Corrections to the Fick-Jacobs equation

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Diffusion in a quasi-one-dimensional channel, with cross section varying along the longitudinal coordinate, is considered. Using a rigorous mapping of the diffusion equation onto one dimension, eliminating transients in transverse direction(s), we derive an expansion of the effective diffusion coefficient $D(x)$, which represents corrections to the Fick-Jacobs equation.

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I. INTRODUCTION

The key to solving most tasks coming from practice resides in proper simplification of description of the problem, reducing marginal effects, and leaving the substantial ones. Bulk diffusion in quasi-one-dimensional systems [two-dimensional (2D) or 3D narrow channel] of varying cross section $A(x)$ represents a simple example of a transport process, where such reduction is useful and can be qualitatively well understood: relaxation in transverse directions is marginal, but still influences 1D transport along the channel, which is our primary interest. Finding a suitable "low resolution" mathematical formulation, describing only 1D quantities, giving satisfactory results but still remaining simple enough to be used in practical calculations, is the open question.

The problem under consideration is defined as follows: let us study the time development of the 2D probability density $\rho(x,y,t)$ in a domain bounded by the x axis and the upper boundary, described by a function $A(x)>0$ for $x_L<x<x_R$. The probability density obeys the diffusion equation

$$\partial_t\rho(x,y,t) = D_0(\partial_x^2+\partial_y^2)\rho(x,y,t), \tag{1}$$

with diffusion constant D_0, which will be set to 1 in the sequel. We suppose reflecting boundary conditions (BC) at the lower and upper boundaries $y=0$ and $y=A(x)$; the BC at the ends of the channel x_L, x_R are arbitrary.

We suppose that this domain is narrow [the typical width of the channel $A(x)\ll x_R-x_L$] and only the 1D probability density

$$P(x,t) = \int_0^{A(x)} \rho(x,y,t)dy \tag{2}$$

or corresponding 1D flux $J(x,t)$ is of interest. The question is how to find a differential equation governing $P(x,t)$ giving (at least for certain sets of initial conditions) the same result as solving first the original diffusion equation (1) and then calculating the 1D density $P(x,t)$ according to Eq. (2).

The simplest equation of this kind is the Fick-Jacobs (FJ) equation [1]

$$\partial_t P(x,t) = \partial_x A(x)\partial_x P(x,t)/A(x), \tag{3}$$

respecting mass conservation in the longitudinal direction. This approximation neglects the influence of relaxation in transverse direction(s), supposing that it is infinitely fast, and so the transverse profile of the 2D (3D) density ρ is always flat. In a more detailed view, we have to notice that diffusing particles pile up, or miss, at the curved wall if the channel is getting narrower or wider in the direction of the local 1D flux $J(x,t)$, because they can flow out from and/or to the wall in the y direction only at finite rate. The real transverse profile of 2D (3D) density ρ depends on the transverse coordinates and this causes additional terms in the FJ equation.

Among various attempts to find these corrections, we mention Zwanzig's work [2], where he derived equations

$$\partial_t P(x,t) = \partial_x A(x)[1-A'^2(x)/3]\partial_x P(x,t)/A(x),$$

$$\partial_t P(x,t) = \partial_x A(x)[1-R'^2(x)/2]\partial_x P(x,t)/A(x) \tag{4}$$

for 2D and 3D channels with cylindrical symmetry, respectively; $R(x)$ is the radius and the cross section $A(x)=\pi R(x)^2$ in the 3D case.

Tests on channels with exactly solvable geometries showed that this correction does not suffice; Zwanzig estimated that the factors $(1-A'^2/3)$, $(1-R'^2/2)$ are truncated expansions of an effective diffusion coefficient $D(x)$ which could have the forms $1/(1+A'^2/3)$ or $1/(1+R'^2/2)$ in the 2D or 3D case, respectively.

The concept of the effective diffusion coefficient $D(x)$ was supported by Reguera and Rubí [3]; they presented consistent reasons for the corrected FJ equation in form

$$\partial_t P(x,t) = \partial_x A(x)D(x)\partial_x P(x)/A(x), \tag{5}$$

within the framework of mesoscopic nonequilibrium thermodynamics. They also improved Zwanzig's estimates of $D(x)$, proposing

$$D(x) = (1+A'^2)^{-1/3} \quad \text{and } D(x) = (1+R'^2)^{-1/2} \tag{6}$$

for 2D and symmetric 3D channels, respectively, with rather heuristic reasoning.

