Asymptotic solution of the diffusion equation in slender impermeable tubes of revolution. I. The leading-term approximations

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Abstract

The anisotropic 3D equation describing the pointlike particles diffusion in slender impermeable tubes of revolution with cross section smoothly depending on the longitudinal coordinate is the object of our study. We use singular perturbations approach to find the rigorous asymptotic expression for the local particles concentration as an expansion in the ratio of the characteristic transversal and longitudinal diffusion relaxation times. The corresponding leading-term approximation is a generalization of well-known Fick-Jacobs approximation. This result allowed us to delineate the conditions on temporal and spatial scales under which the Fick-Jacobs approximation is valid. A striking analogy between solution of our problem and the method of inner-outer expansions for low Knudsen numbers gas kinetic theory is established. With the aid of this analogy we clarify the physical and mathematical meaning of the obtained results.
I. INTRODUCTION

The problem of approximate reduction of the time-dependent 3D equation describing the local concentration field $C(x,t)$ of pointlike particles diffusing in a tube of varying with the longitudinal coordinate $z$ cross section to an effective time-dependent 1D equation appeared to be fairly tricky. For the first time, following the main idea of Fick’s approach, such kind of 1D equation was derived in 1935 by Jacobs. Particularly for a channel with a shape of a surface of revolution the relevant 1D equation reads

$$\frac{\partial c(z,t)}{\partial t} = \frac{\partial}{\partial z} D \left\{ A(z) \frac{\partial}{\partial z} \left[ \frac{c(z,t)}{A(z)} \right] \right\},$$

(1)

where $D$ is the translational diffusion coefficient in space with no constraints, $A(z) = \pi [r(z)]^2$ is the area of the tube cross-section $\Sigma_z$ of radius $r(z)$ at a given point $z$ of the symmetry axis. The corresponding reduced concentration $c(z,t)$ is calculated by the formula

$$c(z,t) = \int_{\Sigma_z} C(x,y,z,t) \, dx \, dy.$$  

(2)

Nowadays the reduced diffusion equation (1) is commonly referred to as the Fick-Jacobs equation (FJE). In addition we will call Eq. (1) a classical form of the FJE. It is interesting that, if we do not take into account a few works on this subject, for decades the FJE remained almost unclaimed. Situation has been changed drastically after 1992 when well-known Zwanzig’s article renewed the problem and stimulated considerable interest to this topic. Soon it turned out that the problem on diffusion in a tube of varying cross section is of great importance for numerous applications dealing with artificial and natural transport processes and thence many researchers studied it within different facets of theory and applications. Even now these kind of investigations are close to the top among hot research topics on the diffusion-influenced processes in confined regions.
In his seminal paper Zwanzig drew attention to the fact that Jacobs derivation is rather heuristic and, besides, it is completely free of impermeable wall boundary condition that should be imposed on the solution of the original higher dimensional diffusion equation. Moreover, Jacobs did not present any reasons for choosing the center line of the tube. Taking into account that the FJE has exactly the same mathematical structure as the Smoluchowski equation for diffusion in a 1D potential field, Zwanzig derived the FJE starting from the general diffusion equation with a potential. According to Zwanzig the FJE may be presented in the form

$$\frac{\partial c(z,t)}{\partial t} = \frac{\partial}{\partial z} D \left\{ e^{-\frac{U(z)}{k_B T}} \frac{\partial}{\partial z} \left[ e^{\frac{U(z)}{k_B T}} c(z,t) \right] \right\}.$$  \hspace{1cm} (3)

In (3) $U(z)$ is so-called entropy potential defined as

$$U(z) = -k_B T \ln A(z),$$

where $k_B$ and $T$ are the Boltzmann constant and the absolute temperature. Assuming that the channel radius varies slowly with increasing of the longitudinal variable $z$, i.e.,

$$\left| r'(z) \right| \ll 1,$$  \hspace{1cm} (4)

hereafter in the paper $\psi'(\zeta) := d\psi(\zeta)/d\zeta$, he also proposed a generalized form of the FJE. For particular case of 3D tube the original diffusion constant $D$ in the FJE (1) was replaced by a spatially dependent effective diffusion coefficient

$$D_{Zw}(z) \approx \frac{D}{1 + \frac{1}{2} \left[ r'(z) \right]^2}.$$  \hspace{1cm} (3)

Later, in 2001 Reguera and Rubi developed this idea using some nonequilibrium thermodynamics reasons and obtained the corrected FJE with

$$D_{R-R}(z) \approx \frac{D}{\sqrt{1 + \left[ r'(z) \right]^2}}.$$
in case of 3D symmetric tubes.\(^{16}\)

Further corrections to the FJE were obtained by Kalnay and Percus with the help of so-called mapping technique, which differs from Zwanzig’s entropy barrier theory.\(^{17–19}\) This mapping procedure has been performed for the anisotropic diffusion equation without a potential

\[
\frac{\partial C}{\partial t} = \nabla \cdot (\mathbf{D} \cdot \nabla C),
\]

where \(\mathbf{D}\) is the translational diffusion tensor matrix. As in Refs. 17 and 19 we suppose here that the diffusion matrix is diagonal with transverse isotropy, i.e., \(\mathbf{D} = \text{diag}(D_x, D_y, D_z)\), and that \(D_x = D_y = D_\perp\) is the transverse and \(D_z = D_\parallel\) is the longitudinal translational diffusion coefficient, respectively. In their study Kalnay and Percus assumed also that

\[
\varepsilon = D_\parallel / D_\perp \ll 1,
\]

which allowed them to suggest that the transverse concentration profile equilibrates quickly and so-called Zwanzig’s factorization holds true. Moreover, this is a quasi steady-state theory, i.e., field \(C(x, t)\) is assumed to be an explicitly time-independent. Time dependence is presented in this function implicitly by functional of the reduced concentration \(c(z, t)\) only. Under given assumptions in the limit \(\varepsilon \to 0\) diffusion equation with reflecting wall condition is reduced to the corresponding FJE. In its turn for higher-order terms in \(\varepsilon\) Kalnay and Percus derived a generalized 1D equation that contains all higher derivatives with respect to \(z\) of the tube radius \(r(z)\) and reduced concentration \(c(z, t)\).\(^{17–19}\) Kalnay and Percus drew attention to the fact that the problem ”requires an analysis of the short-time behavior”, but they did not deal with this question.\(^{17}\) The projection method has been used by Dagdug and Pineda to find more general effective diffusion coefficient for the FJE, describing the unbiased motion of pointlike particles in 2D slender tilted asymmetric...
channels of varying width formed by straight wall. In the subsequent paper of the same authors, to test the validity of obtained formulae, a comparison of these analytical results against Brownian dynamics simulation results were performed.

The biased diffusion transport of pointlike particles under the influence of a constant and uniform force field in 2D and 3D narrow spatially periodic channels of varying cross section is also rather well investigated.

It is worth noting that on account of a mathematical difficulties in solving the original problem for arbitrary tube radius \( r(z) \) an effective 1D description for the simplified case when the tubes composed of some number of contacting equal spheres or cylindrical sections of different diameters was investigated. Further generalization of the previous research to the case of a periodically expanded conical tube was recently reported. It is important that tubes of this shape may be utilized as a controlled drug release device. The interested reader can find numerous references to the previous analytical and numerical studies in a recent paper by Kalnay.

The analysis of the literature showed that, despite the great amount of publications devoted to the topic, rigorous mathematical study of the corresponding boundary value problem for all spatial and temporal scales is still missing. Thus, the purpose of this paper is twofold. Firstly using rigorous technique of the matched asymptotic expansions we consider the 3D anisotropic diffusion equation which describes the diffusion of pointlike particles into a tube with impermeable wall having the shape of a surface of revolution. Secondly accurate asymptotic solution of the original 3D problem for all spatial and temporal scales allows us to elucidate the role, physical and mathematical sense and lastly accuracy of the leading-term approximation and, particularly, the validity of the Fick-Jacobs approximation.
The paper is organized in the following way. Section II contains the full mathematical statement of the corresponding boundary value problem. In Sec. III by means of singular perturbations approach we give the detailed preliminary ideas for asymptotic solution of the posed problem. Section IV devotes to the asymptotic solution in the outer subdomain and, particularly, derivation of the Fick-Jacobs equation. In Sec. V and Sec. VI we study solution in spatial and temporal diffusive boundary layers, respectively, to derive, in particular, the appropriate boundary and initial conditions for solution of the Fick-Jacobs equation. Section VII presents determination of the corner asymptotic solutions. In Sec. VIII the main result of the paper the leading-term approximation is reported. This section also comprises criteria for validity of the Fick-Jacobs approximation and establishes a profound analogy of the problem at issue with the gas kinetic theory for low Knudsen numbers. Finally the main concluding remarks are made in Sec. IX. Some subsidiary classical mathematical facts are given in Appendix.

II. STATEMENT OF THE PROBLEM

Consider the pointlike particles diffusion in a 3D tube of length $L$, which wall is obtained by rotation of the line

$$r (z) = r_M R (z/L)$$

(7)

around the $z$ axis (see Fig. I). We assume function $r (z)$ to be smooth enough and introduced the maximum value of this function

$$r_M := r (z_M) = \max_{z \in [0, L]} r (z)$$

which fully characterizes the transverse size of the tube. It is evident that

$$0 < R (z/L) \leq 1 = R (z_M/L)$$
FIG. 1: Geometric sketch of the problem.

for all \( z \in [0, L] \). By definition we shall call tube slender (narrow) when

\[
\frac{r_M}{L} \ll 1.
\]

In the cylindrical coordinate system \((r, \phi, z)\) connected with the \( z \) axis the tube region is

\[
\Sigma := \{0 < r < r(z)\} \times (0 < z < L) \times (0 < \phi < 2\pi).
\]

A cross section of the tube at any fixed value \( z \) is \( \Sigma_z := \{0 < r < r(z)\} \times (0 < \phi < 2\pi) \) and \( \partial \Sigma_w := \{r = r(z), \phi \in (0, 2\pi), z \in [0, L]\} \) is the tube wall. Moreover we suppose that the local concentration of diffusing particles \( C(x, t) \) possesses the axial symmetry and therefore actually we shall treat here the 2D time-dependent diffusion equation.

