24}$$

$$\kappa(\xi) = \int_{\eta_0}^{\eta_1}d\eta\left(\frac{\partial(x,y)}{\partial(\xi,\eta)}\right)^{-1}\left(\left(\frac{\partial x}{\partial\eta}\right)^2+\left(\frac{\partial y}{\partial\eta}\right)^2\right). \tag{2.25}$$

$x=x(\xi,\eta)$ and $y=y(\xi,\eta)$ are the relations inverse to $\xi=\xi(x,y)$, $\eta=\eta(x,y)$. The condition of stationarity $\delta F_{1D}=0$ then gives the mapped 1D diffusion equation

$$\frac{\partial\rho(\xi,t)}{\partial t} = \frac{1}{\alpha(\xi)}\frac{\partial}{\partial\xi}\kappa(\xi)\frac{\partial}{\partial\xi}\rho(\xi,t). \tag{2.26}$$

The same procedure can be done for a 3D channel with rotational symmetry, transformable to a simple cylinder in some curvilinear coordinates $\xi=\xi(x,r)$, $\eta=\eta(x,r)$; the transverse radius $r=\sqrt{y_1^2+y_2^2}$. The stationary condition of the corresponding functional F_{1D} leads to the same mapped 1D equation (2.26) with redefined α and κ:

$$\alpha(\xi) = \int_{\eta_0}^{\eta_1}d\eta r(\xi,\eta)\frac{\partial(x,r)}{\partial(\xi,\eta)}, \tag{2.27}$$

$$\kappa(\xi) = \int_{\eta_0}^{\eta_1}d\eta r(\xi,\eta)\left(\frac{\partial(x,r)}{\partial(\xi,\eta)}\right)^{-1}\left(\left(\frac{\partial x}{\partial\eta}\right)^2+\left(\frac{\partial r}{\partial\eta}\right)^2\right). \tag{2.28}$$

It is easy to verify that if the coordinates ξ and η form an orthogonal system, the boundary conditions (2.3) and (2.4) in 2D and (2.17) in 3D are automatically satisfied.

III. COMPARISON WITH THE STEADY-STATE APPROXIMATION

The variational method allows us to find the 1D mapped diffusion equation in concise form, and with the spatial operator of only second order, but it is hard to guess how accurate the results are. Therefore in this section, we compare the variational mapping with the steady-state approximation [6], which is the exact mapping of the 2D (3D) diffusion equation onto the longitudinal dimension on a restricted space of eigenfunctions of the 2D (3D) diffusion operator [7].

While the variational method finds the extended Fick-Jacobs equation (2.20) governing 2D (3D) density $\rho(z,t)$ as a function of only the spatial curvilinear variable z, the steady-state approximation constructs the 1D diffusion equation directly for the projected 1D density $\psi(x,t)$ [or $P(x,t)$ as used in [6]]:

$$\psi(x,t) = \frac{P(x,t)}{A(x)} = \frac{1}{A(x)}\int_0^{A(x)}dy\rho(x,y,t) \quad (2D). \tag{3.1}$$

First we have to find conversion relations between these two formulations. In the defining formula for ψ (3.1), we replace $\rho(x,y,t)$ by $\rho(z(x,y),t)$, expand it in λ and carry out the integration over y:

$$\begin{aligned}\psi(x,t) &= \frac{1}{A(x)}\int_0^{A(x)}dy\rho(x+\lambda y^2z_1(x)+\lambda^2y^4z_2(x)+\cdots,t)\\ &= \left[1+\frac{\lambda}{3}A^2(x)z_1(x)\frac{\partial}{\partial x}+\frac{\lambda^2}{5}A^4(x)\left(z_2(x)\frac{\partial}{\partial x}+\frac{1}{2}z_1^2(x)\frac{\partial^2}{\partial x^2}\right)+\cdots\right]\rho(x,0,t)\end{aligned} \tag{3.2}$$

which can be easily inverted, looking for an operator $\hat\omega_0$ in form of an expansion in λ, to obey the inverse relation $\rho(x,0,t)=\hat\omega_0\psi(x,t)$:

$$\hat{\omega}_0 = 1 - \frac{\lambda}{3}A^2(x)z_1(x)\frac{\partial}{\partial x} + \frac{\lambda^2}{90}A^4(x)z_1^2(x)\frac{\partial^2}{\partial x^2} - \frac{\lambda^2}{45}A^3(x) \times(9A(x)z_2(x) - 10A'(x)z_1^2(x) - 5A(x)z_1(x)z_1'(x))\frac{\partial}{\partial x} + \cdots . \quad (3.3)$$