Without any doubt, the true form of the effective diffusion coefficient $D(x)$ can be found only by calculation of the next corrections to the FJ equation. Recently [4], we presented a mapping procedure, enabling us to gain systematically higher order corrections in the parameter $\epsilon = D_x/D_y$, which is the ratio of diffusion constants in the longitudinal and transverse directions. This anisotropy had been imposed on the diffusion equation (1) at the beginning. The result is

$$\partial_t P(x,t) = \partial_x A(x)[1 - \epsilon \hat{Z}(x,\partial_x)]\partial_x P(x)/A(x), \qquad (7)$$

with operator $\hat{Z}(x,\partial_x)$ of the form

$$\hat{Z}(x,\partial_x) = \sum_{k=0}^{\infty} \epsilon^k \zeta_k(x,\epsilon)\partial_x^k = \frac{1}{3}A'^2 + \frac{\epsilon}{45}[A'(AA'A'' + A^2A^{(3)} - 7A'^3) + (A^2A'^2)'\partial_x] + \cdots; \qquad (8)$$

the functions ζ_k are also expressed as Taylor series in ϵ. Notice that the first order term $\sim\epsilon$ recovers the Zwanzig correction (4), the 2D case. The same technique can be applied for mapping diffusion in a 3D channel as well; it is generalized in our following study [5], where we proved that full series of the type such as Eqs. (7) and (8) represent exact dimensional reduction of the original diffusion equation.

The problem is that instead of the expected effective diffusion coefficient $D(x)$, the exact mapping procedure gives an operator $1-\hat{Z}(x,\partial_x)$, containing spatial derivatives of any order, in general. The exact mapped equation (7) is then hard to use in practical calculations. One possible way is to return to the phenomenological description of Eq. (5), and calculate succeeding orders of $D(x)$ using a suitable mapping procedure. This is the aim of our present communication.

II. EXPANSION OF $D(x)$

Both concepts, describing corrections to the FJ equation, either using the operator $\hat{Z}(x,\partial_x)$ or via the effective diffusion coefficient $D(x)$, can meet in the stationary regime, where $\partial_t P(x,t)=0$. The typical task here is to find the total flux J through the channel, if the densities $P(x_L)$ and $P(x_R)$ at both ends are kept fixed. Due to continuity, J is constant in x and Eq. (5) is integrated to

$$J = -A(x)D(x)\partial_x P(x)/A(x), \qquad (9)$$

which can also be understood as an algebraic equation, relating the gradient of P/A and $D(x)$. Similarly, Eq. (7) leads to

$$J = -A(x)[1 - \epsilon\hat{Z}(x,\partial_x)]\partial_x P(x)/A(x), \qquad (10)$$

which is a complicated differential equation of higher order and it needs additional BC's to be solved uniquely; many of its solutions are nonphysical. Our goal is to find $D(x)$ such that the solutions of Eq. (9) also satisfy Eq. (10). We therefore substitute $\partial_x P(x)/A(x)$ from Eq. (9) in Eq. (10),

$$1 = A(x)[1 - \epsilon\hat{Z}(x,\partial_x)][A(x)D(x)]^{-1}. \qquad (11)$$

This relation fixes $D(x)$ uniquely within a recurrence scheme coming from our mapping procedure. To see this, we perform simple algebra:

$$\frac{1}{D(x)} = A(x)[1 - \epsilon\hat{Z}(x,\partial_x)]^{-1}1/A(x) = (1 + \epsilon A\hat{Z}A^{-1} + \epsilon^2 A\hat{Z}A^{-1}A\hat{Z}A^{-1} + \cdots)1 = [1 - \epsilon A(x)\hat{Z}(x,\partial_x)A^{-1}(x)]^{-1}1 \qquad (12)$$

(where the brackets enclose an operator, acting on the unit function 1).

