outside; q_1, q_2, effective flux densities at walls; q_1^*, q_2^*, densities of emitted fluxes at walls; $R(y_0)$, radius of curvature of contour L at point y_0; R_1, R_2, internal and external radii of annular gap; r, coordinate; S, two-dimensional region; $u = q_1 + q_2$, $v = q_2 - q_1$; W_1, W_2, probabilities that a flux incident respectively on the external and internal cylindrical surface will pass through the gap; W_1^*, W_2^*, probabilities that the emitted flux will exit through the internal and external cylindrical surface, respectively; w, discrepancy in the equation; x, coordinate; y, point of region S; Δ, Laplacian; Δ_u, Δ_v, absolute errors; δ_u, δ_v, relative errors; $\Pi^{(\alpha)}$, transmission-coefficient tensor. Indices: α, number of the representation for the transmission coefficient; j, number of gap wall.

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NEW APPROXIMATE ANALYTIC METHODS OF INVESTIGATING PROBLEMS OF PHYSICOCHEMICAL MECHANICS

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UDC 518.12:541.1

New approximate analytic methods are suggested for investigating problems of physicochemical mechanics. Specific examples are provided, illustrating the use of these methods.

1. Asymptotic Correction Method. Various engineering equations, obtained empirically or by approximate solution of the corresponding (boundary-value) problems, are often used in practice. The validity region of these equations is usually restricted, and is separately established in each specific case. Below we suggest a simple universal method of substantial improvement of the approximate engineering equations, based on using the exact asymptotic of the original boundary-value problem.

Let the unknown quantity S be obtained by the approximate expression

$$S = S(k, P), \tag{1}$$

which usually reflects the qualitative behavior of S as a function of the change in the dominant parameters of the problem k and P (here and later it is assumed for simplicity that there are two such parameters). Let the main terms of the asymptotic approximate expression (1) be in the limiting cases $k \to \infty$ (P = const) and $P \to \infty$ (k = const)

$$k \to \infty,\ S \to S^*_{\infty P};\ P \to \infty,\ S \to S^*_{k\infty}; \tag{2}$$

$$S^*_{\infty P} = S^*_{\infty P}(k,\ P),\ S^*_{k\infty} = S^*_{k\infty}(k,\ P) \tag{3}$$

(instead of (2) one can consider any other limiting cases; see the specific examples provided below).

If similar exact asymptotic solutions of the original problem are known

$$k \to \infty,\ S \to S_{\infty P};\ P \to \infty,\ S \to S_{k\infty}, \tag{4}$$

the approximate Eq. (1) can be improved by the following simple method. In expression (3) we

State Research Institute of Nitrogen Industry and Organic Synthesis Products, Moscow.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 46, No. 3, pp. 415-424, March, 1984. Original article submitted November 11, 1982.

0022-0841/84/4603-0295$08.50

express the parameters k and P in terms of $S^*_{k\infty}$ and $S^*_{\infty P}$ (it is assumed that the corresponding transformation is nondegenerate) and substitute them in Eq. (1). As a result, we obtain

$$S = F(S^*_{\infty P},\ S^*_{k\infty}) \quad (F(S^*_{\infty P}(k,\ P),\ S^*_{k\infty}(k,\ P)) \equiv S(k,\ P)). \tag{5}$$

If now one substitutes the corresponding asymptotic exact solution of the original problem (4) instead of the asymptotic (3) of the approximate Eq. (1), one then obtains the equation

$$S = F(S_{\infty P},\ S_{k\infty}), \tag{6}$$

which along with the correct qualitative description of the quantity S now also guarantees an exact result in the limitng cases $k \to \infty$ and $P \to \infty$ (unlike Eq. (1)).

It must be noted that if Eq. (1) is exact, Eq. (6) will also be correct (i.e., the procedure suggested does not worsen the original result). Moreover, it is easily verified that if Eq. (1) undergoes an arbitrary stretch of the parameters k and P ($k \to \alpha k$, $P \to \beta P$, α, β = const) differing from the accurate one (i.e., Eq. (1) is "spoiled" by stretching), then the procedure indicated reconstructs it fully from the known exact asymptotic and renders it exact. It is also easy to mention a wider class of transformations, following which the procedure suggested also reconstructs the "spoiled" equation.