Thus the anisotropic diffusion equation (5), for the chosen cylindrical coordinates reads

\[
\frac{\partial C}{\partial t} = D_1 \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r}\right) + D_\parallel \frac{\partial^2 C}{\partial z^2} \tag{8}
\]

in the space-time domain \( \Sigma_t := \Sigma \times (t > 0) \). It is clear that at the \( z \) axis one should take into consideration conditions of regularity and axial symmetry of solution, respectively

\[
\lim_{r \to 0} C < \infty, \quad \lim_{r \to 0} \frac{\partial C}{\partial r} = 0. \tag{9}
\]

On the wall of the tube \( \partial \Sigma_w \) we impose the common reflecting boundary condition

\[
(n \cdot j)|_{\partial \Sigma_w} = 0, \tag{10}
\]
where \( \mathbf{n} \) being the outer-pointing unit normal with respect to \( \partial \Sigma_w \) (see Fig. 1) and \( \mathbf{j} = -\mathbf{D} \cdot \nabla C \) is the local diffusing flux of particles. One can see that the tube wall \( \partial \Sigma_w \) may be defined analytically as

\[
w(r, z) = r - r_M R(z/L) = 0.
\]

It is well known that for all nonsingular points \( (r, z) \in \partial \Sigma_w \) \( (\nabla w(r, z) \neq 0) \) the unit normal may be calculated as \( \mathbf{n} = \nabla w / \| \nabla w \| \). Taking this into account we can rewrite condition (10) as the orthogonality condition in cylindrical coordinates

\[
\left[ \frac{\partial C}{\partial r} - r M \frac{D_{||}}{D_{\perp}} \frac{\partial C}{\partial z} \frac{d}{dz} R(z/L) \right] \bigg|_{w=0} = 0. \tag{11}
\]

To complete the problem statement one has to impose the initial condition

\[
C|_{t=0} = C_0(r, z) \quad \text{in } \Sigma \tag{12}
\]

and, for definiteness, Dirichlet boundary conditions on the ends of the tube

\[
C|_{z=0} = C_1(r, t), \quad C|_{z=L} = C_2(r, t). \tag{13}
\]

We assume that all given functions \( C_0(r, z) \), \( C_1(r, t) \) and \( C_2(r, t) \) are continuous in their domains of definition. Hence according to the maximum principle for the diffusion equation we see that \( C \in [C_m, C_M] \), where \( C_m := \min_{\partial \Sigma_t} \{C_0(r, z), C_1(r, t), C_2(r, t)\} \) and \( C_M := \max_{\partial \Sigma_t} \{C_0(r, z), C_1(r, t), C_2(r, t)\} \).

One can see that, due to complex geometry of the tube wall, analytical solution of the posed boundary value problem (8)-(13) is not feasible in general case. That is why the FJE corresponding to Eq. (8)

\[
\frac{\partial c(z,t)}{\partial t} = D \frac{\partial}{\partial z} \left\{ A(z) \frac{\partial}{\partial z} \left[ \frac{c(z, t)}{A(z)} \right] \right\} \tag{14}
\]
plays an important role in applications. Note that in a special case of round cylindrical channel the FJE (14) simplifies to the common 1D second Fick’s equation

$$\frac{\partial c(z, t)}{\partial t} = D_\parallel \frac{\partial^2 c(z, t)}{\partial z^2}. \quad (15)$$

Our main objective with this paper is to construct a rigorous iterative procedure for asymptotic solution of the problem (8)-(13) in case of a slender tube. Particularly this solution entails straightforwardly the FJE (14) with appropriate initial and boundary conditions. Besides, we will find criteria for validity of the corresponding approximation $c(z, t)$.

III. FORMULATION AS A SINGULAR PERTURBED PROBLEM

A. Non-dimensionalization of the problem

In order to perform the asymptotic solution of the posed boundary value problem (8)-(13), we need to nondimensionalize it. It is expedient to rewrite this problem for dimensionless variables using the following scales

$$\rho = r/r_M, \quad \xi = z/L, \quad \tau = t/t_L,$$

where $t_L = L^2/D_\parallel$ is the characteristic longitudinal time for the diffusion length $L$. Moreover it is also convenient to treat the normalized dimensionless local concentration

$$u(\rho, \xi, \tau) = c(\rho, \xi, \tau) / C_M.$$

Accordingly, Eq. (8) takes the form

$$(\mathcal{L}_\rho + \epsilon \mathcal{L}_F) u = 0, \quad \text{in } \Sigma_\tau, \quad (16)$$

where the unperturbed operator

$$\mathcal{L}_\rho := -\frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) \quad (17)$$
is the radial part of the 2D Laplacian in polar coordinates. For the notation convenience in Eq. (16) and hereafter we define the dimensionless 1D Fick operator

$$\mathcal{L}_F := \frac{\partial}{\partial \tau} - \frac{\partial^2}{\partial \xi^2}. $$

It is evident that for this problem $\epsilon\mathcal{L}_F$ being the perturbation operator. We shall show below that as $\epsilon \to 0$ unperturbed operator $\mathcal{L}_\rho$ and perturbation $\epsilon\mathcal{L}_F$ determine the fast and slow behavior of the desired solution $u(\rho, \xi, \tau)$, respectively.

Initial and boundary conditions now read

$$u|_{\tau=0} = g_0(\rho, \xi),$$

$$u|_{\xi=0} = g_1(\rho, \tau), \quad u|_{\xi=1} = g_2(\rho, \tau),$$

$$\left[ \frac{\partial u}{\partial \rho} - \epsilon \frac{\partial u}{\partial \xi} R'(\xi) \right]_{\rho=R(\xi)} = 0,$$

$$u|_{\rho=0} < \infty, \quad \frac{\partial u}{\partial \rho}|_{\rho=0} = 0. $$

Hereafter we denote $g_\gamma = C_\gamma/C_M (\gamma = 0, 1, 2)$.

In Eq. (16) and boundary condition (20) we introduced a new dimensionless parameter $\epsilon$ describing well the system under study

$$\epsilon = \epsilon_s \frac{D_\parallel}{D_\perp},$$

where

$$\epsilon_s = \frac{r_M}{L} \ll 1$$

is the slenderness ratio (the relative thickness of the tube) for a narrow tube. Note that, to make the Zwanzig’s factorization more plausible, it is usually assumed that relationship (6) holds true. However it often happens in applications that $D_\parallel/D_\perp > 1$. In any case we consider here the slenderness ratio $\epsilon_s$ is small enough to make $\epsilon$ small. Furthermore there
is another important physical meaning of the introduced parameter \( \epsilon \). To clarify this we rewrite (22) as

\[
\epsilon = \frac{t_{tr}}{t_L} \ll 1,
\]

where \( t_{tr} = r_{M}^2 / D_{\perp} \) is the characteristic transversal time for the diffusion length \( r_{M} \). Physically inequality (24) means that the diffusive relaxation along the transversal direction occurs much faster than that along axis \( z \). In this connection we can call \( \epsilon \) a relaxation parameter.

Simple inspection shows that for \( \epsilon \to 0 \) the posed problem (16)-(21) is a singularly perturbed one. Really, if we just set \( \epsilon = 0 \) in (16) we obtain unperturbed equation with a general solution, which cannot satisfy nor initial nor boundary conditions (18)-(20). To study this problem we shall apply method of matched asymptotic expansions, which proved to be a powerful tool for solution of many singularly perturbed problems concerning the diffusion-influenced processes.

B. Subdomains for the asymptotic solution. Diffusion boundary layers

Taking into account singularity of the perturbed problem (16)-(21) one can see that the diffusion equation exhibits certain diffusion boundary layers, i.e., subdomains of rapid change in the solution and its derivatives. The location and thickness of the boundary layer depends on a small parameter inherent in the problem under consideration (in our case this is \( \epsilon \)). For instance, it follows immediately from the general form of perturbed operator and conditions (18) and (19) that our problem possesses one temporal and two spatial boundary layers.

To facilitate an understanding of the further study we shall use another decomposition
of the space-time domain \( \Sigma_r = \{0 < \rho < R(\xi)\} \times \Omega \), where the semi-infinite strip \( \Omega := (0 < \xi < 1) \times (\tau > 0) \) is its 2D cross section. For the boundary of the domain \( \Omega \) we have \( \partial \Omega = \partial \Omega_\tau \cup \partial \Omega_\xi \), where
\[
\partial \Omega_\tau := \{ (\xi, \tau) : \tau = 0 \}
\]
is the temporal boundary
\[
\partial \Omega_\xi = \partial \Omega_0 \cup \partial \Omega_1
\]
is the spatial boundary comprising two connected components at the endpoints of the tube
\[
\partial \Omega_0 := \{ (\xi, \tau) : \xi = 0 \}, \quad \partial \Omega_1 := \{ (\xi, \tau) : \xi = 1 \}.
\]
Consider the structure of the diffusion boundary layer (see Fig. 2). It is clear that we can decompose the 2D domain of variables \((\xi, \tau)\) as follows:
\[
\Omega = \Omega^{(0)} \cup \Omega^{(b)}.
\]
(25)

Here \( \Omega^{(0)} \) is a subdomain, where one does not expect rapid change in the solution and its derivatives and so relevant solution depends on slow variables \((\xi, \tau)\) only. On the other hand a subdomain \( \Omega^{(b)} \) is the diffusion boundary layer that abutted the boundary \( \partial \Omega \). Usually in perturbations theory the boundary layer subdomain \( \Omega^{(b)} \) and \( \Omega^{(0)} \) are called inner and outer subdomains, respectively.\(^{30}\)

Structure of the perturbed equation (16) allows us to define entirely the boundary layer
\[
\Omega^{(b)} = \Omega^{(b)}_\xi \cup \Omega^{(b)}_\tau,
\]
(26)

where \( \Omega^{(b)}_\tau \) is the temporal boundary layer subdomain abutted the initial values part of the boundary \( \partial \Omega_\tau \). In decomposition (26) the spatial subdomain \( \Omega^{(b)}_\xi \) consists of two strips in the semi-vicinities of the endpoints \( \xi = 0 \) and \( \xi = 1 \), respectively
\[
\Omega^{(b)}_\xi = \Omega^{(b)}_0 \cup \Omega^{(b)}_1.
\]
(27)
FIG. 2: Depiction of the relationship of the boundary layers to the outer subdomain $\Omega^{(0)}$: spatial boundary layers $\Omega_0^{(1)}, \Omega_1^{(1)}$; corner boundary layers $\Omega_0^{(2)}, \Omega_1^{(2)}$ and temporal boundary layer $\Omega_0^{(3)}$.