Using the expansion (8) of the operator $\hat{Z}(x,\partial_x)$, we obtain directly the expansion of $1/D(x)$ or $D(x)$ in ϵ; the first few terms are

$$D(x) = 1 - \frac{\epsilon}{3}A'^2 + \frac{\epsilon^2 A'}{45}(9A'^3 + AA'A'' - A^2A^{(3)}) - \frac{\epsilon^3 A'}{945}(135A'^5 + 45AA'^3A'' - 58A^2A'A''^2 - 41A^2A'^2A^{(3)} - 12A^3A''A^{(3)} + 8A^3A'A^{(4)} + 2A^4A^{(5)}) + \cdots. \qquad (13)$$

This method gives $D(x)$ exactly, but it is rather tedious and one cannot go to high orders in ϵ. The following approximation results in a formula, which can be treated much more easily: If we relax the rule that operators act on everything to the right in products and suppose that factors $A(x)\hat{Z}(x,\partial_x)A^{-1}(x)$ in Eq. (12) are only numbers, i.e., $\hat{Z}$ acts only on the following A^{-1}, we can perform the final inversion of $1/D(x)$ and write

$$D(x) \simeq 1 - \epsilon A(x)\hat{Z}(x,\partial_x)A^{-1}(x). \qquad (14)$$

The difference appears at order ϵ^3. For determining the expansion of $A\hat{Z}A^{-1}$, it is possible to use the same recurrence scheme as for generating $\hat{Z}$ (see Appendix); specific terms then have simple structure and can be summed to infinity. In the simplest approximation, one may neglect the second and higher derivatives of $A(x)$. The result is

$$D(x) \simeq 1 - \frac{\epsilon}{3}A'^2 + \frac{\epsilon^2}{5}A'^4 + \cdots + \frac{(-\epsilon)^n}{2n+1}A'^{2n} + \cdots = \frac{\arctan\sqrt{\epsilon}A'(x)}{\sqrt{\epsilon}A'(x)}. \qquad (15)$$

The same procedure can be performed in the case of a 3D channel with cylindrical symmetry. The corresponding operator $\hat{Z}$ is given by the expansion

$$\hat{Z}(x,\partial_x) = \frac{1}{2}R'^2 + \frac{\epsilon}{48}[R'(R^2R^{(3)} + RR'R'' - 14R'^3) + (R^2R'^2)'\partial_x] + \cdots, \qquad (16)$$

and one can find similar formulas for $D(x)$,

$$\frac{1}{D(x)} = [1 - \epsilon R(x)\hat{Z}(x,\partial_x)R^{-1}(x)]^{-1}1 \quad \text{or}$$

$$D(x) \simeq 1 - \epsilon R(x)\hat{Z}(x,\partial_x)R^{-1}(x). \tag{17}$$

The first few terms of the exact expansion are

$$D(x) = 1 - \frac{\epsilon}{2}R'^2 + \frac{\epsilon^2}{48}R'(18R'^3 + 3RR'R'' - R^2R^{(3)}) - \frac{\epsilon^3}{768}R'(240R'^5 + 120RR'^3R'' - 36R^2R'R''^2 - 40R^2R'^2R^{(3)} - 14R^3R''R^{(3)} + R^3R'R^{(4)} + R^4R^{(5)}) + \cdots . \tag{18}$$

As expected, the approximation neglecting the second and higher derivatives of radius $R(x)$ allows us to express $D(x)$ in closed form

$$D(x) \simeq 1 - \frac{\epsilon}{2}R'^2 + \frac{3}{8}\epsilon^2R'^4 + \cdots + \frac{(2n-1)\,!!}{(2n)\,!!}(-\epsilon A'^2)^n + \cdots = \frac{1}{\sqrt{1+\epsilon R'^2}}, \tag{19}$$

which is the same formula (as opposed to the 2D case) as the one proposed by Reguera and Rubí [3] for the 3D channel. The quality of this approximation was demonstrated on the exactly solvable example of calculating the stationary flux through a 3D hyperboloidal cone with fixed 3D density $\rho(x,y_1,y_2)=\rho_0$ as $x\to\infty$ and $\rho(x=0)=0$. Comparison with other methods can be found also in Ref. [6].