Hence, after substituting for $z_1, z_2, \ldots$ according to (2.15) in the Taylor series of $\rho(z(x,y),t)$ in λ, we get the inverse relation producing 2D density $\rho(z,t)$ from $\psi(x,t)$:

$$\rho(z(x,y),t) = \left[1 + \lambda\left(\frac{y^2}{2A} - \frac{A}{6}\right)A'\frac{\partial}{\partial x} + \lambda^2 A'^2\left(\frac{y^4}{8A^2} - \frac{y^2}{12} + \frac{A^2}{360}\right)\frac{\partial^2}{\partial x^2} + \lambda^2\left(\frac{y^4}{8A^3}(AA'A'' - A'^3) - \frac{y^2}{12A} \times(AA'A'' + A'^3) + \frac{AA'}{360}(AA'' + 19A'^2)\right)\frac{\partial}{\partial x} + \cdots\right]\psi(x,t). \quad (3.4)$$

This relation can be compared with the analogous formula in the steady-state approximation, transforming $\psi(x,t)$ to the 2D density ρ:

$$\rho(x,y,t) = \left[1 + \lambda\left(\frac{y^2}{2A} - \frac{A}{6}\right)A'\frac{\partial}{\partial x} + \lambda^2\left(\frac{y^4}{24A^2}(3A'^2 - 2AA'') + \frac{y^2}{12}(2AA'' - A'^2) - \frac{A^2}{360}(14AA'' - A'^2)\right)\frac{\partial^2}{\partial x^2} + \lambda^2\left(\frac{y^4}{24A^2}\left(-AA^{(3)} + 4A'A'' - 3\frac{A'^3}{A}\right) + \frac{y^2}{12}\left(AA^{(3)} - 2A'A'' - \frac{A'^3}{A}\right) - \frac{A^2}{360} \times\left(7AA^{(3)} - 8A'A'' - 19\frac{A'^3}{A}\right)\right)\frac{\partial}{\partial x} + \cdots\right]\psi(x,t). \quad (3.5)$$

The transformation formulas coincide up to the first order in λ. Both satisfy the boundary conditions (2.3) and (2.4) and do not violate the defining relation (3.1). But only the steady-state density ρ (3.5) satisfies the exact 2D diffusion equation (2.2) at any point (x,y); the variational ρ exhibits an error in second order.

Next, we compare the projected 1D diffusion equations. We must transform the extended Fick-Jacobs equation (2.11) from the coordinates (z,y) back to (x,y) and integrate both sides over y

$$\frac{\partial\psi(x,t)}{\partial t} = \frac{1}{A(x)}\int_0^{A(x)} dy \frac{1}{\alpha(z(x,y))}\frac{\partial x}{\partial z}\frac{\partial}{\partial x} \times\kappa(z(x,y))\frac{\partial x}{\partial z}\frac{\partial}{\partial x}\rho(z(x,y),t). \quad (3.6)$$

If we substitute for $\rho(z(x,y),t)$ according to the transformation relation (3.4), expand the terms to the desired order in λ and integrate the right-hand side (RHS) over y, we get the mapped equation for 1D density $\psi(x,t)$ coming from the variational method:

$$\frac{\partial\psi(x,t)}{\partial t} = \frac{1}{A(x)}\frac{\partial}{\partial x}\left[A - \frac{\lambda}{3}AA'^2 - \frac{\lambda^2}{45}AA'\left(2A(AA'' + A'^2)\frac{\partial}{\partial x} + AA'A'' + A^2A^{(3)} - 7A'^3\right) + \cdots\right]\frac{\partial}{\partial x}\psi(x,t). \quad (3.7)$$

This equation coincides with the 1D steady-state equation (1.5) up to second order. In higher orders (we tested up to fourth order), the structure of both equations remains the same, the nth order in λ contains the derivatives of ψ up to $\partial_x^{n+1}\psi$, but the corresponding coefficients differ except for the terms containing only products of $A(x)$ and $A'(x)$. On the other hand, the terms with higher derivatives of $A(x)$ are missing in the equation coming from the variational method.