The subsequent partition may be obtained if we introduce the corner subdomains near vertices $(0, 0)$ and $(1, 0)$: $\Omega_0^{(2)} = \Omega_0^{(b)} \cap \Omega_\tau^{(b)}$ and $\Omega_1^{(2)} = \Omega_1^{(b)} \cap \Omega_\tau^{(b)}$, where we have intersection of spatial and temporal boundary layers. Whence we can represent a strip near the left endpoint $\xi = 0$ as $\Omega_0^{(b)} = \Omega_0^{(1)} \cup \Omega_0^{(2)}$ and similarly a strip near the right endpoint $\xi = 1$ as $\Omega_1^{(b)} = \Omega_1^{(1)} \cup \Omega_1^{(2)}$. Finally for the problem under study we obtain the following five fold partition of the diffusion boundary layer (see Fig. 2)

$$\Omega^{(b)} = \Omega_0^{(1)} \cup \Omega_0^{(2)} \cup \Omega_0^{(3)} \cup \Omega_1^{(1)} \cup \Omega_1^{(2)},$$

where $\Omega_0^{(3)} := \Omega_\tau^{(b)} \setminus \left( \Omega_0^{(2)} \cup \Omega_1^{(2)} \right)$.

Analysis of the posed boundary value problem (16)-(21) leads to the following asymptotic definitions of the subdomains at issue.

(1) Outer subdomain for the slow spatial and temporal variables $\xi$ and $\tau$

$$\Omega^{(0)} := \{ \mathcal{O}(\sqrt{\epsilon}) < \xi, \mathcal{O}(\epsilon) < \tau \};$$

(2) Left boundary layer subdomain for the fast spatial variable and for slow time $\tau$

$$\Omega_0^{(1)} := \{ \xi < \mathcal{O}(\sqrt{\epsilon}), \tau \};$$
(3) Right boundary layer subdomain for the fast spatial variable and for slow time $\tau$

$$\Omega_1^{(1)} := \{1 - \xi < O(\sqrt{\epsilon}) , \tau \};$$

(4) Left corner boundary layer subdomain for the fast spatial and temporal variables

$$\Omega_0^{(2)} := \{\xi < O(\sqrt{\epsilon}) , \tau < O(\epsilon) \};$$

(5) Right corner boundary layer subdomain for the fast spatial and temporal variables

$$\Omega_1^{(2)} := \{1 - \xi < O(\sqrt{\epsilon}) , \tau < O(\epsilon) \};$$

(6) Initial boundary layer: Low inner subdomain for the fast temporal variable and slow spatial coordinate $\xi$

$$\Omega_0^{(3)} := \{\xi, \tau < O(\epsilon) \}.$$

Note that in order to reduce the original singular perturbed problem to a set of simpler regular problems it is necessary to use inner (rescaled) variable in the relevant subdomains. However, it is expedient to perform this procedure during investigation of the boundary value problem (16)-(21) in appropriate subdomains of the diffusion boundary layer.

C. General form of asymptotic solution

Our aim is to find the leading-term asymptotic solution of the problem (16)-(21) $u_a (\rho, \xi, \tau; \epsilon)$ uniformly valid to order $O(1)$ in the whole domain $\Sigma_\tau$ (see Appendix).

It is convenient to divide the desired asymptotic solution $u$ in three parts: outer $u^{(0)}$ (regular in $\Omega^{(0)}$), boundary layer $u^{(b)}$ and corner boundary layer $u^{(c)}$. Thus the asymptotic solution $u$ may be sought in the form

$$u = u^{(0)} + u^{(b)} + u^{(c)}.$$  (29)
In its turn the boundary layer solution is

\[ u^{(b)} = u^{(1)} + \tilde{u}^{(1)} + u^{(3)}, \]

where \( u^{(1)} \) and \( \tilde{u}^{(1)} \) are the left and right boundary layer solutions given in \( \Omega_0^{(1)} \) and \( \Omega_1^{(1)} \), respectively; \( u^{(3)} \) is the initial boundary layer solution in \( \Omega_0^{(3)} \). Finally the corner boundary layer solution \( u^{(c)} \) naturally is divided into the sum

\[ u^{(c)} = u^{(2)} + \tilde{u}^{(2)}, \]

where \( u^{(2)} \) and \( \tilde{u}^{(2)} \) are the left and right corner boundary layer solutions in \( \Omega_0^{(2)} \) and \( \Omega_1^{(2)} \), respectively. To find explicit form of the above asymptotic solutions one should rewrite original boundary value problem in corresponding subdomains using so-called stretched (or inner) variables inherent in these subdomains (see Sec. V).

The relevant boundary and initial conditions must also take into account the discrepancies arising for the boundary layer solutions \( u^{(1)} \), \( \tilde{u}^{(1)} \) and \( u^{(3)} \) due to the function \( u^{(0)} \). Furthermore the corner functions \( u^{(2)} \) and \( \tilde{u}^{(2)} \) should correct discrepancies caused by functions \( u^{(1)} \), \( \tilde{u}^{(1)} \) and \( u^{(3)} \). This procedure is represented by the diagram

\[
\begin{align*}
\downarrow & \downarrow & \downarrow \\
u^{(1)} & \leftarrow u^{(0)} & \rightarrow \tilde{u}^{(1)} \\
u^{(2)} & \leftarrow u^{(3)} & \rightarrow \tilde{u}^{(2)}
\end{align*}
\]

(30)

It is worth noting here that the above procedure is similar to that used in the reflections method. On the other hand the matching conditions describe exponentially small influence of the appropriate solutions in the opposite directions

\[
\begin{align*}
\uparrow & \uparrow & \uparrow \\
u^{(1)} & \rightarrow u^{(0)} & \leftarrow \tilde{u}^{(1)} \\
u^{(2)} & \rightarrow u^{(3)} & \leftarrow \tilde{u}^{(2)}
\end{align*}
\]

(31)
The explicit form of functions included in (29) will be found during the asymptotic solution iterative procedure.

IV. SOLUTION IN THE OUTER SUBDOMAIN $\Omega^{(0)}$.

A. Zeroth-order outer approximation. The Fick-Jacobs equation

According to common matched asymptotic expansions method technique consider first the diffusion equation for slow variables $\xi$ and $\tau$ in the outer subdomain $\Omega^{(0)}$.\textsuperscript{29,30} Let us look for the asymptotic solution to Eq. (16) with conditions (18)-(21) in $\Omega^{(0)}$ as a regular perturbation expansion in the relaxation parameter

$$ u^{(0)}(\rho, \xi, \tau) = \sum_{n=0}^{\infty} u_{n}^{(0)}(\rho, \xi, \tau) \epsilon^n \quad \text{as } \epsilon \to 0. \quad (32) $$

So outer subdomain $\Omega^{(0)}$ sometimes is called regular one. Note that, although here we limit ourselves by determination of the leading order term $O(1)$, using the proposed approach, one can find functions $u_{n}^{(0)}(\rho, \xi, \tau)$ of any reasonable number $n$. Substitution of (32) in Eq. (16) leads to the following iterative equations

$$ L_{\rho}u^{(0)}_{0} = 0, \quad (33) $$

$$ L_{\rho}u^{(0)}_{n} = -L_{F}u^{(0)}_{n-1}, \quad n \geq 1 \quad (34) $$

and in its turn conditions (21) read

$$ u^{(0)}_{n} \big|_{\rho=0} < \infty, \quad \frac{\partial u^{(0)}_{n}}{\partial \rho} \big|_{\rho=0} = 0, \quad n \geq 0. \quad (35) $$

Similarly, inserting (32) into the reflecting wall condition (20), we get the following recurrence relations

$$ \frac{\partial u^{(0)}_{0}}{\partial \rho} \bigg|_{\rho=R(\xi)} = 0, \quad (36) $$
\[ \left[ \frac{\partial u_0}{\partial \rho} - \frac{\partial u_{n-1}}{\partial \xi} R' (\xi) \right]_{\rho=R(\xi)} = 0, \quad n \geq 1. \] (37)

One can see that the general solution to the quasi steady-state Eq. (33) is

\[ u_0^{(0)} (\rho, \xi, \tau) = u_{00}^{(0)} (\xi, \tau) + u_{01}^{(0)} (\xi, \tau) \ln \rho. \] (38)

Here \( u_{00}^{(0)} (\xi, \tau) \) and \( u_{01}^{(0)} (\xi, \tau) \) are unknown functions to be determined from the boundary conditions (35) and (37). With the aid of conditions (35) we see that \( u_{01}^{(0)} (\xi, \tau) \equiv 0 \) and therefore \( u_0^{(0)} (\rho, \xi, \tau) = u_{00}^{(0)} (\xi, \tau) \), which automatically obeys condition (36).

Consider now the general iterative problem (34), (35) and (37) for \( n \geq 1 \). It is clear that this problem may be insoluble because the unperturbed operator \( L_\rho \) is in spectrum (see Appendix). This circumstance leads to the fact that the approximations in (32) cannot be given explicitly, and they are determined by some unknown functions \( u_n^{(0)} (\rho, \xi, \tau) \). Let us find the solvability condition for the iterative problem (34), (35) and (37). Multiplying Eq. (34) by \( \rho \) and integrating then with respect to \( \rho \) from \( \rho = 0 \) we arrive at

\[ \int_0^\rho \rho L_F u_n^{(0)} d\rho = \rho \frac{\partial u_n^{(0)}}{\partial \rho}. \]

Hence, utilizing the recurrence boundary condition (37), the desired solvability condition for \( u_n^{(0)} (\rho, \xi, \tau) \) reads

\[ \int_0^{R(\xi)} \rho L_F u_{n-1}^{(0)} d\rho = R (\xi) R' (\xi) \frac{\partial u_{n-1}^{(0)}}{\partial \xi} \bigg|_{\rho=R(\xi)}, \quad n \geq 1. \] (39)

It is important to underline that solvability condition (39) eventually follows from the reflecting boundary condition (20) imposed on the tube wall \( \partial \Sigma_w \). In specific case at \( n = 1 \) from (39) we get straightforwardly the following condition

\[ L_F u_0^{(0)} = 2 \frac{R' (\xi) \partial u_0^{(0)}}{R (\xi) \partial \xi}. \] (40)
One can readily see that obtained condition (40) is a dimensionless form of the FJE (see Sec. X).

For further treatment it is convenient to put down the dimensionless FJE (40) in a compact form

$$\mathcal{L}_{FJ} u_0^{(0)} = 0,$$

introducing the dimensionless Fick-Jacobs operator

$$\mathcal{L}_{FJ} := \mathcal{L}_F - 2 R' (\xi) \frac{\partial}{R (\xi) \partial \xi}.$$  

Moreover the zeroth-order approximation in the outer solution $u_0^{(0)} (\xi, \tau)$ we can naturally call the Fick-Jacobs approximation (FJA). To complete the derivation of the FJA one needs to infer the appropriate initial and boundary conditions using the asymptotic solutions of the posed problem in the diffusion boundary layer $\Omega^{(b)}$. Thus it follows from the above treatment that mathematically the FJE is nothing other than a condition of solvability for the function $u_1^{(0)} (\rho, \xi, \tau)$. This feature of $u_1^{(0)} (\rho, \xi, \tau)$ is common with the Hilbert approximation in the kinetic theory for low Knudsen numbers (see Sec. VIII).