Verification of the formulas (15) and (19) in the Appendix shows that there is no better approximation for $D(x)$ involving only the first derivative of the cross section $A(x)$; we have collected here all the terms of this kind. Further improvement can be achieved only by including the terms with higher derivatives of $A(x)$. Finding the relevant infinite series in the expansions (13) or (18) that can be summed into a simple formula like Eq. (18) is not an easy task.

Another way to find $D(x)$ is by the supposition that the 2D (3D) density ρ depends only on one spatial, but curvilinear, coordinate $z=z(x,y)$; $\rho(x,y,t)=\rho(z,t)$. A variational approach [6] showed that $\rho(z,t)$ then obeys the equation

$$\partial_t\rho(z,t) = 1/\alpha(z)\partial_z\kappa(z)\partial_z\rho(z,t), \tag{20}$$

for suitable functions $\alpha(z)$ and $\kappa(z)$ [fixed together with the transformation relation $z=z(x,y)$ within the method [6]], depending on $A(x)$ (2D) or $R(x)$ (3D). Then finding the effective diffusion coefficient $D(x)$ becomes in fact a matter of a coordinate transformation which can be carried out in the following manner: In the stationary regime $\partial_t\rho=0$, the general stationary solution of Eq. (20) is

$$\rho(z) = C_1\int\frac{dz}{\kappa(z)} + C_0, \tag{21}$$

where C_0, C_1 are integration constants. Hence the total flux $J(x)=J$ is

$$J = -\int_0^{A(x)} dy\,\partial_x\rho(z(x,y))\ (2\text{D});$$

$$J = -\int_0^{R(x)} 2\pi r dr\,\partial_x\rho(z(x,r))\ (3\text{D}). \tag{22}$$

On the other hand, we can calculate the stationary 1D density $P(x)$, Eq. (2), from $\rho(z(x,y))$, Eq. (21), and then a comparison of the flux J, Eq. (9), with Eq. (22) gives $D(x)$.

For the form $A(x)=ax$, this calculation quickly verifies the formula (15). According to Ref. [6], the proper curvilinear coordinate is $z=\sqrt{x^2+\epsilon y^2}$ and the corresponding $\kappa(z)=z$. Then the stationary density $\rho(z)=C_1\ln z+C_0$ and the flux $J=-C_1\arctan(\sqrt{\epsilon}a)/\sqrt{\epsilon}$ comes from Eq. (22). In Cartesian coordinates, the corresponding stationary 1D density $P(x)$ is

$$\frac{P(x)}{A(x)} = C_1\left(\frac{\arctan(\sqrt{\epsilon}a)}{\sqrt{\epsilon}a} - 1 + \frac{1}{2}\ln(1+\epsilon a^2) + \ln x\right) + C_0, \tag{23}$$

so substituting into Eq. (9) and comparing with the result of Eq. (22) gives

$$D(x) = \frac{\arctan(\sqrt{\epsilon}a)}{\sqrt{\epsilon}a}. \tag{24}$$

The 3D case with $R(x)=ax$ can be treated in the same way: the curvilinear coordinate $z=\sqrt{x^2+\epsilon r^2}$ and the corresponding $\kappa(z)=z^2$ take place in this geometry. Following the same steps, we arrive at the formula

$$D(x) = \frac{1}{\sqrt{1+\epsilon a^2}}. \tag{25}$$

These results have exactly the form of Eqs. (15) and (19). The parameter a can be interpreted as the local slope of the width $A'(x)$ (2D) or radius $R'(x)$ (3D) in the general case; in this context, the formulas (15) and (19) represent an approximation of a locally linearized channel.

The variational method, using transformation to the curvilinear coordinate z, enables us to avoid complicated expansions and so it may help to suggest better approximations for the effective diffusion coefficient $D(x)$, including higher derivatives of $A(x)$. On the other hand, Eq. (20) in the higher orders of ϵ is not equivalent to the perturbation expansion (7), which represents the exact mapping. It is worth then to check any approximation of $D(x)$ against its exact expansion (13) or (18).