The same comparison can be done for diffusion in a 3D channel with cylindrical symmetry. The 1D density $\psi(x,t)$ is now defined as

$$\psi(x,t) = \frac{2\pi}{A(x)}\int_0^{R(x)} r dr \rho(x,r,t), \quad (3.8)$$

where $r=\sqrt{y_1^2+y_2^2}$ is the transverse radius and $A(x)$ denotes the area of the cross section at the point x: $A(x)=\pi R^2(x)$. The relation transforming $\psi(x,t)$ to $\rho(z,t)$

$$\rho(z(x,r),t) = \left[1 + \lambda\left(r^2 - \frac{A}{2\pi}\right)\frac{A'}{4A}\frac{\partial}{\partial x} + \frac{\lambda^2 A'^2}{192\pi^2 A^2}(6\pi^2 r^4 - 6\pi r^2 A + A^2)\frac{\partial^2}{\partial x^2} + \lambda^2\left(\frac{r^4}{32A^3}(AA'A'' - A'^3) - \frac{r^2}{32\pi A}A'A'' + \frac{1}{192\pi^2 A}(AA'A'' + 2A'^3)\right)\frac{\partial}{\partial x} + \cdots\right]\psi(x,t) \quad (3.9)$$

differs from the transformation formula of the steady-state approximation in second order and the 1D diffusion equations coincide up to second order in λ

$$\frac{\partial\psi(x,t)}{\partial t} = \frac{1}{A(x)}\frac{\partial}{\partial x}\left[A - \frac{\lambda}{8\pi}A'^2 - \frac{\lambda^2}{192\pi^2}\frac{A'}{A}\left(2A^2A''\frac{\partial}{\partial x} + A^2A^{(3)} - AA'A'' - 3A'^3\right) + \cdots\right]\frac{\partial\psi(x,t)}{\partial x}. \quad (3.10)$$

IV. EXACTLY SOLVABLE EXAMPLES

In this section, we test the extended Fick-Jacobs equation on two examples: a 2D channel with $A(x)=x$, which is exactly solvable (the exact Green's function of the 2D diffusion equation is known [6]) and the 3D tube shaped as a rotational hyperboloid, for which the stationary flux has been calculated exactly [2].

A. 2D channel with $A(x)=x$

The calculation of the extended Fick-Jacobs equation for this geometry is very simple, so we can easily demonstrate the variational mapping, and the result is comparable with the known solution.

Following the recurrence scheme (2.14), we find the relation for the curvilinear coordinate z:

$$z(x,y) = x + \frac{\lambda y^2}{2x} - \frac{\lambda^2 y^4}{8x^3} + \cdots = \sqrt{x^2 + \lambda y^2}. \qquad (4.1)$$

The sum of the series is correct; if it is substituted into the boundary condition (2.12), we get the identity

$$\frac{1}{\lambda}\partial_y \sqrt{x^2 + \lambda y^2}\big|_{y=x} = \partial_x \sqrt{x^2 + \lambda y^2}\big|_{y=x} = \frac{1}{\sqrt{1+\lambda}}. \qquad (4.2)$$

Then the inverse relation is $x(z,y)=\sqrt{z^2-\lambda y^2}$ and the Jacobian $\partial x/\partial z = z/\sqrt{z^2-\lambda y^2}$. The upper limit in the integrations, defining α and κ is $A(x_z)=x_z$, which is given by the implicit equation

$$x_z = x(z, A(x_z)) = \sqrt{z^2 - \lambda x_z^2}, \quad \text{hence } x_z = \frac{z}{\sqrt{1+\lambda}}. \qquad (4.3)$$

Finally we can calculate the coefficients α (2.8) and κ (2.9)

$$\alpha(z) = \int_0^{A(x_z)} \frac{\partial x}{\partial z} dy = \int_0^{z/\sqrt{1+\lambda}} \frac{z dy}{\sqrt{z^2 - \lambda y^2}} = \frac{z}{\sqrt{\lambda}} \arctan \sqrt{\lambda}, \qquad (4.4)$$

$$\kappa(z) = \int_0^{z/\sqrt{1+\lambda}} dy \frac{\sqrt{z^2 - \lambda y^2}}{z}\left[1 + \frac{1}{\lambda}\left(\frac{\lambda y}{\sqrt{z^2-\lambda y^2}}\right)^2\right]$$

