

INTEGRAL TRANSFORM "INFIXING" METHOD FOR NONLINEAR TRANSIENT  
MASS-TRANSFER PROBLEMS

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An approximate method is proposed for solving nonlinear problems of transient mass transfer between a wall and a motionless fluid for an arbitrary concentration dependence of the diffusion coefficient. Nonlinear problems compounded with a volume or surface chemical reaction are investigated.

1. DESCRIPTION OF THE METHOD

Various integral transforms of an unknown function (Laplace-Carson, Mellin, Bessel, and other transforms [1]) are often used in the solution of linear problems; they can be written conditionally in the form

$$u = L*c, \quad (1)$$

where  $c$  is the unknown function (inverse transform),  $L$  is a certain integral operator, and  $u$  is the transform.

In particular, the Laplace-Carson transform is defined as

$$u = p \int_0^{\infty} e^{-p\tau} c d\tau, \quad (2)$$

where  $p$  is a complex parameter.

In some cases transforms of the type (1) and (2) can also be used successfully for the approximate analysis of nonlinear boundary-value problems by "infixing" the transform in the argument of the function according to the rule [2, 3]

$$L*f(c) \simeq f(L*c) = f(u), \quad (3)$$

where  $f = f(c)$  is a certain nonlinear function of the argument  $c$ .

The domain of validity of the approximate operation (3) must be established separately in each specific instance. We note, however, that this approach yields a correct asymptotic result at large times in transient problems whose solution stabilizes in the limit  $\tau \rightarrow \infty$ . Moreover, the method ensures satisfaction of the initial and boundary conditions and gives an exact solution for linear problems.

We now illustrate the application of the "infixing" of integral transforms in specific examples of independent interest. As usual, we focus mainly on the derivation of diffusion flux equations.

2. MASS TRANSFER FOR AN ARBITRARY CONCENTRATION DEPENDENCE  
OF THE DIFFUSION COEFFICIENT

We consider the transient problem of mass transfer between a wall and motionless medium for an arbitrary dependence of the diffusion coefficient  $D$  on the concentration  $C$ .

The distribution of the concentration is described by the nonlinear equation

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial x} \bar{D}(c) \frac{\partial c}{\partial x} \quad (4)$$

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subject to the initial and boundary conditions

$$\tau = 0, c = 0; \quad x = 0, c = 1; \quad x \rightarrow \infty, c \rightarrow 0. \quad (5)$$

Dimensionless variables are expressed here in terms of dimensioned variables by means of the relations

$$c = \frac{C}{C_s}, \quad \bar{D}(c) = \frac{D(C)}{D(C_s)}, \quad x = \frac{X}{a}, \quad \tau = \frac{tD(0)}{a^2}.$$

We take the Laplace-Carson transforms of Eq. (4) and the initial and boundary conditions (5). Infixing the transform in the argument of the function  $\bar{D}$  according to rule (3), we have

$$pu = \frac{d}{dx} \bar{D}(u) \frac{du}{dx}, \quad (6)$$

$$x = 0, u = 1; \quad x \rightarrow \infty, u \rightarrow 0. \quad (7)$$

Making use of the fact that the ordinary differential equation (6) does not depend explicitly on  $x$ , we lower its order by the standard substitution

$$w = \frac{du}{dx}, \quad \left( \frac{d}{dx} = w \frac{d}{du} \right). \quad (8)$$

As a result, we obtain

$$pu = w \frac{d}{du} [\bar{D}(u) w]. \quad (9)$$

It is directly verifiable that the general solution of this equation has the form

$$2p \int_0^u \bar{D}(u) u du = [\bar{D}(u) w]^2 + A, \quad (10)$$

where  $A$  is an arbitrary constant.

It follows from the boundary condition at infinity (7) that  $w = du/dx \rightarrow 0$  as  $x \rightarrow \infty$ . Consequently, passing to the limit  $x \rightarrow \infty$  in Eq. (10), which corresponds to  $u = w = 0$ , we find the constant  $A = 0$ .