Let us notice that (for the reason of testing) the effective diffusion coefficient $D(x)$ for the channels with exactly solvable geometries can be also expressed exactly. As an example, we do it for the 3D hyperboloidal cone: In oblate spheroidal coordinates (ξ,η), $x=a\xi\eta$, $r^2=a^2(1+\xi^2)(1-\eta^2)$, the cone is defined as a rectangle $\xi_L<\xi<\xi_R$ and $\eta_0<\eta<1$ ($\eta=1$ coincides with the x axis); $\xi_{L,R}$ denotes the ends of the channel, the parameter $\eta_0>0$ sets the opening of the cone, and a is a length scale. $\xi=\xi(x,r)$ becomes the spatial variable, in which the stationary density $\rho(\xi)$ is considered. Using the Laplaceian in oblate spheroidal coordinates in the

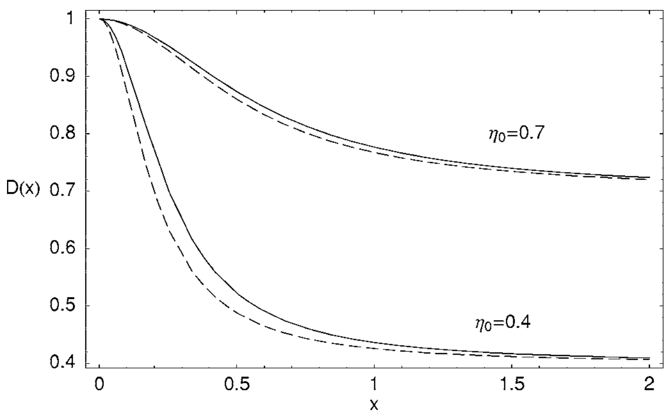

FIG. 1. Effective diffusion coefficient $D(x)$, depending on the longitudinal coordinate x, for the 3D hyperboloidal cone ($a=1$, $\eta_0=0.4$ and 0.7). The solid lines represent the exact function (27), the dashed lines depict the approximation equation (19).

diffusion equation [2] or applying the variational method [6],we arrive at $\kappa=1+\xi^2$, hence $\rho(\xi)=C_1\arctan\xi+C_0$. The total flux according to Eq. (22) is then $J=-2\pi a(1-\eta_0)C_1$.

In Cartesian coordinates, the boundary of the cone is given by $R^2(x)=(a^2\eta_0^2+x^2)(1/\eta_0^2-1)$ and $\rho(\xi)$ transforms to

$$\frac{P(x)}{A(x)}=C_1\arctan\frac{x}{\eta_0 a}+C_0-\frac{C_1 x a\eta_0(1-\eta_0)}{(x^2+\eta_0^2a^2)(1+\eta_0)}. \tag{26}$$

After substituting into Eq. (9) and comparing J, we obtain the exact effective diffusion coefficient for this geometry

$$D(x)=\frac{\eta_0(x^2+\eta_0^2a^2)}{x^2+\eta_0^3a^2}. \tag{27}$$

This function compared with the approximate formula (19) for the hyperboloidal cone is described in Fig. 1.

III. CONCLUSION

Our present analysis demonstrates that the mapping procedure, recently developed to project the 2D (3D) diffusion in a narrow channel onto the longitudinal direction, can be adopted to calculate the effective diffusion coefficient $D(x)$, defined within the framework of nonequilibrium thermodynamics. $D(x)$ involves corrections to the Fick-Jacobs equation, caused by the finite rate of relaxation in the transverse directions. Although the exact mapping leads to a correction operator, including derivatives ∂_x instead of the pure correction function $D(x)$, both descriptions become equivalent in the limit of stationary regime that is used in this calculation.

Our result is a perturbation expansion of $D(x)$ in a parameter ϵ, which can be carried out to any desired order for an arbitrarily shaped 2D or 3D channel with cylindrical symmetry. (Until now, only the first order correction has been known.) If the second and higher derivatives of the cross section $A(x)$ are neglected, the perturbation series can be summed to infinity and we obtain simple approximate formulas for $D(x)$. In the 3D case, this calculation proves the formula of Reguera and Rubí [3], argued originally only heuristically.

For practical purposes, it is worthwhile to look for a more complex infinite series of terms in the expansion of $D(x)$, which could be summed and expressed in closed form, containing also higher derivatives of $A(x)$. We suppose that considering the 2D (3D) density as a function of one curvilinear coordinate might be helpful in this effort.

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APPENDIX

We want to present here more technical details concerning construction of the recurrence schemes for expansion of $D(x)$ and to prove the expansions leading to formulas (15) and (19).