$$= \frac{z}{\sqrt{\lambda}} \arctan \sqrt{\lambda} \qquad (4.5)$$

so the extended Fick-Jacobs equation is very simple:

$$\frac{\partial \rho(z,t)}{\partial t} = \frac{1}{z}\frac{\partial}{\partial z} z \frac{\partial}{\partial z}\rho(z,t) \qquad (4.6)$$

and its solution, starting from the initial condition $\rho(z,0) = \delta(z-z_0)$ is given by

$$\rho(z,t) = \frac{\sqrt{\lambda}}{\arctan \sqrt{\lambda}} \frac{1}{2t} I_0\left(\frac{z z_0}{2t}\right) e^{-(z^2+z_0^2)/4t}, \qquad (4.7)$$

where I_0 denotes the Bessel function of the first kind with imaginary argument. This result is known, it is the solution of the 1D diffusion equation in the steady-state approximation [formula (3.4) in [6]].

Equivalence of the results obtained from the steady-state approximation and by the variational method for the geometry $A(x)=x$ can also be understood as proof that the current extended Fick-Jacobs equation includes correctly all terms in any order of λ, which do not depend on higher derivatives of $A(x)$ than the first, $A'(x)$. In other words, in comparison with the steady-state approximation, the extended Fick-Jacobs equation sums up a certain class of contributions to the exactly mapped 1D equation. These contributions are related to the first derivative of $A(x)$; if the higher derivatives of $A(x)$ are zero, the sum produces correctly all nonzero terms.

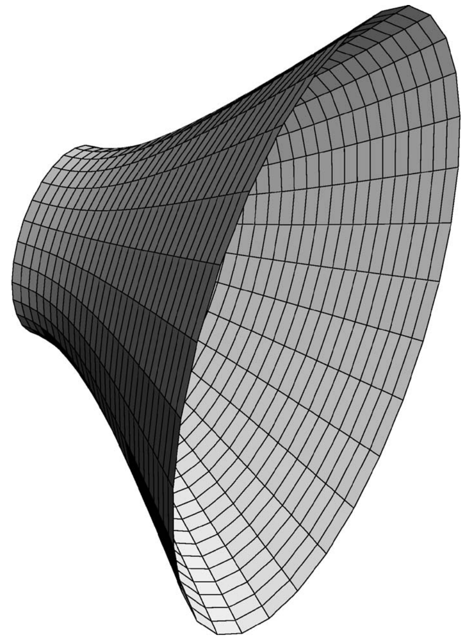

FIG. 2. Hyperboloidal cone with cylindrical symmetry.

B. Hyperboloidal tube in natural coordinates

The hyperboloidal tube (Fig. 2) is an object defined by simple rectangular relations in oblate spheroidal coordinates (ξ, η, ϕ)

$$x = a\xi\eta, \quad r^2 = y_1^2 + y_2^2 = a^2(1+\xi^2)(1-\eta^2). \qquad (4.8)$$

$\xi_L < \xi < \xi_R$ and $\eta_0 < \eta < \eta_1$ with ξ_L, ξ_R, η_0, η_1 and a constant. As we suppose also the cylindrical symmetry of ρ, there is no dependence on the angle $\phi = \arctan(y_2/y_1)$ anywhere in the next calculation.

The coordinate η represents now the transverse coordinate; the points with $\eta = \eta_1 = 1$ lie on the x axis. The lower bound η_0 $(0 < \eta_0 < 1)$ determines how much the tube is opened. While $\eta_0 \to 1$ makes the tube flat, the limit case $\eta_0 \to 0$ changes the hyperboloid to two half-spaces separated by the plane $x=0$, communicating only through the circular hole of radius a.

For this geometry, Zwanzig [2] derived the exact flux through the bottleneck $(\xi = x = 0)$ under stationary conditions, when the density at infinity $\rho(\xi \to \infty)$ is kept constant. The diffusing particles can pass through the bottleneck only once, there is an absorbing BC at $\xi_L = 0$: $\rho(\xi=0)=0$, while on the walls of the hyperboloidal tube, the reflecting (Neumann) BC holds.