Taking the foregoing considerations into account, we rewrite (10) in the form

$$\bar{D}(u) \frac{du}{dx} = -\sqrt{2p \int_0^u \bar{D}(u) u du}. \quad (11)$$

We now derive an equation for calculating the dimensionless diffusion flux at the wall  $j = -\bar{D}(1) (\partial c / \partial x)_{x=0}$ . For this purpose we substitute  $x = 0$  in both sides of Eq. (11), which by virtue of the first boundary condition (7) corresponds to the value  $u = 1$ . Then, taking the inverse Laplace-Carson transform, we arrive at the required approximate expression for the flux

$$j = \sqrt{\frac{2}{\pi\tau} \int_0^1 \bar{D}(c) c dc}. \quad (12)$$

This equation gives the exact result for a constant diffusion coefficient.

We estimate the error of Eq. (12) for certain specific concentration dependences of the diffusion coefficient.

We first consider the nonlinear problem (4), (5) for

$$\bar{D}(c) = 1 - c. \quad (13)$$

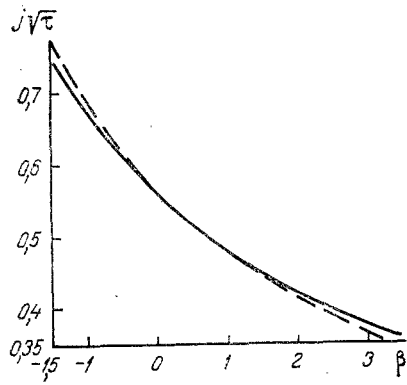


Fig. 1. Graph of  $j\sqrt{\tau}$  vs parameter  $\beta$ .

It has been solved previously [4] and leads to the expression for the diffusion flux

$$j = 0,332/\sqrt{V\tau}. \quad (14)$$

On the other hand, substituting Eq. (13) in (12), we obtain

$$j = \frac{1}{\sqrt{3\pi\tau}} \approx \frac{0,326}{\sqrt{\tau}}. \quad (15)$$

It follows from a comparison of relations (14) and (15) that the error of the proposed approximate method is less than 2% in the given situation.

We now consider an exponential dependence of the diffusion coefficient on the concentration

$$\bar{D}(c) = \exp\{\beta(c-1)\}. \quad (16)$$

A numerically obtained solution of problem (4), (5), (16) is given in [5]. The following equation is also proposed there for the diffusion flux:

$$j = \frac{0,564}{1 + 0,177\beta} \frac{1}{\sqrt{\tau}}, \quad (17)$$

which "works" well in the interval  $-1.5 \leq \beta \leq 3.5$ .

Substituting Eq. (16) in the integrand of Eq. (12), we obtain

$$j = \frac{1}{|\beta|} \sqrt{\frac{2}{\pi\tau} (\beta + e^{-\beta} - 1)}. \quad (18)$$

The dependences (18) and (17) are compared in Fig. 1 (solid and dashed curves, respectively). We see that the maximum disparity between these equations is ~4%.

It is important to note that the outer problem (either steady-state or transient) of mass transfer between droplets or bubbles and laminar flow at large Péclet numbers leads to the equation and boundary conditions (4), (5) for an arbitrary concentration dependence of the diffusion coefficient [6, 7]. In this light, the results obtained above can be used to derive an approximate expression for calculating the average Sherwood number for droplets and bubbles:

$$\frac{\text{Sh}(\bar{D})}{\text{Sh}(1)} = \sqrt{2 \int_0^1 \bar{D}(c) c dc}. \quad (19)$$

Here  $\text{Sh}(\bar{D})$  is the average Sherwood number for an arbitrary concentration dependence of the diffusion coefficient  $\bar{D} = \bar{D}(c)$ , and  $\text{Sh}(1)$  is the average Sherwood number for a constant diffusion coefficient  $\bar{D} = 1$ .

### 3. TRANSIENT MASS TRANSFER COMPOUNDED WITH A VOLUME CHEMICAL REACTION

We now consider mass transfer between a wall and a motionless medium with a chemical reaction taking place in its volume at the rate  $W_V = K_V F_V(C)$ . The corresponding transient

problem is formulated as follows in dimensionless variables:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial x^2} - k_v f_v(c), \quad (20)$$

$$\tau = 0, c = 0; \quad x = 0, c = 1; \quad x \rightarrow \infty, c \rightarrow 0,$$

where

$$c = \frac{C}{C_s}, \quad k_v = \frac{a^2 K_v F_v(C_s)}{D C_s}, \quad f_v(c) = \frac{F_v(C)}{F_v(C_s)}, \quad x = \frac{X}{a}, \quad \tau = \frac{D t}{a^2}.$$

