DIFFUSION-LAYER THEORY FOR FLOWS UNDER APPARENT WALL SLIP

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An explicit analytical formula is given for the overall mass transfer coefficient between the bulk of flowing microdisperse liquid and a small but finite active part of a solid surface. The apparent wall slip effect inside a diffusion layer is reflected through the local power-law velocity profile, $v_x(z) = Bz^p$, and a distribution $B = B(x,y)$ over the solid surface.
Key words: Diffusion layer; Microdisperse liquids; Apparent wall slip.

The theory of a small heat or mass transfer probe, embedded in an inactive body or wall in a stream of liquid, provides a common basis for various experimental techniques: thermal anemometers[1] (mainly for the bulk velocity measurements), electrodiffusion sensors[2] (mainly for the wall friction measurements), and electroanalytical measurements in flowing liquids[3] (mainly for the concentration measurements under conditions of limiting diffusion currents). All the mentioned references deal with flows of microhomogeneous Newtonian liquids. This means that they all are limited to linear velocity profiles close to the probe surface, represented locally by a single quantity, the wall shear rate. The classic result[4], which considers unidirectional flows with the constant shear rate, was generalized to planar[5] and axisymmetric[6,7] flows with one-dimensional distributions of the wall shear rate, tacitly assuming the same symmetry of the probe territory. This approach was generalized[8] for any three-dimensional flow of Newtonian liquids and any shape of the probe. In the present paper, this approach is further generalized for a class of non-linear profiles close to the wall which appear in the theory of apparent wall slip effects[9–11]. The theory is based on an idea recently sketched by the author[9].

THEORETICAL

Recently it has been argued[10,11] that, for any actual velocity profile $v_x = u(z)$ close the probe surface, a systematic theory of convective diffusion for a class of mass transfer probes can be based on a power-law representation of the velocity profiles,

$$u(z) = Bz^p \quad . \tag{1}$$

For a series of the probes with known transport lengths h and mass transfer coefficients $\bar{k}$, the parameters B, p can be adjusted in the following way:

$$p = \left.\frac{\mathrm{d}\ln u}{\mathrm{d}\ln z}\right|_{z=0.4\delta} = \frac{\mathrm{d}\ln h}{\mathrm{d}\ln \delta} - 2 \ , \qquad (2)$$

$$B = \left.\frac{\mathrm{d}u(z)}{\mathrm{d}z^p}\right|_{z=0.4\delta} = \frac{0.8hD}{0.4^p\,\delta^{2+p}} \ , \qquad (3)$$

where $\delta = D/\bar{k}$ stands here for the mean diffusion layer thickness, available, *e.g.*, from electrodiffusion experiments[10].

Basic theory[11] of convective diffusion with a space-independent power-law velocity profile, *i.e.*, in unidirectional viscometric flows with constant shear stress at the wall, was generalized[12] to include the transport configurations with planar symmetry. However, only a local distribution of mass transfer coefficients was given. A general theory for any surface distribution $B = B(x,y)$ at constant p is given here for the first time.

Problem Statement in the Diffusion-Layer Approximation

The mathematical problem[8] of steady convective diffusion from the bulk of a flowing liquid to the probe, *i.e.*, a small active surface A embedded in an inactive wall N (see Fig. 1) consists of the transport equation for an active component, $\boldsymbol{v} \cdot \nabla c = D\,\nabla^2 c$, with a given coefficient of diffusion D and a velocity field $\boldsymbol{v} = \boldsymbol{v}(\boldsymbol{r})$, accompanied by several boundary conditions which express:

1. the existence of the bulk liquid far away from the probe,

$$c \to c^{\mathrm{b}} \qquad \text{for } |\boldsymbol{r}| \to \infty \ , \qquad (4a)$$