Our goal in this section is to test our variational mapping on this exactly solvable example. First we derive the extended Fick-Jacobs equation in the "natural" coordinates ξ, η (4.8). We make the supposition that ξ is the longitudinal coordinate and so our ansatz density ρ in the functional F (2.16) depends only on it: $\rho(x, y_1, y_2, t) = \rho(\xi, t)$. Having expressed the Jacobian of the transformation

$$\frac{\partial(x,r)}{\partial(\xi,\eta)} = -\frac{a^3}{r(\xi,\eta)}(\xi^2+\eta^2), \tag{4.9}$$

we can calculate α and κ according to (2.27) and (2.28):

$$\alpha(\xi) = \int_{\eta_0}^{1} a^3(\xi^2+\eta^2)d\eta = a^3\left[\xi^2(1-\eta_0) + \frac{1}{3}(1-\eta_0^3)\right], \tag{4.10}$$

$$\kappa(\xi) = \int_{\eta_0}^{1} \frac{r^2(\xi,\eta)d\eta}{a^3(\xi^2+\eta^2)}\left[(a\xi)^2 + \left(\frac{\eta a^2}{r(\xi,\eta)}(\xi^2+1)\right)^2\right] = a(1-\eta_0)(1+\xi^2), \tag{4.11}$$

that gives finally the extended Fick-Jacobs equation in the form

$$\frac{\partial\rho(\xi,t)}{\partial t} = \frac{1}{a^2\big(\xi^2+(1+\eta_0+\eta_0^2)/3\big)}\frac{\partial}{\partial\xi}(1+\xi^2)\frac{\partial}{\partial\xi}\rho(\xi,t). \tag{4.12}$$

In the stationary case $\partial_t\rho(\xi,t)=0$, so the prefactor $1/\alpha(\xi)$ in (4.12) becomes irrelevant and we have to solve the stationary equation

$$0 = \frac{\partial}{\partial\xi}(1+\xi^2)\frac{\partial}{\partial\xi}\rho(\xi), \tag{4.13}$$

which is identical with the equation solved by Zwanzig, giving the same result

$$\rho(\xi) = \rho_0\left(1 - \frac{2}{\pi}\arctan\frac{1}{\xi}\right) \tag{4.14}$$

if the same Dirichlet BC $\rho(0)=0$ and $\rho(\infty)=\rho_0$ are required. Following his calculation, we get the same formula for the total steady-state flux

$$J_0 = 4Da(1-\eta_0)\rho_0 \tag{4.15}$$

(we have the time rescaled by the diffusion constant D).

This calculation demonstrates that the extended Fick-Jacobs equation derived in natural coordinates gives an exact result under stationary conditions. It is not a surprise; the stationary condition leaves only one "natural" longitudinal coordinate in which the density varies. So the transients in η are quenched from the beginning.

C. Hyperboloidal tube; the λ expansion

Nevertheless, in the general case we do not know the "natural" longitudinal variable and we have to use a method which is able to find the mapped equation for arbitrary cross-section of the channel $A(x)$. One possibility is the expansion of $z(x,r)$ in λ, as we proposed in the previous section. Now we shall test it on the example of the hyperboloidal tube.

Starting from the definition of the hyperboloidal surface in oblate spheroidal coordinates (4.8) $\eta=\eta_0$, the function $R(x)$, bounding the radius of the channel in the cylindrical coordinates, reads

$$R^2(x) = \left(\frac{1}{\eta_0^2} - 1\right)(x^2+\eta_0^2a^2). \tag{4.16}$$

The first step is that of finding the transformation relation from (x,r) to the curvilinear coordinate z. We use the possibility of choosing $z_0(x)$ to cut off the series (2.21); if

$$z'_0(x) = \frac{2R(x)}{R'(x)} = \frac{2}{x}(x^2+\eta_0^2a^2), \quad \text{hence}$$

$$z_0(x) = x^2 + 2\eta_0^2a^2\log x + \text{const}, \tag{4.17}$$

then $z_1(x)=1$ and any next coefficient $z_j(x)$ is zero, so the relation $z=z(x,r)$ can be expressed in the closed form

$$z = z(x,r) = x^2 + \eta_0^2a^2\log\frac{x^2}{\eta_0^2a^2} + \lambda r^2. \tag{4.18}$$

The inverse relation $x=x(z,r)$ can be written as

$$x^2 = \eta_0^2a^2\text{PLog}(e^{(z-\lambda r^2)/\eta_0^2a^2}), \tag{4.19}$$

where we used the function Product Logarithm: $u=\text{PLog}(v)$, which is inverse to $v=ue^u$.