We illustrate the method suggested on several specific examples. It is well-known [1] that in analyzing mass exchange of a drop with laminar flow in the diffuse boundary layer approximation an analytic solution of the problem can be obtained only in the limiting cases of relatively small and infinitely large values of the ratio of the drop viscosity to the surrounding liquid β. This is due to the fact that the asymptotic expansions for the concentration and the mean Sherwood number in terms of the large Peclet number $Pe = aU_\infty D^{-1}$ for the drop are not uniformly valid in the parameter β. In particular, the asymptotic values for the mean Sherwood number at $Pe \gg 1$ for a drop of moderate viscosity ($\beta = O(1)$) and a solid sphere ($\beta = \infty$) are [1]

$$\beta = O(1),\ Sh = Sh_\beta;\ \beta \to \infty,\ Sh \to Sh_\infty; \tag{7}$$

$$Sh_\beta = (2Pe)^{1/2}[3\pi(1+\beta)]^{-1/2},\ Sh_\infty = \frac{3}{8}(3\pi)^{2/3}\Gamma^{-1}\left(\frac{1}{3}\right) Pe^{1/3} \approx 0{,}624 Pe^{1/3}$$

A consequence of the nonuniformity of the results (7) in the parameter β is the property $Sh_\infty \neq \lim_{\beta\to\infty} Sh_\beta = 0$.

It was shown in [2, 3] that the validity region of the equations obtained in the diffuse boundary layer approximation for drops $Sh = Sh_\beta$ (7) is limited from above in the parameter β by the inequality $\beta < O(Pe^{1/3})$. The problem mentioned in [4] was investigated approximately over the whole interval of variation of the drop viscosity $0 \leqslant \beta \leqslant \infty$. Additional considerations were included in this case, which are not directly related to the equation of convective diffusion.

We now show how, using the procedure suggested, one can improve on the results of [4], where the following approximate cubic equation was obtained for the mean Sherwood number

$$Sh^3 - \frac{Pe}{16\ln 2(1+\beta)}(2Sh + 3\beta + 1) = 0. \tag{8}$$

The following two basic asymptotic relations take place for the mean Sherwood number of (8):

$$\beta = O(1),\ Sh = Sh^*_\beta;\ \beta \to \infty,\ Sh \to Sh^*_\infty;$$

$$Sh^*_\beta = \left[\frac{Pe}{8\ln 2(1+\beta)}\right]^{1/2},\quad Sh^*_\infty = \left(\frac{3Pe}{16\ln 2}\right)^{1/3}, \tag{9}$$

which correspond to a drop with moderate viscosity $\beta = O(1)$ and a solid sphere $\beta = \infty$; in deriving Eq. (9) it was taken into account that the Peclet number is large, $Pe \gg 1$.

It is seen that the limiting approximate expressions (9) obtained from (8) are such that only the coefficients differ from the asymptotically correct (7). We now express the parameters β and Pe in terms of Sh^*_β and Sh^*_∞, and we further substitute them into Eq. (8). As a result, we obtain

$$Sh^3 - Sh^{*2}_\beta(Sh - 1) - Sh^{*3}_\infty = 0. \tag{10}$$

The exact asymptotic solutions of the original problem corresponding to (9) are given above and have the shape (7).

Taking into account that for large Peclet numbers $Sh \gg 1$ and $Sh - 1 \approx Sh$, and replacing in (10) Sh_β^* and Sh_∞^* by Sh_β and Sh_∞, we obtain the following approximate equation for determining the mean Sherwood number:

$$Sh^3 - Sh_\beta^2 Sh - Sh_\infty^3 = 0, \tag{11}$$

which correctly reflects the qualitative behavior of Sh, and leads to the exact asymptotic result for $\beta = O(1)$ and $\beta = \infty$ ($Pe \gg 1$).