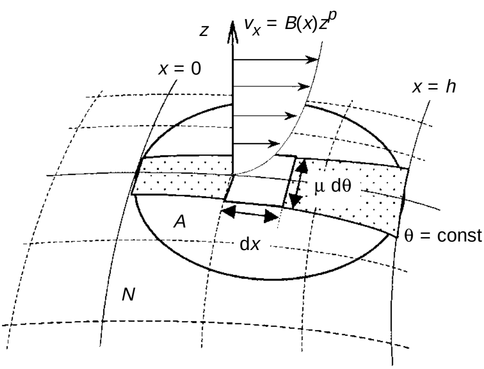

FIG. 1
Natural coordinates for the equation of convective diffusion. A Probe surface; N inert surface in a probe neighbourghood; z normal coordinate; x local longitudinal coordinate starting in the local forward edge on a given surface streamline; θ lateral coordinate: θ = const, z = 0 (corresponds to a surface streamline); μ metric coefficient of the mapping from Cartesian to natural coordinates, $\mathrm{d}A = \mu\,\mathrm{d}\theta\,\mathrm{d}x$ gives the area differential

2. the limiting diffusion conditions at the probe surface,

$$c = 0 \qquad \text{for } \boldsymbol{r} \in A \ , \tag{5a}$$

3. the zero-flux condition across the inert neighbouring surface,

$$\boldsymbol{n}_N \cdot \nabla c = 0 \qquad \text{for } \boldsymbol{r} \in N \ . \tag{6a}$$

Solving this problem, one obtains the concentration profile, $c = c(\boldsymbol{r})$, and the corresponding surface distribution of the local mass transfer coefficients,

$$k(\boldsymbol{r}) = D\boldsymbol{n}_N \cdot \nabla c / c^{\mathrm{b}} \ , \qquad \boldsymbol{r} \in A \ , \tag{7}$$

which is, in the next step, integrated over the probe surface A to provide the total (surface averaged) mass transfer coefficient of the probe,

$$\overline{k} = A^{-1} \iint_A k(\boldsymbol{r}) \, \mathrm{d}A(\boldsymbol{r}) \ . \tag{8}$$

The diffusion-layer approximation to this problem, in analogy to well-known boundary-layer theories of flow and heat transfer, assumes that the mass transfer resistance is concentrated in a thin layer close to the probe[13]. Using the common scaling arguments, as suggested by Prandtl, the only diffusion term is preserved which represents the diffusion flux normal to the surface. Assuming also the curvature of the probe surface to be negligible comparing with the local diffusion layer thickness $\delta = D/k$ as a local length scale, and choosing appropriate curvilinear orthogonal coordinates[8], the transport equation for the concentration field $c(x,z,\theta)$ can be written in a parabolic form

$$v_x \, \partial_x c + v_z \, \partial_z c = D \, \partial^2_{zz} c \ . \tag{9}$$

The transversal coordinate θ does not enter this equation in an explicit way as the direction $\boldsymbol{e}_x$ *by definition* as the local flow direction close to the surface. In other words, the line (θ = const, $z = 0$) corresponds to a surface streamline and θ is a parameter in description of the non-zero velocity components $v_x = v_x(x,z,\theta)$, $v_z = v_z(x,z,\theta)$ along this streamline. The continuity equation in the boundary-layer approximation for a smooth surface can be written in the form[8]

$$\partial_x(\mu v_x) + \mu \, \partial_z v_z + 0 \ , \tag{10a}$$

where the metric coefficient $\mu = \mu(x,\theta)$ specifies also the local differential area in the new coordinates,

$$dA(x,\theta) = \mu(x,\theta)\, dx\, d\theta \quad . \tag{11}$$

Let us assume the local profiles of longitudinal velocity in the form suggested in Eq. (*1*),

$$v_x(x,z,\theta) = B(x,\theta) z^p \quad , \tag{12}$$

with a constant exponent p. The continuity equation (*10a*) can be integrated to provide the profile of normal velocity component,

$$v_z(x,z,\theta) = -(1+p)^{-1}\, B(x,\theta)\, \partial_x \ln\,[\mu(x,\theta) B(x,\theta)]\, z^{p+1} \tag{10b}$$

and the corresponding form of the equation of convective diffusion:

$$Bz^p \left\{\partial_x - (1+p)^{-1}\, \partial_x \ln\,(\mu B)\, z\, \partial_z\right\} c = D\, \partial^2_{zz} c \quad . \tag{13}$$