From now on, we do not need λ as an expansion parameter and we set it to 1, having restored isotropy of the diffusion in the channel. The upper limit of integration $R(x_z)$ in α and κ can then be obtained from the equation

$$z = z(x_z,R(x_z)) = \frac{x_z^2}{\eta_0^2} + \eta_0^2a^2\log\frac{x_z^2}{\eta_0^2a^2} + a^2(1-\eta_0^2) \tag{4.20}$$

in a simpler form

$$R^2(x_z) = a^2(1-\eta_0^2)\left[1 + \eta_0^2\text{PLog}\left(\frac{1}{\eta_0^2}e^{(z/a^2-1)/\eta_0^2+1}\right)\right]. \tag{4.21}$$

The integration over y can be carried out analytically, but the formulas for the functions $\alpha(z)$ and $\kappa(z)$ are rather complicated

$$\alpha(z) = \eta_0 a\int_0^{R(x_z)} rdr\frac{\partial}{\partial z}\sqrt{\text{PLog}e^{(z-r^2)/\eta_0^2a^2}} = -\frac{\eta_0 a}{2}[\sqrt{\text{PLog}(e^u)}]_{u_0}^{u_R}, \tag{4.22}$$

$$\kappa(z) = -2(\eta_0 a)^3\left[(\text{PLog}(e^u))^{3/2} - \frac{1}{\sqrt{\text{PLog}(e^u)}} + \left(4 + \frac{z}{\eta_0^2a^2} - u\right)\sqrt{\text{PLog}(e^u)}\right]_{u_0}^{u_R}, \tag{4.23}$$

where we have introduced an auxiliary variable $u=(z-r^2)/\eta_0^2a^2$, so the boundaries u_0 and u_R are

$$u_R = \frac{z-R^2(x_z)}{\eta_0^2a^2} \quad\text{and}\quad u_0 = \frac{z}{\eta_0^2a^2}. \tag{4.24}$$

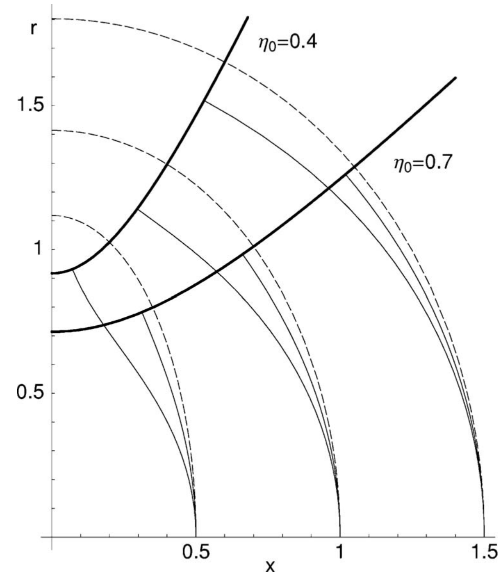

FIG. 3. The curves with constant $z=z(x,r)$ (thin full lines) in the hyperboloid. The functions $z(x,r)$ have the form (2.21) and obey the boundary condition (2.17) at $\lambda=1$. The thick lines depict the walls of the hyperboloid for $\eta_0=0.4$ and 0.7. The dashed curves are ellipses, defined as ξ=const according to the defining relation (4.8). While the ellipses are orthogonal to the hyperboloidal boundaries of any η_0, the curves $z=z(x,r)$ are orthogonal only to the boundary of specific η_0, for which they have been calculated.