The mean Sherwood number corresponding to (11) can be represented in a form more convenient for analysis:

$$Sh = Sh_\beta x(Q),\ Q = \frac{Sh_\infty}{Sh_\beta} = \mathrm{const}\frac{Pe^{1/3}}{1+\beta}, \tag{12}$$

where $x = x(Q)$ is the root of the equation

$$x^3 - x - Q^3 = 0. \tag{13}$$

Consider one specific example, when the procedure suggested above makes it possible to improve substantially the approximate equation. Stationary convective diffusion was investigated in [5], consisting of a complicated exchange chemical reaction of arbitrary order n. The following expression was obtained for the mean Sherwood number corresponding to Stokes flow of a spherical drop (Hadamard–Rybchinskii flow)

$$Sh = Sh(k,\ Pe,\ \beta) = \left(\frac{1}{8\ln 2}\frac{Pe}{\beta+1} + \frac{2k}{n+1}\right)^{1/2}. \tag{14}$$

In deriving Eq. (14) it was assumed that $Pe \gg 1$.

For $k \to \infty$ ($Pe = \mathrm{const}$) the approximate expression (14) describes correctly the asymptotic behavior of the mean Sherwood number, and in the other limiting case we have

$$k \to 0,\ Sh \to Sh_0 = Pe^{1/2}[8\ln 2(1+\beta)]^{-1/2}. \tag{15}$$

Here and later the asterisk above the corresponding asymptotics of the approximate solution will be omitted: $Sh_0 = Sh\ (0,\ Pe,\ \beta)$. We now express by means of (15) the Peclet number in terms of Sh_0, and substitute it into (14). As a result, we reach the equation

$$Sh = [Sh_0^2 + 2k(n+1)^{-1}]^{1/2}, \tag{16}$$

which was earlier obtained by other considerations in [6]. In using this equation for Sh_0 one must choose the exact value of the mean Sherwood number, corresponding to the pure diffusion regime without chemical reactions ($k = 0$). It must be noted that the validity region of the improved equation (16) is substantially wider than that of the original approximation (14), and it can also be used for approximate determination of the mean Sherwood number, both for a drop and for a solid particle of arbitrary shape in any flow. In particular, for large Peclet numbers and for translational flow of a solid sphere one must put in expression (16) $Sh_0 = Sh_\infty$, where Sh_∞ has been determined in (7).

We note that in the given case the parameter k was not eliminated in terms of the asymptotic approximate equation (14) for $k \to \infty$ due to the fact that this asymptotic coincided with the corresponding expression.

In the case of translational Stokes flow of a spherical drop and for first order reactions $n = 1$ comparison of the approximate equation (16) with results of numerical integration [7], obtained in the approximation of a diffuse boundary layer expressed for a local diffusion flow [8], was carried out in [6]; in this case the maximum error of Eq. (16) was around 7%. Table 1 provides a comparison of the approximate equation (16) with results of numerical analysis [9], obtained for translational flow of a spherical drop in the case of volumetric chemical reactions of half-integral order $n = 1/2$ for various values of the parameters k, Pe, and β. It is seen that in this case the error was around 5%.

2. Method of Model Equations and Analogies. In many problems of convective mass and heat transfer, it is of basic practical interest to determine the mean integral characteristics of the solution, the mean Sherwood Sh and Nusselt Nu numbers, while at the same time direct determination of the concentration and temperature fields is often of lower priority,