This is a two-dimensional parabolic equation, which cannot satisfy the complete set of boundary conditions (*4a*), (*5a*), (*6a*) accompanying the original elliptic three-dimensional problem. Since the two-dimensional domain under consideration is a semi-infinite quadrant $x > 0$, $z > 0$, the modified boundary conditions are

$$c \to c^{\mathrm{b}} \qquad \text{for } z \to \infty \text{ and } x > 0 \quad , \tag{4b}$$

$$c = 0 \qquad \text{for } z = 0 \text{ and } x > 0 \quad , \tag{5b}$$

$$c \to c^{\mathrm{b}} \qquad \text{for } z > 0 \text{ and } x\mu B \to 0 \quad . \tag{6b}$$

The set (*4b*)–(*6b*) implies a singularity at the starting point ($x = 0$, $z = 0$) with a discontinuous change of the concentration from 0 to c^{b}.

Similarity Solution to the Problem

The transport equation (*13*) with the boundary conditions (*4b*)–(*6b*) allows an exact solution in the similarity form

$$c(x,z,\theta)/c^{\mathrm{b}} = C(w)\ ; \quad w = z/\delta(x,\theta)\ . \tag{14}$$

The similarity concentration profile $C(w)$ is a solution to the second-order linear differential equation with an indeterminated constant m,

$$C'(w) + qmw^{1+p}C''(w) = 0\ , \qquad q \equiv 1/(2+p)\ , \qquad (15a,\ 15b)$$

and the boundary conditions

$$C(0) = 0\ , \quad C(\infty) = 1\ , \quad C'(0) = 1\ . \qquad (16a\text{–}16c)$$

From the solution,

$$C(w) = \int_0^w \exp\,(-mq^2s^{2+p})\ \mathrm{d}s \tag{17}$$

and the normalizing condition (*16c*), it follows:

$$1 = \int_0^\infty \exp\,(-mq^2s^{2+p})\ \mathrm{d}s = \Gamma(1+q)/(mq^2)^q\ . \tag{18}$$

The local diffusion layer thickness $\delta(x,\theta)$ along a surface streamline θ = const is a solution to the first-order non-linear differential equation,

$$mqD\ \mathrm{d}x = B(x)\ \delta^{2+p}(x)\ [\mathrm{d}\ln\delta(x) + \frac{1}{1+p}\ \mathrm{d}\ln(\mu(x)B(x))]\ , \tag{19}$$

with the initial condition

$$\mu B\delta^{1+p} \to 0 \qquad \text{for}\ \ x \to 0\ . \tag{20}$$

For probes with a forward critical point, $B = 0$, lying on their territory A, the initial diffusion layer thickness can be non-zero. In a more common case, with the forward edge, $x = 0$, lying on a single surface streamline, $B > 0$, the initial diffusion layer thickness is zero. The resulting longitudinal profiles of the local mass transfer coefficient along individual surface streamlines, θ = const, can be expressed analytically:

$$k(x,\theta) \equiv D/\delta(x,\theta) = D^{1-q}\,[\mu(x,\theta)B(x,\theta)]^{q/(1-q)}/[Q(x,\theta)]^{q}\ , \qquad (21)$$

$$Q(x,\theta) \equiv m\int_0^x \mu^{1/(1-q)}(\xi,\theta)B^{q/(1-q)}(\xi,\theta)\,\mathrm{d}\xi\ . \qquad (22)$$