We use the Laplace-Carson transform (2) for the approximate solution of this nonlinear problem. Infixing the integral operator in the argument of the function  $f_v$  according to rule (3), we obtain the ordinary differential equation

$$\frac{d^2 u}{dx^2} = pu + k_v f_v(u). \quad (21)$$

$$x = 0, u = 1; \quad x \rightarrow \infty, u \rightarrow 0. \quad (22)$$

The introduction of the new variable  $w$  according to Eq. (8) enables us to reduce the order of Eq. (21). As a result, we arrive at an equation in separable variables, whose integral has the form

$$2 \int_0^u [pu + k_v f_v(u)] du = w^2, \quad w = \frac{du}{dx}. \quad (23)$$

Using Eq. (23) and the boundary condition (22) at  $x = 0$ , we calculate the derivative at the wall:

$$\left( \frac{du}{dx} \right)_{x=0} = - \sqrt{p + 2k_v \int_0^1 f_v(u) du}. \quad (24)$$

Now, taking the inverse Laplace-Carson transform of both sides of Eq. (24), we find the diffusion flux  $j = -(\partial c / \partial x)_{x=0}$ :

$$i = \frac{e^{-\xi \tau}}{\sqrt{\pi \tau}} + V \bar{\xi} \operatorname{erf}(V \bar{\xi} \tau), \quad \xi = 2k_v \int_0^1 f_v(c) dc. \quad (25)$$

It is readily verified that the approximate functional relation (25) gives exact asymptotic results for small and large values of the dimensions time  $\tau$ . In the other two limiting cases  $k_v \rightarrow 0$  and  $k_v \rightarrow \infty$  Eq. (25) also gives the correct result. In addition, Eq. (25) is exact for a first-order reaction  $f_v = c$ .

#### 4. TRANSIENT DIFFUSION COMPOUNDED WITH A SURFACE CHEMICAL REACTION

Here we investigate the nonlinear problem of transient mass transfer between a motionless fluid and a wall when a heterogeneous chemical reaction takes place on the surface of the latter at the rate  $W_s = K_s F_s(C)$ . We assume that the concentration in the volume of the fluid is constant and equal to  $C_0$  at the initial time. The corresponding equation and initial and boundary conditions for the concentration are written in the form

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial x^2}, \quad (26)$$

$$\tau = 0, c = 0; \quad x = 0, \frac{\partial c}{\partial x} = -k_s f_s(c); \quad x \rightarrow \infty, c \rightarrow 0, \quad (27)$$

where the dimensionless variables are defined as

$$c = \frac{C_0 - C}{C_0}, \quad \tau = \frac{\sqrt{Dt}}{a}, \quad x = \frac{X}{a}, \quad k_s = \frac{aK_s F_s(C_0)}{DC_0}, \quad f_s(c) = \frac{F_s(C)}{F_s(C_0)}.$$

Taking the Laplace-Carson transforms (2) with allowance for rule (3), we arrive at the ordinary differential equation subject to a nonlinear boundary condition

$$\frac{d^2 u}{dx^2} = pu, \quad (28)$$

$$x = 0, \quad \frac{du}{dx} = -k_s f_s(u); \quad x \rightarrow \infty, \quad u \rightarrow 0. \quad (29)$$

The general solution of the equation with constant coefficients (28) subject to the extinction condition at infinity (29) is given by the equation

$$u = u_s \exp(-\sqrt{p}x), \quad (30)$$

in which  $u_s = u_s(p)$  is the transform of the surface concentration, which is required to be determined in the course of solving the problem.

Substituting Eq. (30) in the boundary condition (28) at  $x = 0$ , we obtain a nonlinear algebraic equation for the determination of  $u_s$ :

$$\sqrt{p}u_s = k_s f_s(u_s). \quad (31)$$

Taking the inverse Laplace-Carson transform [1] and making use of the correspondence (3)  $f(u_s) \approx L * f(c_s)$ , we derive an integral equation for the surface concentration:

$$\frac{d}{d\tau} \int_0^\tau \frac{c_s(\lambda) d\lambda}{\sqrt{\tau - \lambda}} = k_s f_s(c_s). \quad (32)$$

This equation can be integrated numerically according to a scheme described by Gupalo et al. [8]. The diffusion flux is expressed in terms of the surface concentration according to the equation

$$j = k_s f_s(c_s), \quad (33)$$

which is a consequence of the nonlinear boundary condition (27) on the wall at  $x = 0$ .