First, we have to recall briefly the recurrence scheme generating the operator $\hat{Z}(x,\partial_x)$ (see Refs. [4,5]). In the mapping procedure, there are two important operators, which are to be found: aside from the operator $\hat{Z}$, defining the dynamics in the space of 1D functions $P(x,t)/A(x)$, Eq. (7), there is also an operator $\hat{\omega}(x,y,\partial_x)$, mapping the space of functions $P(x,t)/A(x)$ back onto the space of the original 2D densities $\rho(x,y,t)$, $\rho(x,y,t)=\hat{\omega}(x,y,\partial_x)P(x,t)/A(x)$, resulting in the inverse relation

$$P(x)=\int_0^{A(x)}dy\,\hat{\omega}(x,y,\partial_x)P(x)/A(x). \tag{A1}$$

Both operators are written as expansions in the parameter ϵ

$$\hat{\omega}(x,y,\partial_x)=\sum_{j=0}^{\infty}\epsilon^j\hat{\omega}_j(x,y,\partial_x),\quad \epsilon\hat{Z}(x,\partial_x)=\sum_{j=1}^{\infty}\epsilon^j\hat{Z}_j(x,\partial_x), \tag{A2}$$

and the operators $\hat{\omega}_j$ and $\hat{Z}_j$ are calculated simultaneously according to the pair of recurrence relations

$$\partial_y^2\hat{\omega}_{j+1}(x,y,\partial_x)=-\sum_{k=0}^{j}\hat{\omega}_{j-k}(x,y,\partial_x)\frac{1}{A(x)}\partial_x A(x)\hat{Z}_k(x,\partial_x)\partial_x - \partial_x^2\hat{\omega}_j(x,y,\partial_x) \tag{A3}$$

and

$$\hat{Z}_j(x,\partial_x)\partial_x=\frac{A'(x)}{A(x)}\hat{\omega}_j(x,y=A(x),\partial_x)\quad \text{for } j>0, \tag{A4}$$

starting from $\hat{\omega}_0(x,y,\partial_x)=1$ and $\hat{Z}_0(x,\partial_x)=-1$ to be used in Eq. (A3).

Having determined $\partial_y^2\hat{\omega}_{j+1}$, we integrate it twice over y, fix the integration constants to satisfy two conditions: BC in the y direction $\partial_y\hat{\omega}_{j+1}(x,y,\partial_x)|_{y=0}=0$ and normalization $\int_0^{A(x)}dy\,\hat{\omega}_j(x,y,\partial_x)=0$, coming from Eq. (A1), and finally find the next $\hat{Z}_{j+1}(x,\partial_x)$ according to Eq. (A4).

This scheme leads to very complicated formulas after a few iterations, if applied to find the operators $\hat{\omega}_j$ and $\hat{Z}_j$. The result can be reduced to a much simpler form, if only $\hat{\omega}_j f(x)$ and $\hat{Z}_j\partial_x f(x)$ for some specific functions $f(x)$ are needed. This is the case in calculating $D(x)$ according to the approximate relation Eq. (14), i.e., the terms $A(x)\hat{Z}_j(x,\partial_x)A^{-1}(x)$.

In the simplest case, if we neglect the second and higher derivatives of $A(x)$, it is enough to take only $f(x) = \int dx/A(x)$. Let us follow the first steps of the iterative procedure for this function,

$$\partial_y^2\hat{\omega}_1 f(x) = \frac{1}{A(x)}\partial_x A(x)\partial_x f(x) - \partial_x^2 f(x) = \frac{1}{A(x)}\partial_x 1 - \partial_x\frac{1}{A(x)} = \frac{A'(x)}{A^2(x)}. \tag{A5}$$

After double integration over y and fixing the integration constants, we have

$$\hat{\omega}_1 f(x) = \left(\frac{y^2}{2} - \frac{A(x)^2}{6}\right)\frac{A'(x)}{A(x)^2},$$

$$\text{so } \hat{\omega}_1(x,A(x),\partial_x)f(x) = \frac{1}{3}A'(x) \tag{A6}$$

and finally, we obtain the first correction term according to Eq. (A4),

$$A(x)\hat{Z}_1 A^{-1}(x) = A(x)\hat{Z}_1\partial_x f(x) = \frac{1}{3}A'(x)^2. \tag{A7}$$