Some authors[7,14] who have presented various modifications and generalizations of the original Lighthill's theory overlooked a chance to obtain an analytical expression also for the total fluxes and the corresponding mean mass transfer coefficients. For a simple (single-segment) probe, the resulting formula follows from Eqs (*21*) and (*22*):

$$A\bar{k} \equiv \int_A k(x,\theta)\,\mathrm{d}A(x,\theta) = \frac{D^{1-q}}{(1-q)m}\int_{\theta\in A} Q^{1-q}[h(\theta),\theta]\,\mathrm{d}\theta\ , \qquad (23)$$

$h(q)$ standing for the geodetic lengths, $0 < x < h(\theta)$, of individual surface streamlines on the probe territory, $(x,\theta) \in A$. Note that, with the present formalism, the probe area is given as

$$A \equiv \int_A \mathrm{d}A(x,\theta) = \int_{\theta\in A}\mathrm{d}\theta\int_0^{h(\theta)}\mu(x,\theta)\,\mathrm{d}x\ . \qquad (24)$$

For multi-segmented probes, the theory can easily be modified by applying the approach described in our preceding communication[8].

RESULTS AND DISCUSSION

The resulting formulas (*21*)–(*23*) cover all the cases of steady-state convective diffusion studied so far within the diffusion layer (*i.e.*, the concentration boundary layer) approximation:

1. for $p = 1$ (*i.e.*, $q = 1/3$), they correspond to the general case of Newtonian liquids[8],

2. for m = const, they correspond to a rectilinear viscometric flow with a constant non-linear velocity profile according to ref.[12], see Eq. (*1*),

3. for $\mu = r(x)$, where r gives the local radius of an axisymmetric surface with an embedded axisymmetric probe (*e.g.*, a pole electrode on rotating sphere or a ring electrode on a rotating disk) surrounded in a flowing microdisperse liquid with axisymmetric velocity field, the *local* mass transfer coefficients were given in ref.[14]. The corresponding total mass transfer coefficients for an axisymmetric probe of a constant geodetic length h (see Fig. 2) can simply be deduced from Eq. (*21*):

$$A\bar{k} = \frac{D^{1-q}}{(1-q)m}\, 2\pi \left(m \int_0^h [r^{2+p}(x)B(x)]^{1/(1+p)}\, \mathrm{d}x \right)^{1-q} . \qquad (25)$$

4. A particular case of planar convective diffusion under ideal slip conditions, $p = 0$, was mentioned in a study[15] of unsteady heat transfer of liquid metals.

An interesting question[16] arises about a general kinematic condition of the uniformly accessible configurations, with constant diffusion layer thickness and local mass transfer coefficients, $k(x) = \bar{k}$ = const. It follows from Eqs (*21*) and (*22*) that, even under the apparent wall slip conditions, there is a sufficient condition for uniform accessibility in the form

$$B \sim \mu^{-1} \int_0^x \mu\, \mathrm{d}x \ . \qquad (26)$$

The diffusion-layer approximation to a complete theory of convective diffusion is often characterized as an asymptotic theory for a large Schmidt number. This is correct only for convective diffusion to a body in an external flow at a high Reynolds number, when the diffusion layer is located inside the hydrodynamic boundary layer. In general, the local transport regime for a heat/mass transfer microprobe of length h in a Newtonian fluid is characterized by the modified Peclet number, $Pe = h^2\dot{\gamma}/D$. For the power-law velocity profiles, this dimensionless criterion can be generalized, *e.g.*, to $Pe = (h/\lambda)^{1+p}$, where λ is a length parameter. A recent study[17] of the convective diffusion in microdisperse liquids at low Pe has shown that the effect of longitudinal diffusion is of