Assuming that (41) holds true, it is clear that the general solution to inhomogenous Eq. (34), which satisfies conditions (35) is

$$u_1^{(0)} (\rho, \xi, \tau) = u_{10}^{(0)} (\xi, \tau) - \frac{1}{4} \rho^2 \mathcal{L}_F u_0^{(0)},$$

where $u_{10}^{(0)} (\xi, \tau)$ is an arbitrary function to be found during asymptotic solution. Hence it is important to note that the outer approximation of order $O (\epsilon)$ contains a term depending on the transversal variable $\rho$.

To end this subsection, we observe that solution $u (\rho, \xi, \tau)$ is nonanalytic in the relaxation parameter $\epsilon$ and, therefore, regular expansion (32) in powers of $\epsilon$ fails to give uniformly valid approximation in the whole domain $\Sigma_\tau$. In this connection we note that expansion (32) is
an analog of the Hilbert expansion for solution of the Boltzmann equation (see Sec. VIII for details). Thus, as we mentioned in Sec. III, to find the uniformly valid approximation, one has to solve appropriate boundary value problems concerning the diffusion boundary layers.

B. Forms of the Fick-Jacobs equation

Analysis of the literature showed that the classical form of FJE (1) (or in case of anisotropic diffusion (14)) is the most common in theoretical and applied papers. However we believe that the most natural form of the FJE for the axially symmetric tubes is the following divergent form

\[
\frac{\partial u_0(0)}{\partial \tau} = \frac{1}{R(\xi)^2} \frac{\partial}{\partial \xi} \left[ R(\xi)^2 \frac{\partial u_0(0)}{\partial \xi} \right].
\] (43)

It seems interesting that the right hand side of Eq. (43) resembles the Laplacian action in conformally flat metric, which was rather widely investigated in theoretical physics. The connection of this equation with classical FJE (14) is known. Utilizing the cylindrical coordinates we can write relation (2) as follows:

\[
c(z, t) = 2\pi \int_0^{r(z)} C(r, z, t) \, rdr
\] (44)

and making notation

\[
C_M u_0^{(0)}(z, t) = c_0^{(0)}(z, t) := \frac{1}{A(z)} \lim_{\epsilon \to 0} c(z, t)
\] (45)

we obtain the FJE in the classical form (1).

The FJE in the form (43) may be useful, g.e., to describe diffusion in a long conical tube of the radius given by linear function

\[
R(\xi) = a\xi + b,
\] (46)
where $a$ and $b$ are some constants. Indeed, assuming for definiteness that $a$ and $b$ are positive, by means of substitution (46) we can reduce the FJE (13) to well-known spherically symmetric diffusion equation

$$\frac{\partial u_0^{(0)}}{\partial \tau} = a^2 \frac{1}{R^2} \frac{\partial}{\partial R} \left[ R^2 \frac{\partial u_0^{(0)}}{\partial R} \right]$$

in a hollow sphere $b < R < a + b$.\(^{38}\)

To present one more example rewrite Eq. (43) in the dimensional form

$$R^2(z) \frac{\partial c_0^{(0)}}{\partial t} = D_\parallel \frac{\partial}{\partial z} \left[ R^2(z) \frac{\partial c_0^{(0)}}{\partial z} \right].$$

One can see that multiplication of (48) by $\pi$ and integration with respect to $z$ from 0 to any current $z$ gives

$$\Phi(z, t) = \Phi(0, t) - \int_0^z \frac{\partial c_0^{(0)}}{\partial t} dV,$$

where $dV = \pi R^2(z) \, dz$ and

$$\Phi(z, t) := -D_\parallel \pi R^2(z) \frac{\partial}{\partial z} c_0^{(0)}(z, t)$$

is the total flux of diffusing particles through the cross section at point $z$. For the steady state flux $\Phi_s(z) \ (t \gg t_L)$ relationship (49) takes the simplest form

$$\Phi_s(z) = \Phi_s(0).$$

Thus, the FJE is similar to continuity equation and Eq. (50) is an analog to known Bernoulli’s principle in ideal fluid dynamics. The latter fact supports the analogy between the FJA $u_0^{(0)}$ and the Hilbert solution to the Boltzmann equation at low Knudsen numbers (see Sec. IV and below).

Eq. (41) represents one more convenient form of the FJE, which for dimensional variables reads

$$\frac{\partial c_0^{(0)}}{\partial \tau} - D_\parallel \frac{\partial^2 c_0^{(0)}}{\partial z^2} = V(z) \frac{\partial c_0^{(0)}}{\partial z},$$

20
Here we denote \( V(z) := V_L A^{-1} dA/dz \) the effective drift velocity of diffusing particles along the \( z \) axis, and \( V_L = D || / L \) the characteristic longitudinal diffusion velocity. It seems that convective diffusion interpretation (51) appeared to be even more appropriate for investigation of the FJE than widely used entropy potential form (3). This ensues from the fact that nowadays mathematical theory of convective diffusion equation is thoroughly elaborated in all aspects.

V. SOLUTION IN THE SUBDOMAINS \( \Omega^{(1)}_0 \) AND \( \Omega^{(1)}_1 \). BOUNDARY CONDITIONS FOR THE FICK-JACOBS EQUATION

Let us study the solution of the problem (16)-(21) in the spatial diffusion boundary layer subdomains \( \Omega^{(1)}_0 \) and \( \Omega^{(1)}_1 \) attached to the endpoints (\( \xi = \{0, 1\} \)) (see Fig. 2). In subdomains \( \Omega^{(1)}_0 \) and \( \Omega^{(1)}_1 \) we introduce so-called inner coordinates: new stretched spatial variables \( \xi^* = \xi/\sqrt{\epsilon} \) and \( \tilde{\xi} = (1 - \xi)/\sqrt{\epsilon} \), respectively, leaving slow time \( \tau \) unscaled. So in the left and right subdomains \( \Omega^{(1)}_0 \) and \( \Omega^{(1)}_1 \) one has \( \xi^* = \mathcal{O}(1) \) and \( \tilde{\xi} = \mathcal{O}(1) \) as \( \epsilon \to 0 \).

Asymptotic solutions to the problem (16)-(21) behave similarly in \( \Omega^{(1)}_0 \) and \( \Omega^{(1)}_1 \), therefore, for definiteness we consider in detail the solution corresponding to the left subdomain \( \Omega^{(1)}_0 \) only. Rewriting the boundary value problem (16)-(21) in the inner coordinates \( (\rho, \xi^*, \tau) \) of \( \Omega^{(1)}_0 \) for the inner solution \( u^{(1)}(\rho, \xi^*; \tau) \) we obtain

\[
\frac{\partial^2 u^{(1)}}{\partial \xi^*^2} - \mathcal{L}_\rho u^{(1)} = \epsilon \frac{\partial u^{(1)}}{\partial \tau} \quad \text{in} \quad \Omega^{(1)}_0, \tag{52}
\]

\[
u^{(1)} \bigg|_{\rho=0} < \infty, \quad \frac{\partial u^{(1)}}{\partial \rho} \bigg|_{\rho=0} = 0, \tag{53}
\]

\[
\left[ \frac{\partial u^{(1)}(\rho, \xi^*; \tau)}{\partial \rho} - \sqrt{\epsilon} \frac{\partial u^{(1)}}{\partial \xi^*} R' \left( \sqrt{\epsilon} \xi^* \right) \right] \bigg|_{\rho=R(\sqrt{\epsilon} \xi^*)} = 0. \tag{54}
\]

Let us observe that conditions on the \( z \) axis (53) must be satisfied in all other subdomains of the boundary layer (\( \Omega^{(1)}_1, \Omega^{(2)}_0, \Omega^{(2)}_1, \text{and} \Omega^{(3)}_0 \)), so for brief henceforward we omit them.
later in the text. Due to the type of Eq. (52) subdomain $\Omega_0^{(1)}$ ($\Omega_1^{(1)}$) is often termed as elliptic boundary layer.

Find now the appropriate boundary conditions for $u^{(1)}$. Bearing in mind the derivation of uniformly valid approximation (29), consider the partial sum

$$u^{(0,1)}(\rho, \xi, \xi^*, \tau) = u^{(0)}(\rho, \xi, \tau) + u^{(1)}(\rho, \xi^*; \tau)$$  \hspace{1cm} (55)$$

which is defined in $\Omega^{(0)} \cup \Omega_0^{(1)}$ with appropriate matching conditions. It is worth noting that both outer $u^{(0)}(\rho, \xi, \tau)$ and inner $u^{(1)}(\rho, \xi^*; \tau)$ solutions are approximations to the same solution but defined in outer $\Omega^{(0)}$ and inner $\Omega_0^{(1)}$ subdomains, respectively. So the compound approximation $u^{(0,1)}$ should obeys the left boundary condition (19) and satisfies the corresponding diffusion equation (16) in $\Omega^{(0)} \cup \Omega_0^{(1)}$. Substitution of approximation (55) into Eq. (16) yields

$$\left(\mathcal{L}_\rho + \epsilon \mathcal{L}_F\right)u^{(0)}(\rho, \xi, \tau) = \left(\frac{\partial^2}{\partial \xi^*^2} - \mathcal{L}_\rho - \epsilon \frac{\partial}{\partial \tau}\right)u^{(1)}(\rho, \xi^*; \tau).$$

Hence, employing the fact, that $\xi$ and $\xi^*$ are independent variables, we obtain Eqs (16) and (52). In its turn from the left boundary condition (19) we have

$$u^{(1)}|_{\xi^*=0} = g_1(\rho, \tau) - u^{(0)}(\rho, \xi, \tau)|_{\xi=0}. \hspace{1cm} (56)$$

Missing right boundary condition for $u^{(1)}$ may be found using the matching condition between inner and outer solutions (30), i.e.

$$u^{(0,1)}(\rho, \xi, \xi^*, \tau)|_{\xi^* \to \infty} \to u^{(0)}(\rho, \xi, \tau)$$

that immediately leads to the desired boundary condition

$$u^{(1)}(\rho, \xi^*; \tau)|_{\xi^* \to \infty} \to 0. \hspace{1cm} (57)$$
Note that hereafter the limit as $\xi^* \to \infty$ means that $\epsilon \to 0$ provided $\xi$ is fixed.