Continuing the same way gives

$$\hat{\omega}_j f(x) = (-1)^{j-1}\left(\frac{y^{2j}}{2j} - \frac{A^{2j}}{2j(2j+1)}\right)\frac{A'^{2j-1}}{A^{2j}} \tag{A8}$$

and

$$A(x)\hat{Z}_j A^{-1}(x) = A(x)\hat{Z}_j\partial_x f(x) = \frac{(-1)^{j-1}}{2j+1}A'^{2j}, \tag{A9}$$

if $A''(x)$ and its derivatives are neglected. The proof is by mathematical induction. In $j+1$ order

$$\partial_y^2\hat{\omega}_{j+1}f = \hat{\omega}_j\frac{1}{A}\partial_x 1 - \sum_{k=0}^{j-1}\hat{\omega}_{j-k}\frac{1}{A}\partial_x A\hat{Z}_k\partial_x f - \partial_x^2\hat{\omega}_j f = (-1)^j(2j+1)y^{2j}\frac{A'^{2j-1}}{A^{2j+2}} + \text{terms with } A'', \tag{A10}$$

the derivative ∂_x in the sum acts on $A\hat{Z}_k\partial_x f$, which contains only A'. Neglecting A'', performing double integration over y, and fixing integration constants, we obtain expression (A8) for $j\to j+1$ and using Eq. (A4), we arrive at the corresponding Eq. (A9).

Mapping a 3D channel with cylindrical symmetry is carried out in the same way. We suppose the 3D density $\rho(x,r,t)$ to not depend on the angle ϕ in the cylindrical coordinate system, connected with the axis of symmetry x, as well as the boundary, defined by the local radius $R(x)$. The density ρ then satisfies the original diffusion equation

$$\partial_t\rho(x,r,t) = \left(\partial_x^2 + \frac{1}{\epsilon r}\partial_r r\partial_r\right)\rho(x,r,t), \tag{A11}$$

with reflecting boundary condition on the wall and arbitrary conditions at the ends of the tube, $x=x_L,x_R$. The mapping procedure generates again a differential equation for 1D density $P(x,t)$, defined now as

$$P(x,t) = 2\pi\int_0^{R(x)} rdr\rho(x,r,t), \tag{A12}$$

of the form (7) with $A(x)=\pi R^2(x)$. Aside from the operator $\hat{Z}(x,\partial_x)$, we have to look also for the operator $\hat{\omega}(x,r,\partial_x)$, mapping P/A back onto the space of ρ. Both operators are expressed as series [Eq. (A2)] in ϵ and calculated simultaneously according to the recurrence relations

$$\frac{1}{r}\partial_r r\partial_r\hat{\omega}_{j+1}(x,r,\partial_x) = -\sum_{k=0}^{j}\hat{\omega}_{j-k}(x,r,\partial_x)\frac{1}{A(x)}\partial_x A(x)\hat{Z}_k(x,\partial_x)\partial_x - \partial_x^2\hat{\omega}_j(x,r,\partial_x) \tag{A13}$$

and

$$\hat{Z}_j(x,\partial_x)\partial_x = \frac{A'(x)}{A(x)}\hat{\omega}_j(x,R(x),\partial_x) = \frac{2R'(x)}{R(x)}\hat{\omega}_j(x,R(x),\partial_x) \tag{A14}$$

for $j>0$, with the same starting values $\hat{\omega}_0(x,r,\partial_x)=1$ and $\hat{Z}_0(x,\partial_x)=-1$ as in the 2D case. Fixing two integration constants in 3D, we provide regularity of $\hat{\omega}_j$ on the x axis and the normalization condition $\int_0^{R(x)} rdr\hat{\omega}_j(x,r,\partial_x)=0$ for $j>0$, coming from Eq. (A12).