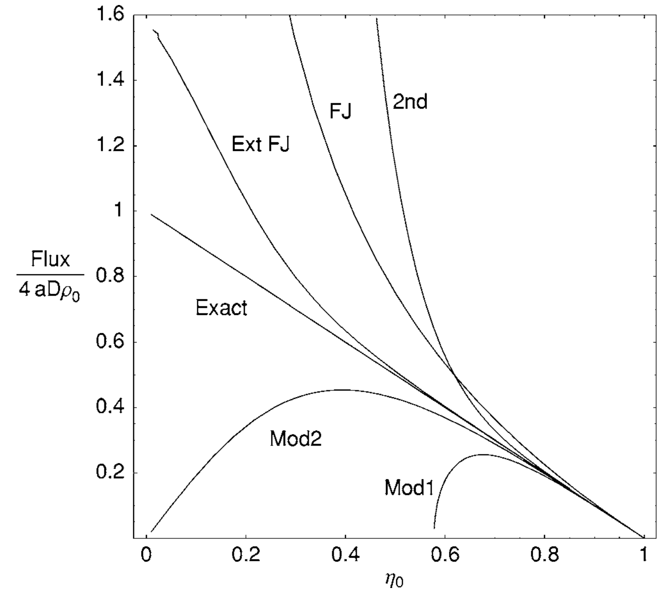

FIG. 4. Total stationary flux through the bottleneck of the hyperboloidal cone J_0 (normalized by $4aD\rho_0$) versus the parameter η_0. The variational method using the natural coordinates (4.8) gives the exact result (4.15). Extended Fick-Jacobs equation based on the λ-expansion of the transformation relation $z=z(x,r)$ leads to values that are close to the exact ones for $\eta_0>0.5$ (Ext FJ). For comparison, there are also plots of J_0 coming from the Fick-Jacobs equation (FJ), the Fick-Jacobs equation with the first order correction (Mod1), steady-state approximation up to the second order (2nd) and Zwanzig's intuitive modification of the corrected Fick-Jacobs equation (Mod2) [2] in the graph.

Also the corresponding extended Fick-Jacobs equation based on the variable z (2.20) is much more complicated than that derived in the natural coordinate ξ (4.12). These approximations are not equivalent: the curvilinear variable z cannot be transformed to ξ by some function $\xi(z)$. Notice that the variable ξ (4.8) reduces to x/a at the x axis, when $\eta=1$. However, we can transform z to a variable ζ, having the same property:

$$a^2\left(\zeta^2+\eta_0^2\log\frac{\zeta^2}{\eta_0^2}\right)=z\left(=x^2+\eta_0^2a^2\log\frac{x^2}{\eta_0^2a^2}+r^2\right), \tag{4.25}$$

but keeping $\xi=\zeta$=const, the curves $\xi=\xi(x,r)$ and $\zeta=\zeta(x,r)$ are not the same, they meet each other only at the x axis; see Fig. 3. While $\xi=\xi(x,r)$ (dashed lines) are ellipses focused in $(0,a)$, $(0,-a)$ and perpendicular to the hyperbolic boundaries (bold curves) for any η_0, the curves $\zeta=\zeta(x,r)$ are perpendicular only to the boundary of specific η_0, as required by the boundary condition (2.17) with $\lambda=1$.

Finally, we calculate the total flux through the bottleneck of the hyperboloidal tube. In this stationary case, the prefactor $1/\alpha(z)$ is again irrelevant, so we solve a simpler equation for $\rho(z)$:

$$0=\frac{\partial}{\partial z}\kappa(z)\frac{\partial}{\partial z}\rho(z),\quad \text{hence } \rho(z)=C_0\int_{-\infty}^{z}\frac{dz'}{\kappa(z')} \tag{4.26}$$

for the BC defined in the previous paragraph. C_0 is an integration constant fixed to set the desired value of $\rho=\rho_0$ in $z\to\infty$

$$C_0=\rho_0\int_{-\infty}^{\infty}\frac{dz}{\kappa(z)}. \tag{4.27}$$

The longitudinal component of the local flux density $j_x(x,r)$, from its defining relation

$$j_x(x,r)=-D\frac{\partial\rho(x,r)}{\partial x}=-D\frac{\partial z}{\partial x}\frac{\partial\rho(z)}{\partial z}=-D\frac{\partial z}{\partial x}\frac{C_0}{\kappa(z)} \tag{4.28}$$

gives

$$j_x(x\to 0,r)=-DC_0\frac{1}{(a\eta_0)^2}(e^{(1/\eta_0^2-1)/2}-1)^{-1}e^{r^2/2a^2\eta_0^2} \tag{4.29}$$

at the bottleneck, after having calculated the limit of $(\partial z/\partial x)\kappa^{-1}(z)$ for $z\to-\infty$. The total flux J_0 is then given by simple integration over the cross section of the tube

$$J_0=\int_0^{R(0)}2\pi j_x(x\to 0,r)r\,dr=-2\pi D\rho_0\left(\int_{-\infty}^{\infty}\frac{dz}{\kappa(z)}\right)^{-1}. \tag{4.30}$$