It is clear that inside $\Omega_0^{(1)}$ the problem under study becomes regular, so we can seek the solution $u^{(1)}(\rho, \xi^*, \tau)$ in the form of the expansion

$$u^{(1)}(\rho, \xi^*, \tau) = \sum_{m=0}^{\infty} u_m^{(1)}(\rho, \xi^*, \tau) \epsilon^{m/2} \quad \text{as } \epsilon \to 0,$$

where $u_m^{(1)}(\rho, \xi^*, \tau)$ are so-called functions of the boundary layer. One can see that implicitly the dependence on slow time $\tau$ arises in the second order approximation ($m = 2$) only. In this way we formally reduced the problem in the inner subdomain $\Omega_0^{(1)}$ to the quasi steady-state problem (we have only parametric dependence upon time $\tau$) posed on the semi-infinite tube bounded at $\xi^* = 0$.

Hence for the zeroth-order approximation we gain the problem

$$\frac{\partial^2 u_0^{(1)}}{\partial \xi^*^2} - \mathcal{L}_\rho u_0^{(1)} = 0, \quad 0 < \rho < R_0,$$

$$u_0^{(1)}|_{\xi^* = 0} = g_1(\rho, \tau) - u_0^{(0)}|_{\xi^* = 0},$$

$$u_0^{(1)}|_{\xi^* \to \infty} \to 0,$$

$$\frac{\partial u_0^{(1)}}{\partial \rho} \bigg|_{\rho = R_0} = 0.$$

Therefore for $u_0^{(1)}$ the reflecting wall condition (54) simplifies to the relevant condition (62) on the circular cylinder of constant radius $R_0 := R(0)$.

The general solution to Eq. (59) satisfying the reflecting condition (62) is

$$u_0^{(1)}(\rho, \xi^*; \tau) = \sum_{k=0}^{\infty} b_k(\tau) e^{-\lambda_k \xi^*} \hat{J}_0 \left( \lambda_k \frac{\rho}{R_0} \right),$$

where $\left\{ \hat{J}_0 \left( \lambda_k \rho / R_0 \right) \right\}_{k=0}^{\infty}$ is the complete orthonormal system defined in Appendix.
Matching condition (61) leads to $b_0 (\tau) = 0$ that yields the desired boundary condition for the solution of the FJE $u_0^{(0)} (\xi, \tau)$ at the left endpoint ($\xi = 0$)

$$u_0^{(0)} (\xi, \tau) \bigg|_{\xi=0} = \left< g_1, \tilde{J}_0 (0) \right> \tilde{J}_0 (0) = \frac{2}{R_0} \int_0^{R_0} \rho g_1 (\rho, \tau) \, d\rho. \quad (64)$$

For $k \geq 1$ unknown coefficients $b_k (\tau)$ are

$$b_k (\tau) = \left< g_1, \tilde{J}_0 \left( \lambda_k \frac{\rho}{R_0} \right) \right> \tilde{J}_0 . \quad (65)$$

Similar treatment of the inner solution in the right subdomain $\Omega_1^{(1)}$ gives

$$\tilde{u}_0^{(1)} (\rho, \xi; \tau) = \sum_{k=0}^{\infty} \tilde{b}_k (\tau) e^{-\lambda_k \xi} \tilde{J}_0 \left( \lambda_k \frac{\rho}{R_1} \right), \quad (66)$$

Hence $\tilde{b}_0 (\tau) = 0$ and the second boundary condition for the FJA $u_0^{(0)} (\xi, \tau)$ at the right endpoint ($\xi = 1$) is

$$u_0^{(0)} (\xi, \tau) \bigg|_{\xi=1} = \left< g_2, \tilde{J}_0 (0) \right> \tilde{J}_0 (0) = \frac{2}{R_1} \int_0^{R_1} \rho g_2 (\rho, \tau) \, d\rho, \quad (67)$$

where $R_1 := R (1)$ and

$$\tilde{b}_k (\tau) = \left< g_2, \tilde{J}_0 \left( \lambda_k \frac{\rho}{R_1} \right) \right> \tilde{J}_0 , \quad k \geq 1. \quad (68)$$

VI. SOLUTION IN THE SUBDOMAIN $\Omega_0^{(3)}$. INITIAL CONDITIONS FOR THE FICK-JACOBS EQUATION

Now we dwell on the solution to problem (16)-(21) in the initial diffusion boundary layer subdomain $\Omega_0^{(3)}$ attached to the the initial time $\tau = 0$ (see Fig. 2). In this subdomain inner variables are $\xi$ and the stretched (fast) time $\tau^* = \tau / \epsilon$ ($\tau^* = \mathcal{O} (1)$ as $\epsilon \to 0$). Using these variables in the original problem (16)-(21) similarly to the previous case we arrive at

$$\frac{\partial u^{(3)}}{\partial \tau^*} + \mathcal{L}_\rho u^{(3)} = \epsilon \frac{\partial^2 u^{(3)}}{\partial \xi^2}, \quad (69)$$
\[
\frac{\partial u^{(3)}}{\partial \rho} - \epsilon \frac{\partial u^{(3)}}{\partial \xi} R' (\xi)|_{\rho=R(\xi)} = 0.
\]

(71)

One can see that now we obtained effectively the boundary value problem for the infinitely long solid of revolution. According to the type of Eq. (69) the subdomain \(\Omega_0^{(3)}\) is often called as parabolic boundary layer.\(^{30}\) We also must add to (70) and (71) the matching condition for the inner solution

\[
\frac{\partial u^{(3)}}{\partial \tau^*} = 0.
\]

(72)

The corresponding regular expansion of the inner solution in \(\Omega_0^{(3)}\) reads

\[
u^{(3)} (\rho, \xi, \tau^*) = \sum_{m=0}^{\infty} u_m^{(3)} (\rho, \tau^*; \xi) \epsilon^m \quad \text{as} \quad \epsilon \to 0.
\]

(73)

Here the functions of the boundary layer \(u_m^{(3)} (\rho, \tau^*; \xi)\) depend upon \(\xi\) as a parameter. So for the zeroth-order function \(u_0^{(3)} (\rho, \tau^*; \xi)\) we get the following boundary value problem

\[
\frac{\partial u_0^{(3)}}{\partial \tau^*} + \mathcal{L}_{\rho} u_0^{(3)} = 0,
\]

(74)

\[
u_0^{(3)} |_{\tau^*=0} = g_0 (\rho, \xi) - u_0^{(0)} |_{\tau=0},
\]

(75)

\[
\frac{\partial u_0^{(3)}}{\partial \rho} |_{\rho=R(\xi)} = 0.
\]

(76)

One can see that the obtained problem (74)-(76) describes the diffusion into the infinite circular cylinder of radius \(R (\xi)\). It is clear that general solution to Eq. (74), which obey the reflecting condition (76), may be expressed as

\[
u_0^{(3)} (\rho, \tau^*; \xi) = \sum_{k=0}^{\infty} a_k (\xi) e^{-\lambda_k^2 \tau^*} \tilde{J}_0 \left( \lambda_k \frac{\rho}{R (\xi)} \right).
\]

(77)

Setting \(\tau^* = 0\), this implies that to satisfy the matching condition

\[
u_0^{(3)} |_{\tau^* \to \infty} \to 0
\]

(78)
we should impose $a_0(\xi) = 0$ at that, utilizing initial condition (75), we have the desired initial condition for the FJA

$$u_0^0(\xi, \tau) \big|_{\tau=0} = \left< g_0, \tilde{J}_0(0) \right>_{H_\xi}, \quad \tilde{J}_0(0) = \frac{2}{R^2(\xi)} \int_0^{R(\xi)} \rho g_0(\rho, \xi) \, d\rho.$$ (79)

and expression for unknown coefficients $a_k(\xi) \ (k \geq 1)$

$$a_k(\xi) = \left< g_0, \tilde{J}_0 \left( \lambda_k \frac{\rho}{R(\xi)} \right) \right>_{H_\xi}.$$ (80)

For the problem under study this formula gives the answer to the question posed by Kalnay and Percus: "Having projected 2D equation to the 1D one ..., one may ask the question: how then is the projected 1D initial density $P(x, 0)$ related to the original $\rho(x, y, 0)$, and is there some reasonable projection algorithm?"17

VII. SOLUTION IN THE CORNER SUBDOMAINS $\Omega_0^{(2)}$ AND $\Omega_1^{(2)}$

It is clear that behavior of inner solution in the corner subdomains $\Omega_0^{(2)}$ and $\Omega_1^{(2)}$ (see Fig. 2) is similar, therefore, for briefness we give the detailed treatment of the relevant boundary value problem only in $\Omega_0^{(2)}$. For this purpose we define inner variables $(\xi^*, \tau^*)$ and rewrite Eq. (16) for the corner boundary layer function $u^{(2)}(\rho, \xi^*, \tau^*)$ as

$$\frac{\partial^2 u^{(2)}}{\partial \xi^{*2}} - \mathcal{L}_\rho u^{(2)} = \frac{\partial u^{(2)}}{\partial \tau^*}, \quad 0 < \rho < R_0.$$ (81)

Similarly to the previous case the subdomain $\Omega_0^{(2)}$ (or $\Omega_1^{(2)}$) is also called as parabolic boundary layer.30 The reflecting wall condition (20) in $\Omega_0^{(2)}$ takes the form

$$\left[ \frac{\partial u^{(2)}(\rho, \xi^*, \tau^*)}{\partial \rho} - \sqrt{\epsilon} \frac{\partial u^{(2)}}{\partial \xi^*} R' \left( \sqrt{\epsilon \xi^*} \right) \right]_{\rho=R(\sqrt{\epsilon \xi^*})} = 0.$$ (82)

One can see immediately from geometry of the problem that desired solution $u^{(2)}(\rho, \xi^*, \tau^*)$ does not affect directly to the outer solution $u^{(0)}(\xi, \tau)$ in $\Omega^{(0)}$. According to scheme (30)
function \( u^{(2)}(\rho, \xi^*, \tau^*) \) should be matched with \( u^{(1)}(\rho, \xi^*, \tau) \) and \( u^{(3)}(\rho, \xi, \tau^*) \) in order to correct discrepancies due to these functions for initial and boundary conditions, respectively

\[
    u^{(2)}|_{\tau^*=0} = - u^{(1)}|_{\tau=0}, \quad u^{(2)}|_{\xi^*=0} = - u^{(3)}|_{\xi=0}.
\] (83)

The relevant matching conditions (see scheme (31)) for the corner boundary layer function \( u^{(2)}(\rho, \xi^*, \tau^*) \) in \( \Omega_0^{(1)} \) and \( \Omega_0^{(3)} \) are

\[
    u^{(2)}|_{\tau^* \to \infty} \to 0, \quad u^{(2)}|_{\xi^* \to \infty} \to 0. \] (84)

One can see that obtained problem (81)-(84) effectively describes the time-dependent diffusion in a semi-infinite circular cylinder of radius \( R_0 \).