Calculation of the effective diffusion coefficient $D(x)$ according to Eq. (14) requires again taking $f(x)=\int dx/A(x)$ and iterating for $\hat{\omega}_j f(x)$ and $A(x)\hat{Z}_j\partial_x f(x)$. The first step is obvious:

$$\frac{1}{r}\partial_r r\partial_r\hat{\omega}_1 f(x) = \frac{1}{A(x)}\partial_x A(x)\partial_x f(x) - \partial_x^2 f(x) = -\partial_x\frac{1}{A(x)} = \frac{2R'(x)}{\pi R^3(x)}. \tag{A15}$$

After double integration over r and fixing the integration constants, we have

$$\hat{\omega}_1 f(x) = \left(\frac{r^2}{2R^2(x)} - \frac{1}{4}\right)\frac{R'(x)}{\pi R(x)};$$

$$\text{so } \hat{\omega}_1(x,R(x),\partial_x)f(x) = \frac{R'(x)}{4\pi R(x)}, \tag{A16}$$

and according to Eq. (A14), the first correction term to $D(x)$ is

$$A(x)\hat{Z}_1 A^{-1}(x) = A(x)\hat{Z}_1 \partial_x f(x) = \frac{1}{2}R'(x)^2. \quad \text{(A17)}$$

If continued to higher orders, in the simplest approximation when $R''(x)$ and higher derivatives are neglected, the functions $\hat{\omega}_j f(x)$ have a bit more complicated structure,

$$\hat{\omega}_j(x,r,\partial_x)f(x) = \frac{R'^{2j-1}(x)}{4^j\pi}\sum_{k=0}^{j}\frac{(-1)^k(2k)!}{(k!)^2}c_{j-k}\frac{r^{2k}}{R^{2k+1}(x)}, \quad \text{(A18)}$$

to fit Eq. (A13) applied on $f(x)$, together with

$$A(x)\hat{Z}_j\partial_x f(x) = 2\left(\frac{R'^2}{4}\right)^j\sum_{k=0}^{j}\frac{(-1)^j(2k)!}{(k!)^2}c_{j-k}, \quad \text{(A19)}$$

depending only on $R'(x)$ as in 2D, so the sum in Eq. (A13) contains only terms with $R''(x)$ and higher, which are to be neglected in this approximation.

Integration constants c_j are fixed from the normalization conditions in successive orders. Starting from $c_0=-1$, we obtain the following sequence of equations

$$\sum_{k=0}^{j-1}\frac{(-1)^{k+1}(2k)!}{k!(k+1)!}c_{j-k} = \frac{(-1)^{j+1}(2j)!}{j!(j+1)!}. \quad \text{(A20)}$$

Its solution

$$c_{j+1} = \frac{(-1)^{j+1}(2j)!}{j!(j+1)!} \quad j \geq 0 \quad \text{(A21)}$$

can be easily verified, having constructed a function $g(\tau)$,

$$g(\tau) = \sum_{j=0}^{\infty}\frac{(2j)!}{j!(j+1)!}(-\tau)^{j+1} = \frac{1}{2}(1-\sqrt{1+4\tau}). \quad \text{(A22)}$$

Using the property of g that $g^2(\tau)=g(\tau)+\tau$, expanding both sides of this relation in τ and comparing the coefficients at τ^{j+1}, we obtain Eq. (A20) with Eq. (A21).

The function $g(\tau)$ also enables us to find the approximate formula for $D(x)$. If we set $\epsilon R'^2(x)/4=\tau$,

$$\begin{aligned} D(x) &\simeq 1 - \sum_{j=1}^{\infty}\epsilon^j A(x)\hat{Z}_j\partial_x f(x) \\ &\simeq 1 - 2\sum_{j=1}^{\infty}\left(\sum_{k=0}^{j-1}\frac{(-\tau)^k(2k)!}{(k!)^2}\frac{(-\tau)^{j-k}[2(j-k-1)]!}{(j-k-1)!(j-k)!} - \frac{(-\tau)^j(2j)!}{(j!)^2}\right) = 1-2[-g'(\tau)g(\tau)+g'(\tau)+1] \\ &= -g'(\tau) = \frac{1}{\sqrt{1+4\tau}}. \end{aligned} \quad \text{(A23)}$$

Better approximations could be made, if one could find next functions $f(x)$, which help express $\hat{\omega}_{j-k}A^{-1}\partial_x A\hat{Z}_k\partial_x f$ terms with higher accuracy. We leave this question open.

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