Having transformed from z to the dimensionless variable ζ (4.25), we find that the integral in this simple looking result is proportional to $1/a$, but still too complicated to be calculated analytically. For comparison with other approximations, we have calculated it numerically and the final values of $J_0/4Da\rho_0$, depending on the parameter η_0, are plotted in Fig. 4 together with the exact solution (4.15), the Fick-Jacobs result, the first order (Zwanzig) correction "Mod1," the second order steady-state approximation calculated from Eq. (3.10) and Zwanzig's intuitive formula "Mod2." Both curves, "Mod1" and "second" bear signs of a truncated expansion: they improve the results in the region of good convergence (η_0 close to 1, corresponding to very smooth channels), but for smaller η_0, the corrections make the results even worse than those from the Fick-Jacobs equation.

Our extended Fick-Jacobs equation, on the other hand, gives values very close to the exact ones for $\eta_0 > 0.5$, and even in the limit $\eta_0 \to 0$ goes to a finite nonzero value ~ 1.57.

V. CONCLUSION

In this paper, we have presented a mapping of the diffusion equation in a 2D or 3D channel of varying cross-section $A(x)$ onto a 1D differential equation using a variational method. As a variational ansatz, we have considered that the 2D (3D) density $\rho(x,y_1,(y_2),t)$ is a function of only one spatial (longitudinal) curvilinear variable z. The mapped 1D equation then always has the concise form

$$\frac{\partial\rho(z,t)}{\partial t} = \frac{1}{\alpha(z)}\frac{\partial}{\partial z}\kappa(z)\frac{\partial}{\partial z}\rho(z,t), \tag{5.1}$$

reminding one of the Fick-Jacobs equation, so we called it an extended Fick-Jacobs equation. The coefficients α and κ, depend on the geometry of the channel and also on the transformation between the coordinates $(x,y_1,\ldots)$ and $(z,y_1,\ldots)$.

The choice of the transformation relation $z=z(x,y_1,\ldots)$ appears to be crucial for the quality of the approximation. We proposed two possibilities. The first one is the transformation to the "natural" orthogonal coordinates, in which the channel turns into a simple rectangle (or a cylinder in 3D rotational symmetric case). One of them is declared as a longitudinal one, considered as z, on which the density ρ depends; the others are integrated out. This choice of z gave the exact result in the task we have solved: calculation of the total stationary flux through a hyperboloidal tube.

In the general case of an arbitrary cross section $A(x)$, we proposed $z=z(x,y)$ in the form of expansion

$$z(x,y) = x + \lambda y^2 z_1(x) + \lambda^2 y^4 z_2(x) + \cdots \tag{5.2}$$

in the parameter $\lambda = D/D_y$, expressing anisotropy of the diffusion constant in the longitudinal (D) and transverse (D_y) directions. Its coefficients z_j are fixed to obey the Neumann boundary conditions, requiring that the local flux density is parallel to the walls of the channel. This choice of z leads to the extended Fick-Jacobs equation (5.1), which is equivalent to the steady-state approximation [6] up to second order in λ and it sums properly all the terms depending only on $A(x)$ and $A'(x)$ in the higher orders of λ. Also, it gave a very good result in the test of calculating the stationary flux through the hyperboloidal tube (Fig. 4).

Nevertheless the density $\rho(z(x,y),t)$ does not satisfy the exact 2D (3D) diffusion equation (2.2) since the second order in λ—in contrast to the density $\rho(x,\vec{y},t)$ in the steady-state approximation [6]. Although taking the full expansion in our test example, we have not reconstructed the extended Fick-Jacobs equation as it comes out using natural coordinates. This raises the question of whether and how our variational mapping can be improved. Currently we see the fixing the transformation relation using ansatz (5.2) as the weakest point of our calculation. Finding the curvilinear coordinate $z=z(x,\vec{y})$ directly from within the variational method would make the result more consistent. Also, the question of how exact results can be achieved supposing 2D (3D) density ρ to be a function of only one spatial variable remains open.

As we have emphasized, the models studied here are very simple "toy models," chosen to evaluate strategies for analyzing diffusion in confined, i.e., quasi-one-dimensional spaces. These strategies extend without difficulty to many-body diffusion, and so the information obtained in the above fashion will be invaluable in the understanding at a quantitative level of the phenomenology of the more complex systems. Work along these lines is now under way.

ACKNOWLEDGMENTS

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