Inside the corner boundary layer subdomain at issue \( \Omega_0^{(2)} \) we can seek the solution in the regular form

\[
    u^{(2)}(\rho, \xi^*, \tau^*) = \sum_{m=0}^{\infty} u^{(2)}_m(\rho, \xi^*, \tau^*) \epsilon^{m/2} \quad \text{as } \epsilon \to 0.
\] (85)

Employing expressions (77) and (63) it is clear that the zeroth-order approximation \( u_0^{(2)} \) to the corner function \( u^{(2)} \) in \( \Omega_0^{(2)} \) governs by the problem

\[
    \frac{\partial^2 u_0^{(2)}}{\partial \xi^{*2}} - \mathcal{L} u_0^{(2)} = \frac{\partial u_0^{(2)}}{\partial \tau^*}, \quad 0 < \rho < R_0,
\] (86)

\[
    u_0^{(2)}|_{\tau^*=0} = - \sum_{k=1}^{\infty} b_k(0) e^{-\lambda_k^* \xi^*} \mathcal{J}_0\left( \lambda_k^* \frac{\rho}{R_0} \right),
\] (87)

\[
    u_0^{(2)}|_{\xi^*=0} = - \sum_{k=1}^{\infty} a_k(0) e^{-\lambda_k^* \tau^*} \mathcal{J}_0\left( \lambda_k^* \frac{\rho}{R_0} \right),
\] (88)

\[
    u_0^{(2)}|_{\xi^* \to \infty} \to 0,
\] (89)

\[
    \frac{\partial u_0^{(2)}}{\partial \rho} \bigg|_{\rho=R_0} = 0.
\] (90)

It is convenient to look for solution of the obtained boundary value problem (86)-(90) by means of projection method with respect to the orthonormal basis \( \left\{ \mathcal{J}_0\left( \lambda_k^* \frac{\rho}{R_0} \right) \right\}_{k=0}^{\infty} \) (see
Multiplying Eq. (86) by \( \hat{J}_0 \left( \lambda_k \frac{\rho}{R_0} \right) \) and using formulae (A.116) and (A.117) one gets

\[
 u^{(2)}_{0k} \equiv 0, \quad k = 0;
\]

\[
 \frac{\partial^2 u^{(2)}_{0k}}{\partial \xi^*{}^2} - \lambda_k^2 u^{(2)}_{0k} = \frac{\partial u^{(2)}_{0k}}{\partial \tau^*}, \quad k \geq 1;
\]

where

\[
 u^{(2)}_{0k} (\xi^*, \tau^*) = \left\langle u^{(2)}_{0k}, \hat{J}_0 \left( \lambda_k \frac{\rho}{R_0} \right) \right\rangle_{\mathcal{H}_0}.
\]

Introducing for \( k \geq 1 \) a subsidiary function

\[
 w_k (\xi^*, \tau^*) = e^{\lambda_k^2 \tau^*} u^{(2)}_{0k} (\xi^*, \tau^*)
\]

we finally reduce problem (86)-(90) to

\[
 \frac{\partial^2 w_k}{\partial \xi^*{}^2} = \frac{\partial w_k}{\partial \tau^*}, \quad (91)
\]

\[
 w_k|_{\tau^*=0} = -b_k (0) e^{-\lambda_k \xi^*}, \quad (92)
\]

\[
 w_k|_{\xi^*=0} = -a_k (0), \quad w_k|_{\xi^* \to \infty} \to 0. \quad (93)
\]

One can easily derive that solution to the boundary value problem (91)-(93) reads

\[
 w_k (\xi^*, \tau^*) = -a_k (0) \operatorname{erfc} \left( \frac{\xi^*}{2 \sqrt{\tau^*}} \right)
\]

\[
 -\frac{1}{2} b_k (0) e^{\lambda_k^2 \tau^*} \left[ e^{-\lambda_k \xi^*} \operatorname{erfc} \left( \lambda_k \sqrt{\tau^*} - \frac{\xi^*}{2 \sqrt{\tau^*}} \right) - e^{\lambda_k \xi^*} \operatorname{erfc} \left( \lambda_k \sqrt{\tau^*} + \frac{\xi^*}{2 \sqrt{\tau^*}} \right) \right], \quad (94)
\]

where

\[
 \operatorname{erfc} (\zeta) = \frac{2}{\sqrt\pi} \int_{\zeta}^{\infty} e^{-\alpha^2} d\alpha
\]
is the complementary error function. Hence for the zeroth-order corner function we have expansion

\[
  u^{(2)}_0 (\rho, \xi^*, \tau^*) = \sum_{k=1}^{\infty} w_k (\xi^*, \tau^*) e^{-\lambda_k^2 \tau^*} \tilde{J}_0 \left( \lambda_k \frac{\rho}{R_0} \right). \tag{95}
\]

It is obvious that function (95) also satisfies matching condition (84) as \( \tau^* \to \infty \).

The appropriate leading-term approximation for the inner solution \( \tilde{u}^{(2)} (\rho, \tilde{\xi}, \tau^*) \) in the corner subdomain \( \Omega_1^{(2)} \) may be founded with the help of above derivation. For this purpose in (85)-(95) one should implement the following substitutions

\[
  \xi^* \to \tilde{\xi}, \quad R_0 \to R_1, \quad a_k (0) \to a_k (1), \quad b_k (0) \to \tilde{b}_k (0). \tag{96}
\]

Denoting by \( \tilde{w}_k (\tilde{\xi}, \tau^*) \) the result of substitutions (96) in formula (95) we arrive at the zeroth-order right corner approximation

\[
  \tilde{u}^{(2)}_0 (\rho, \tilde{\xi}, \tau^*) = \sum_{k=1}^{\infty} \tilde{w}_k (\tilde{\xi}, \tau^*) e^{-\lambda_k^2 \tau^*} \tilde{J}_0 \left( \lambda_k \frac{\rho}{R_1} \right). \tag{97}
\]

Note in passing that the limit as \( \tilde{\xi} \to \infty \) means that \( \epsilon \to 0 \) provided \( \xi \) is fixed.

VIII. LEADING-TERM APPROXIMATION

A. Explicit form of the general asymptotic solution

Inserting partial expansions (32), (58), (85) and (73) into general formula (29) we have uniformly valid as \( \epsilon \to 0 \) in the whole space-time domain \( \Sigma_\tau \) asymptotic solution

\[
  u (\rho, \xi, \tau; \epsilon) = \sum_{m=0}^{\infty} \left\{ u_m^{(0)} (\rho, \xi, \tau) + u_m^{(3)} (\rho, \tau^*; \xi) \epsilon^m \right. \\
  + \left. \left[ u_m^{(1)} (\rho, \xi^*; \tau) + \tilde{u}_m^{(1)} (\rho, \tilde{\xi}; \tau) \right] \epsilon^{m/2} + \right. \\
  \left. u_m^{(2)} (\rho, \xi^*, \tau^*) + \tilde{u}_m^{(2)} (\rho, \tilde{\xi}, \tau^*) \right\} \epsilon^m. \tag{98}
\]
Finally, collecting here all leading terms, and denoting by \( \mathbf{q} := \{ \rho, \xi, \xi^*, \tilde{\xi}, \tau, \tau^* \} \) the complete set of outer and inner variables inherent in the problem under consideration, we can rewrite expansion (98) in a compact form

\[
 u (\rho, \xi, \tau; \epsilon) = u_a (\mathbf{q}) + \mathcal{O} (\sqrt{\epsilon}) \quad \text{as} \quad \epsilon \to 0,
\]

where \( u_a (\mathbf{q}) \) is the leading-term approximation uniformly valid in domain \( \Sigma_{\tau} \) to order \( \mathcal{O} (1) \).

Accordingly, using the obtained results, function \( u_a (\mathbf{q}) \) may be given as follows:

\[
 u_a (\mathbf{q}) = u_0^{(0)} (\xi, \tau)
 + \sum_{k=1}^{\infty} a_k (\xi) \ e^{-\lambda_k^2 \tau^*} \hat{J}_0 \left( \frac{\lambda_k^2}{R(\xi)} \right)
 + \sum_{k=1}^{\infty} \left[ b_k (\tau) \ e^{-\lambda_k^* \xi^*} + w_k (\xi^*, \tau^*) \ e^{-\lambda_k^2 \tau^*} \right] \hat{J}_0 \left( \frac{\lambda_k^* \rho}{R_0(\xi)} \right)
 + \sum_{k=1}^{\infty} \left[ \tilde{b}_k (\tau) \ e^{-\lambda_k^* \tilde{\xi}} + \tilde{w}_k (\tilde{\xi}, \tau^*) \ e^{-\lambda_k^2 \tau^*} \right] \hat{J}_0 \left( \frac{\lambda_k^* \rho}{R_1(\xi)} \right).
\]

This formula constitutes the main result of the present paper. As an important consequence of formula (100) we infer that within the leading-term approximation the total flux through a tube cross section is entirely determined by the FJA \( u_0^{(0)} (\xi, \tau) \) and initial boundary layer function \( u_0^{(3)} (\rho, \tau^*; \xi) \).

Combining expressions (64), (67), (79) and utilizing the projector \( \mathcal{P}_\xi \) defined by formula (A.127) one can see that the FJA \( u_0^{(0)} (\xi, \tau) \) is uniquely determined by the following 1D boundary value problem

\[
 \mathcal{L}_F \hat{u}_0^{(0)} = 0, \quad (101)
\]

\[
 u_0^{(0)} \bigg|_{\tau=0} = \mathcal{P}_\xi \hat{g}_0, \quad (102)
\]

\[
 u_0^{(0)} \bigg|_{\xi=0} = \mathcal{P}_0 \hat{g}_1, \quad u_0^{(0)} (\xi, \tau) \bigg|_{\xi=1} = \mathcal{P}_1 \hat{g}_2. \quad (103)
\]
Hence one can see that function $u^{(0)}_0(\xi, \tau)$ is the zeroth-order in $\epsilon$ projection of 3D concentration on the unit zero eigenfunction of the unperturbed operator $L_{\rho}$ (see Appendix), that is

$$u^{(0)}_0(\xi, \tau) = \lim_{\epsilon \to 0} P_\xi u(\rho, \xi, \tau; \epsilon).$$

(104)

It is important to note here that we cannot obtain the FJE (101) just by simple projection of the original 3D equation (16) onto the zero eigenfunction of the unperturbed operator $L_{\rho}$ because operators of differentiation with respect to $\xi$ and projection operator (depending on $\xi$) do not commute.\textsuperscript{17}

Thus, provided one has solved problem (101)-(103) with respect to the FJA $u^{(0)}_0(\xi, \tau)$ the desired leading-term approximation $u_a(q)$ is governed explicitly by formula (100).