It is important to note that the nonlinear integral equation (32), which was obtained by an approximate method, is exact for an arbitrary dependence  $f_s = f_s(c)$ . We now prove this assertion.

Taking the Laplace-Carson transform of the linear equation (26) with allowance for the initial condition (27), we arrive at an equation for the transform (28). A solution of this equation, extinct at infinity, is given by Eq. (30). Accordingly, for the transform of the diffusion flux we have

$$\left( \frac{du}{dx} \right)_{x=0} = -\sqrt{p}u_s. \quad (34)$$

Taking the inverse Laplace-Carson transform of both sides of this equation, we find the relation between the surface concentration and its derivative at the wall

$$\left( \frac{\partial c}{\partial x} \right)_{x=0} = -\frac{d}{d\tau} \int_0^\tau \frac{c_s(\lambda) d\lambda}{\sqrt{\tau - \lambda}}. \quad (35)$$

Now, using this expression to eliminate the quantity  $(\partial c / \partial x)_{x=0}$  from the nonlinear boundary condition at the wall (27), we arrive at Eq. (32), Q. E. D.

#### NOTATION

$a$ , linear space scale;  $C$ , concentration;  $C_s$ , surface concentration on wall;  $C_0$ , concentration at initial time;  $c$ , dimensionless concentration;  $D$ , diffusion coefficient  $D = D(C)$ ;

$j$ , dimensionless diffusion flux onto wall;  $K_s$ , rate constant of surface chemical reaction;  $K_v$ , rate constant of volume chemical reaction;  $t$ , time;  $X$ , distance from wall.

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#### ELECTROTHERMAL ANALOGY IN HEREDITARY MEDIA AND ITS APPLICATION

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An electrothermal analogy (ETA) is established for the most common media with a thermal memory. The problem of intensifying thermal perturbations in a system consisting of a plate and a semiinfinite body is examined.

It is currently possible to distinguish a broad range of nonequilibrium physical phenomena in which heat transfer processes cannot be adequately described on the basis of the linear Fourier gradient relation. These cases include the following: heat transfer in liquid helium [1, 2]; heat transfer in media with energy carriers having a low concentration (in low-density gases [3]); heat transfer at low temperatures in crystals and semiconductors by second sound, ballistic phonons, etc. [4-7]; transport phenomena described within the framework of a two-temperature model (in a nonequilibrium gas [8], hot electrons in semiconductors [5, 6]). Mastery of thin-film and laser technologies also requires that allowance be made for memory effects in heat transfer. Similar problems are even more important in mass-transfer processes, where the relaxation time of the processes is several orders greater than in the case of heat transfer. For example, the study [9] described lag effects in various forms of mass transfer (adsorption, drying, heterogeneous catalysis, diffusion processing of porous bodies). Besides transport processes under extreme conditions, it is also possible to see deviations of heat transfer from the Fourier relation under normal conditions for media having a complex structure (polycrystalline materials, polymers, liquid crystals, etc.). Thus, a relaxational effect has been observed [10] in the high-temperature heat capacity of tungsten, this effect being due to the existence of high concentrations of point defects in the metal. The above-mentioned classes of phenomena and materials can be described at the phenomenological level in terms of heat transfer in hereditary media on the basis of integral governing relations (GR) [11, 12] with relaxation functions (RF)  $\lambda_1(t)$ ,  $c_1(t)$  for heat flux and internal energy. These functions account for the history of the thermal process. In the particular case of RFs of the form  $\lambda_1 = 1 - \exp(-t/\tau_0)$ ;  $c_1(t) = H(t)$ , the GRs [11, 12] describe the hypothesis of relaxation of the thermal stress  $q + \tau_0 q = -\lambda_0 \nabla u$ , leading to a hyperbolic heat-conduction equation. The Maxwell relaxation time  $\tau_0$  in solids at normal temperature has the value  $10^{-9}$ - $10^{-11}$  sec [13]. Thus, its effect on heat transfer should be considered when a material is subjected to a laser pulse of nanosecond duration [14, 15]. At low temperatures,  $\tau_0$  may increase by several orders [5] and have a more significant ef-

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