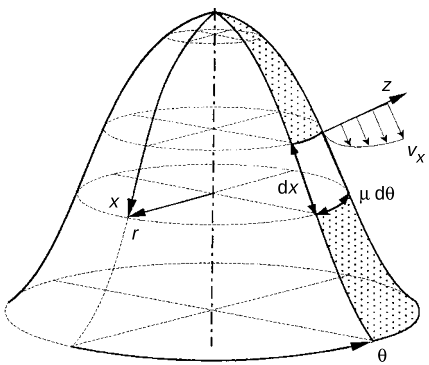

FIG. 2
Natural coordinates for completely axisymmetric problems. z Normal coordinate; θ azimuthal (angular) coordinate; x longitudinal coordinate along an axisymmetric body, the length of a surface streamline from the critical point or the forward edge line; r polar radius; $\mu = r$ metric coefficient, $\mathrm{d}A = r\, \mathrm{d}\theta\, \mathrm{d}x$

some importance close to the probe boundaries, within a narrow boundary band of depth λ in streamwise direction and δ in lateral direction. For a rectangular wall mass transfer probe of length h and width w, the relative effect of spatial diffusion at sufficiently high $H = h/\lambda$ can be represented by the asymptotic formula[17]

$$\overline{k}_{\mathrm{corr}}/\overline{k}_{\mathrm{diff}} \approx 1 + (w/h)\alpha_{\mathrm{S}}\, H^{-(1-q)} + \alpha_{\mathrm{FT}}\, H^{-1} - 0.06H^{-2(1-q)} \ , \qquad (27)$$

where

$$\alpha_{\mathrm{S}} = 0.276 - 0.038(1-p) - 0.016(1-p)^2 \, , \qquad (28)$$

$$\alpha_{\mathrm{FT}} = [0.0705 - 0.0080(1-p)^4](1+p) + 0.153 - 0.072(1-p) - 0.018(1-p)^2 \ . \qquad (29)$$

As it is obvious from this asymptotic formula for $H \rightarrow \infty$, the transversal effect, $\alpha_{\mathrm{S}}\, H^{-(1-q)}$, is asymptotically stronger than the remaining (longitudinal) ones.

Unfortunately, the theory in its present form is merely descriptive, *i.e.*, it predicts the mass transfer response for an *a priori* assumed velocity field in the diffusion layer. For its efficient application, a class of rheodynamical problems should be solved with the implied apparent wall slip condition at walls. Such solutions are only known for viscometric flows with constant shear stress at wall, see, *e.g.*, ref.[12]. Only recently[18], an analogous problem was formulated correctly for a general class of viscometric flows and actually solved for the case of generalized torsional flows.

SYMBOLS

A	surface and area of the probe, m^2
B	magnitude parameter of the velocity profile (*1*), $m^{1-p}\ s^{-1}$
c	concentration field of depolarizer, mol m^{-3}
c^{b}	bulk value of c, mol m^{-3}
D	diffusion coefficient for depolarizer, $m^2\ s^{-1}$
$\boldsymbol{e}_x$, $\boldsymbol{e}_z$, $\boldsymbol{e}_\theta$	base of the natural coordinates $\{x,z,\theta\}$
h	transport length of the probe, m
k	local mass transfer coefficient, m s^{-1}
$\overline{k}$	total (surface-averaged) mass transfer coefficient, m s^{-1}
m	$= q^{-2}\,\Gamma^{1/q}(1+q)$
$\boldsymbol{n}$	unit vector normal to the solid surface
N	inactive solid surface around the probe
p	form parameter of the velocity profile (*1*), $0 \le p \le 1$
q	$= 1/(2+p)$
Q	an auxiliary integral, Eq. (*22*)
r	local radius of an axisymmetric probe, m

r	radius vector, m
$u(z)$	velocity profile close to the wall, m s^{-1}
v	velocity field, m s^{-1}
v_x	longitudinal velocity component, m s^{-1}
x	longitudinal coordinate, m
z	normal-to-surface coordinate, m
$\dot{\gamma}$	wall shear rate, s^{-1}
δ	local diffusion layer thickness, m
$\overline{\delta}$	mean (Nernst) diffusion thickness, m
θ	lateral coordinate
λ	$= [(2 + p)^2 D/B]^{1/(1+p)}$, characteristic internal length within diffusion layer, m
μ	metric coefficient of the natural coordinates $\{x,z,\theta\}$

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