Note in passing that according to expansion (98) the contribution from inner solutions in the spatial boundary layer ($u^{(1)}_m$ and $\tilde{u}^{(1)}_m$) is much more important than that from the solutions for the initial layer ($u^{(3)}_m$), since the influence of the spatial boundary layer at $m = 1$ gives a term of order $O(\sqrt{\epsilon})$.

**B. Validity of the Fick-Jacobs approximation**

Let us delineate the conditions on temporal and spatial scales under which the FJA $u^{(0)}_0(\xi, \tau)$ is valid. One can see that the general condition for validity of the FJA reads

$$\left| u_a - u^{(0)}_0 \right| / u^{(0)}_0 \ll 1.$$  

(105)

To obtain simple validity conditions first we observe that contribution of the corner functions $u^{(2)}_0$ and $\tilde{u}^{(2)}_0$ to $u$ is certainly less than that from the functions of the diffusion spatial $u^{(1)}_0$, $\tilde{u}^{(1)}_0$ and temporal $u^{(3)}_0$ boundary layers. Therefore one can ignore in (99) the corrections due to corner functions.
It is also clear from (99) and (100) that solution \( u_0^{(3)} \) corresponds to initial stage of the concentration evolution in \( \Omega^{(3,0)} := \Omega_0^{(3)} \cup \Omega^{(0)} \) (see Fig. 2), where there is a relaxation to the equilibrium with respect to the transversal variable \( \rho \), that is

\[
\frac{\partial u_0(q)}{\partial \rho} = 0 \quad \text{in } \Omega^{(3,0)}.
\]

This process occurs by exponential damping law with times spectrum \( t_k = t_{tr} \lambda_k^{-2} \), \( (k \geq 1) \) and the characteristic relaxation longitudinal time for homogenization of initially nonuniform in \( r \) distribution of concentration is determined by the lowest eigenvalue

\[
t_1 = \frac{t_{tr}}{\lambda_1^2} \approx 0.0681 \cdot \frac{r_M^2}{D_\perp} \ll t_{tr}.
\]  

Similarly it follows from expression (99) and form of solutions \( u_0^{(1)} \), \( \tilde{u}_0^{(1)} \) (100) that characteristic thickness of the spatial diffusion boundary layers \( l_1 \) along \( z \) axis in \( \Omega_0^{(1)} \cup \Omega^{(0)} \) and \( \Omega_1^{(1)} \cup \Omega^{(0)} \) (see Fig. 2) is

\[
l_1 = \frac{r_M}{\lambda_1} \approx 0.2610 \cdot r_M < r_M.
\]  

One can see from (106) and (107) that there is a simple connection between values \( t_1 \) and \( l_1 \): \( t_1 = \frac{r_M^2}{D_\parallel} \).

Accordingly, combining (106) and (107) the validity of the FJA is determined by the following temporal and spatial conditions

\[
t \gtrsim t_{tr} \gg t_1, \quad z \text{ (or } L - z) \gg r_M > l_1.
\]  

This means that for temporal and spatial scales (108) the explicit dependence of the leading-term approximation \( u_a(q) \) on the initial distribution (12) and boundary conditions (13) depending on the transversal coordinate \( r \) disappeared. In other words the FJA works well under a quasi steady-state regime with respect to the characteristic transversal time \( t_{tr} \), i.e.,
when we can eliminate dependence on fast transversal variable \( \rho \) and consider dependence only upon slow "hydrodynamic" variables \( \xi \) and \( \tau \).

Particularly, for the cylindric tube of radius \( r_M \) all deviations from the "equilibrium function" \( v_0 \) (see Appendix) caused by the initial and boundary conditions depending on transversal coordinate \( \rho \) are vanished within diffusion boundary layer subdomains. Thus the subdomain \( \Omega^{(0)} \) becomes "the equilibrium region", where solution \( u^{(0)} \) does not contain the dependence on \( \rho \). It is clear that this situation occurs due to the wall condition \( (\partial u/\partial \rho)|_{\rho=1} = 0 \).

For general case it is clear that at least in a vicinity near the wall \( \partial u/\partial \xi \neq 0 \) in \( \Sigma \), hence and from the reflection boundary condition (20) we have

\[
\frac{\partial u}{\partial \rho} \bigg|_{\rho=R(\xi)} \propto R' (\xi).
\]

Therefore \( \partial u/\partial \rho \neq 0 \) in a vicinity near the wall and a deviation of \( u(\rho, \xi, \tau) \) from the equilibrium value increases with increasing of function \( |R'(\xi)| \). Nevertheless condition \( |R'(\xi)| \ll 1 \) is not important for validity of the leading-term approximation \( u_a (q) \).

To describe similar heat transfer problem in the semi-bounded cylinder Luikov wrote in his book:\ref{39} "Since there is no loss of heat through the wall of the rod we can treat it as a solid, where heat spreads only in one direction" (see p. 182 of Ref. 39). Then in this book he considered only 1D equation. It infers from our study that this statement correct only out of the corresponding spatial and temporal boundary layers, that is in the outer sundomain \( \Omega^{(0)} \).

Thus, conditions (108) determine the temporal and spatial scales when the FJA holds true, that is

\[
u_a (q) \simeq u^{(0)}_0 (\xi, \tau).
\]
C. Analogy to the gas kinetic theory

Previously, using an analogy with the gas kinetic theory, we proposed a general kinetics equation to describe the kinetics of diffusion-controlled reactions in case of infinite system for all spatial and temporal scales and interpreted some results on diffusive interaction in dense arrays of absorbing particles.\textsuperscript{40,41} It is appropriate to note that idea of the projection method suggested by Kalnay and Percus was inspired by analogy with kinetic theory as well. Concerning their method in Ref. 17 they claimed the following: "It reminds one of Bogolubov’s derivation of the generalized Boltzmann equation, expressing the $n$-particle densities as a functional of the one-particle one; here we reduce similarly the number of coordinates."

For the problem under study we also revealed a profound analogy with the gas kinetic theory at low Knudsen numbers, that helped us to choose an adequate mathematical method to find the desired asymptotic solution. The analogy, we intend to establish, becomes even more profound in the isotropic diffusion case, i.e., when $D_\parallel = D_\perp = D$. Hence we consider this case and, moreover, for the sake of simplicity, here we dwell on 1D gas system only. Denoting by $T$ a typical time for the gas system of a typical length $L$, $w$ a typical molecular velocity, $\lambda$ the mean free path, and $t_\lambda$ the mean free time we have

$$T = L/w, \quad t_\lambda = \lambda/w.$$  \hspace{1cm} (109)

Using these scales one can put down linearized Boltzmann’s equation with respect to the distribution function $f (v, \xi, \tau)$ in the dimensionless form\textsuperscript{42}

$$Q_v f + \text{Kn} \left( \frac{\partial f}{\partial \tau} + \frac{\partial}{\partial \xi} v f \right) = 0,$$  \hspace{1cm} (110)

where $v = v/w$ being the dimensionless velocity, $\tau = t/T$ is the dimensionless time, $-Q_v$ is

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the linearized collision operator and the small parameter $Kn$ is so-called Knudsen number

$$Kn = \frac{t_\lambda}{T} = \frac{\lambda}{L} \ll 1. \quad (111)$$

The analogy between problem (16)-(21) and the relevant problem for Eq. (110) appeared to be striking. Simple comparison of Knudsen number (111) with relaxation parameter (24) shows that the mean free time $t_\lambda$ corresponds to the characteristic transversal time $t_{tr}$. The value $w_{tr} = D/r_M$ may be treated as a typical transversal diffusion velocity and, therefore, $r_M$ corresponds to the mean free path $\lambda$. In both cases the perturbation operators describe the particles transport (with the relevant local fluxes for particles diffusion $- (\partial / \partial \xi) f$ and for particles flow $\nu f$) and unperturbed operators $L_\rho$ and $-Q_\nu$ are in spectrum. Namely for $-Q_\nu$ number $\lambda_0 = 0$ is a degenerate eigenvalue with five associated eigenfunctions, meanwhile for $L_\rho$ there is only one eigenfunction associated with one trivial eigenvalue. That is why in both cases for the zeroth-order outer approximation we can derive only equations for the corresponding projections on the above eigenfunctions (see (104)). Moreover, one can see that so-called Hilbert asymptotic solution (ideal liquid approximation) of Eq. (110) entirely corresponds to the FJA $u_0^{(0)}$ and the normal region$^{42}$ is nothing more than $\Omega^{(0)}$. In the kinetic theory as in the problem under study these terms, however, cannot describe the solutions into initial and boundary layers which naturally arise in both cases as well.$^{42}$

It is well known that the classical Chapman-Enskog method is widely used to reduce the Boltzmann kinetic equation to appropriate hydrodynamic and transport equations. Note-worthy that if we consider higher-order approximations of the Chapman-Enskog method, we obtain differential equations of higher order. Nevertheless, it is long known that the Chapman-Enskog expansion can bring in solutions, which are nonexistent. In order to overcome these difficulties the method of matching inner and outer expansions was also applied in kinetic theory.$^{42}$ It seems that the Kalnay-Percus mapping approach$^{17-19}$ resembles some
features of the Chapman-Enskog method, but this question needs to be investigated.

However, the analogy at issue is limited. The reflecting boundary condition \((20)\) plays an essential role in the diffusion problem \((16)-(21)\). Exactly due to this condition in contrast to the unperturbed operator of kinetics theory \(-Q\), operator \(\mathcal{L}_\rho\) \((17)\) is not self-adjoint (see Appendix). Nevertheless, detected analogy enables us to elucidate a number of the features inherent in the asymptotic solution of the diffusion problem \((16)-(21)\) at small values of the relaxation parameter \(\epsilon\).

\section{IX. CONCLUDING REMARKS}

By means of matched asymptotic expansions approach we gained here the uniformly valid leading-term approximation \((100)\) to solution of the 3D diffusion problem \((16)-(21)\) with respect to small relaxation parameter of the tube \(\epsilon\) \((24)\).

Suggested here derivation elucidates the mathematical sense of the Fick-Jacobs equation as the solvability condition of the lowest order \((39)\) for the first correction in \(\epsilon\) to the Fick-Jacobs approximation. Asymptotic solution also shows that known quasi-cylindrical condition \(|R'(\xi)| \ll 1\) is not necessary for validity of the leading-term approximation including Fick-Jacobs approximation. At the same time matching procedure automatically gave us an exact algorithm for determination of the missing initial and boundary conditions which must be imposed on the Fick-Jacobs approximation and its corrections.

The explicit form of the leading-term approximation allowed us to delineate the conditions on temporal and spatial scales \((108)\) under which the Fick-Jacobs approximation is valid.

One of the most noteworthy features of all previously suggested zeroth-order corrections to the Fick-Jacobs approximation is the absence of dependence on the transverse coordinates. However, as we have shown, even the leading-term approximation comprises the boundary
layers solutions explicitly depending on the transversal coordinate. We also proved that the outer approximation \( u^{(0)}(\rho, \xi, \tau) \) starting from orders \( O(\epsilon) \) contains terms explicitly depending on the transversal variable \( \rho \) (see (42)).

A profound analogy between the problem under consideration and the method of inner-outer expansions for low Knudsen numbers gas kinetic theory is established. This analogy enables us to clarify the physical and mathematical meaning of the obtained results.

It is important to underline that contrary to other known approaches our derivation of the Fick-Jacobs equation was implemented straightforwardly within the scope of asymptotic method procedure without any additional assumptions. In this connection we believe that it is rather inexpedient to exploit any physical arguments during the solution of quite well posed mathematical problem.

Future extension of the present work may include the higher order in \( \epsilon \) corrections to the solution considered here and also the case of tubes of other varying constraint geometry, e.g., without axial symmetry. The results obtained in this paper allow us to hope that the matched asymptotic expansions method may be successfully applied to many other problems concerning diffusion transport of pointlike particles in tubes of varying cross section. For example, the diffusion of particles undergoing the influence of interaction potential, partially penetrable boundary condition on the tube wall and its ends or diffusion equation with a source term may be considered by means of above method.

**ACKNOWLEDGMENTS**

This research has been partially supported by ”Le STUDIUM” (Loire Valley Institute for Advanced Studies). We also personally thank Professors P. Vigny and N. Fazzalari for their interest in this study and Professor F. Piazza for useful discussions.
APPENDIX

For the sake of completeness we recall here some useful classical mathematical definitions and facts.

The boundary layer of a domain $\Sigma_{\tau}$ comprises the set of points from $\Sigma_{\tau}$ such that their distance to the boundary $\partial \Sigma_{\tau}$ does not exceed some given magnitude $\delta > 0$, which is called the thickness of the layer.

In theory of singular perturbed problems a function $u_a (x; \epsilon)$ is said to be an approximation to $u (x; \epsilon)$ uniformly valid in a domain $\Lambda \subset \mathbb{R}^n$ to order $O (\zeta (\epsilon))$ as $\epsilon \to 0$ if

\[
\lim_{\epsilon \to 0} \frac{|u (x; \epsilon) - u_a (x; \epsilon)|}{\zeta (\epsilon)} = 0 \quad (A.112)
\]

uniformly for all $x \in \Lambda$. Here $\zeta (\epsilon)$ is so-called a gauge function.

Let us introduce the space $H_\epsilon$ of twice continuously differentiable real-valued functions $v : (0, R (\xi)) \to \mathbb{R}_+$ given on the cross section of the tube $0 < \rho < R (\xi)$ at any fixed point $(\xi, \tau)$. Additionally we assume that functions $v \in H_\epsilon$ obey the Neumann boundary conditions

\[
|_{\rho=0} < \infty, \quad \left. \frac{\partial v}{\partial \rho} \right|_{\rho=0} = 0, \quad (A.113)
\]

\[
|_{\rho=R(\xi)} = 0 \quad (A.114)
\]

at fixed point $(\xi, \tau)$.

Then for any two functions $f, g \in H_\epsilon$ we can introduce the weighted $L^2_\rho$ scalar product with the weight function $\rho$ as

\[
\langle f, g \rangle_{H_\epsilon} := \int_0^{R(\xi)} \rho f (\rho) g (\rho) \, d\rho. \quad (A.115)
\]

One can show that this defines the weighted Hilbert space $H_\epsilon := L^2_\rho((0, R(\xi)))$ with the
norm \[ \| f \|_{H_\xi} = \left[ \int_0^{R(\xi)} \rho f^2(\rho) \, d\rho \right]^{1/2} < \infty. \]  

Consider the linear operator \( \mathcal{L}_\rho : H_\xi \to C(0, R(\xi)) \) defined by (17). One can see that operator \( \mathcal{L}_\rho \) is self-adjoint in \( H_\xi \), that is

\[ \langle \mathcal{L}_\rho f, g \rangle_{H_\xi} = \langle f, \mathcal{L}_\rho g \rangle_{H_\xi}. \]  

Hence there exists the nontrivial solution of the eigenvalue problem

\[ \mathcal{L}_\rho v = \lambda^2 v \]  

for \( v \in H_\xi \) under the Neumann boundary conditions (A.113) and (A.114).

It has real pure-point spectrum of eigenvalues \( \{ \lambda_k \}_{k=0}^\infty \) such that for all \( k \geq 0 \) we have the ordering

\[ 0 \leq \lambda_0 < \lambda_1 < \ldots < \lambda_k < \ldots \]

at that \( \lambda_k \to \infty \) as \( k \to \infty \).

The associated eigenfunctions \( v_k \in H_\xi \) of the problem (A.117) are

\[ v_k := J_0 \left( \lambda_k \frac{\rho}{R(\xi)} \right). \]  

Here \( J_\nu(\zeta) \) is Bessel’s function of the first kind of order \( \nu \) which may be defined by its Maclaurin series

\[ J_\nu(\zeta) = \sum_{m=0}^\infty \frac{(-1)^m}{\Gamma(m+\nu+1) m!} \left( \frac{\zeta}{2} \right)^{2m+\nu}, \]  

where \( \Gamma(\beta) \) is the gamma function.

Thus the eigenvalues \( \lambda_k \) of the eigenvalue problem (A.117) are determined by the transcendental equation

\[ J'_0(\lambda_k) = 0 \]  

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which follows from the Neumann condition (A.114). Taking advantage of the known relation

\[ J'_0(\zeta) = -J_1(\zeta) \]

we infer that \( \lambda_k \) are also the roots of the transcendental equation

\[ J_1(\lambda_k) = 0. \tag{A.121} \]

It follows from expansion (A.119) and Eq. (A.121) that \( \lambda_0 = 0 \) and \( v_0 = J_0(0) = 1 \). One can see that for \( \lambda_0 = 0 \) there is only one linear independent eigenfunction \( v_0 \equiv \text{const} \).

We have and other eigenvalues, e.g.

\[ \lambda_1 \approx 3.8317, \quad \lambda_2 \approx 7.0156, \quad \lambda_3 \approx 10.1735, \ldots \]

Eigenfunctions \( \{v_k\}_{k=0}^{\infty} \) form a complete orthogonal system in \( \mathcal{H}_\xi \) and the orthogonality property for them holds\(^{44}\)

\[ \langle v_k, v_m \rangle_{\mathcal{H}_\xi} = \delta_{km} \|v_k\|^2_{\mathcal{H}_\xi}, \tag{A.122} \]

where \( \delta_{km} \) is the Kronecker delta and

\[ \|v_k\|^2_{\mathcal{H}_\xi} = \frac{1}{2} R^2(\xi) J_0^2(\lambda_k). \tag{A.123} \]

The corresponding orthonormal system \( \{\hat{v}_k\}_{k=0}^{\infty} \) is defined by

\[ \hat{v}_k = v_k / \|v_k\|_{\mathcal{H}_\xi}. \tag{A.124} \]

For any \( \lambda_k \) there is only one normed eigenfunction \( \hat{v}_k \in \mathcal{H}_\xi \) therefore for any function \( f \in L^2_\rho((0, R(\xi))) \) we have the Fourier series with respect to orthonormal basis \( \{\hat{v}_k\}_{k=0}^{\infty} \), that is

\[ f = \sum_{k=0}^{\infty} c_k \hat{v}_k, \tag{A.125} \]

where \( c_k = \langle f, \hat{v}_k \rangle \). It is known that series (A.125) converges in \( \mathcal{H}_\xi \), so the set of orthonormal functions \( \{\hat{v}_k\}_{k=0}^{\infty} \) is complete.\(^{43}\)
Note that existence of the trivial eigenvalue \( \{ \lambda_0 = 0 \} \) for (A.117) leads to a serious complication for solution of Eq. (16). Operator \( \mathcal{L}_\rho \) is termed to be in spectrum if there is at least one trivial eigenvalue belonging to the spectrum of \( \mathcal{L}_\rho \).

Consider a linear subspace \( V \) of the Hilbert space \( \mathcal{H}_\xi \) spanned on the zero eigenfunction \( v_0 \), that is \( V = \{ v \in V : v = \alpha v_0, \alpha \in \mathbb{R} \} \). It is well known that there exists space \( V^\perp \) orthogonal to \( V \) such that \( (V^\perp)^\perp = V \) and \( \mathcal{H}_\xi = V \oplus V^\perp \). So we can define the linear orthogonal projection operator (projector) \( \mathcal{P}_\xi : \mathcal{H}_\xi \to V \) that maps any \( w \in \mathcal{H}_\xi \) to \( v \in V \) is called the orthogonal projection onto \( V \), i.e.

\[
\mathcal{P}_\xi w = \langle w, v \rangle_{\mathcal{H}_\xi} v. \tag{A.126}
\]

In this paper it is convenient to define the projector as follows:

\[
\mathcal{P}_\xi w = \langle w, \hat{v}_0 \rangle_{\mathcal{H}_\xi} \hat{v}_0, \tag{A.127}
\]

where \( \hat{v}_0 = \hat{J}_0(0) = \sqrt{2}/R(\xi) \).

We observe here that simple Neumann condition (A.114) arises in the simplified problems corresponding to diffusion boundary layers. In general case of functions \( f \) and \( g \) obeying the reflecting boundary condition (20) the unperturbed operator \( \mathcal{L}_\rho \) (17) is not self-adjoint, i.e.

\[
\langle \mathcal{L}_\rho f, g \rangle_{\mathcal{H}_\xi} \neq \langle f, \mathcal{L}_\rho g \rangle_{\mathcal{H}_\xi}. \tag{A.128}
\]

The latter property of the unperturbed operator \( \mathcal{L}_\rho \) greatly complicates the original boundary value problem (16)-(21).
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