TABLE 1. Comparison of the Mean Sherwood Number, Obtained by Approximate and Numerical Methods, for Translational Flow of a Spherical Drop in Case of a Volumetric Chemical Reaction of Fractional Order n = 1/2

k	Pe	β	Sh, results of [9]	Sh, Eq. (15)	Sh_0, [9]	Error, %
50	500	10	9,90	9,39	4,63	5,2
500	5000	10	27,9	28,1	11,2	0,8
50	500	0,01	15,2	15,0	12,6	1,2
500	5000	0,01	49,3	48,7	41,3	1,2
5000	5000	10	82,8	82,4	11,2	0,4
5000	5000	0,01	87,0	91,5	41,3	5,2

supplying less substantial information. In these cases, for approximate description of the unknown mean characteristics it was suggested in [6] to consider, instead of the original complicated equations in partial derivatives, ordinary differential equations — model equations of the problem. Solutions were constructed of these model equations, and by means of the similarity principle one could even obtain an approximate expression for the unknown mean characteristics. In the method of model equations and analogies the approximate solution of the model equation is substantially improved by means of the exact asymptotics of the original boundary-value problem by using the procedure described in Sec. 1.

We illustrate the basic ideas of the method of model equations and analogies on specific examples (a more detailed discussion of the method is given in [6]).

Consider stationary convective diffusion to the surface of a spherical drop, flowing in a translational Stokes flow (Hadamard—Rybchinskii flow). It is assumed that on the surface of the drop there is total absorption of the solution in the liquid material, whose concentration far from the drop is constant. In dimensionless variables and in a spherical coordinate system r, θ, fixed in the drop, the corresponding boundary-value problem is (the last boundary condition in (18) is a consequence of the axial symmetry of the problem)

$$\frac{1}{\sin\theta}\left(-\frac{\partial\psi}{\partial\theta}\frac{\partial c}{\partial y}+\frac{\partial\psi}{\partial y}\frac{\partial c}{\partial\theta}\right)=\frac{1}{\mathrm{Pe}}\frac{\partial^2 c}{\partial y^2};\quad c=\frac{C}{C_\infty};\ y=r-1; \tag{17}$$

$$y=0,\ c=0;\ y\to\infty,\ c\to 1;\ \theta=0,\ \partial c/\partial\theta=0; \tag{18}$$

$$\psi=[\lambda_1(\beta)y+\lambda_2(\beta)y^2]\sin^2\theta,\ \lambda_1=\frac{1}{2(1+\beta)},\ \lambda_2=\frac{3\beta+2}{4(1+\beta)}, \tag{19}$$

and for the stream function in (19) we have selected the two-term quadratic expansion of the concentration in y near the surface of the drop. The solutions obtained in [1] correspond to the values $\lambda_1 = \lambda_1(\beta)$, $\lambda_2 = 0$ (for a drop of moderate viscosity $\beta = O(1)$) and $\lambda_1 = 0$, $\lambda_2 = \lambda_2(\infty) = 3/4$ (for a solid sphere). Since $\lambda_1(\beta) \to 0$ for $\beta \to \infty$, account of the second term in the expansion of the stream function (19) is necessary to obtain the unknown relations, uniformly valid in the parameter β for $\mathrm{Pe} \gg 1$. There is no analytic solution of the problem (17)-(19).

Near the limiting critical point θ = 0, due to the equalities $\psi(y, 0) = 0$ and $(\partial c/\partial\theta)_{\theta=0} = 0$ the second term in the left-hand side of Eq. (17) can be neglected; in this case (17) degenerates into an ordinary differential equation, and the problem is rewritten in the following form:

$$-2[\lambda_1(\beta)y+\lambda_2(\beta)y^2]\frac{dc}{dy}=\frac{1}{\mathrm{Pe}}\frac{d^2c}{dy^2};\ y=0,\ c=0;\ y\to\infty,\ c\to 1. \tag{20}$$

We note that the solution of (20) depends weakly on the shape of the parameter $\lambda_2 = \lambda_2(\beta)$. Indeed, since in the case under consideration $\mathrm{Pe} \gg 1$, for values $\beta < O(\mathrm{Pe}^{1/3})$ the quadratic term in Eq. (20) can be neglected, corresponding to a solution generally independent of λ_2. The necessity of taking into account terms including the λ_2 dependence becomes apparent for values $\beta \geqslant O(\mathrm{Pe}^{1/3})$, when (due to $\mathrm{Pe} \gg 1$) the relationship $\lambda_2(\beta) \approx \lambda_2(\infty) = 3/4$ is valid. The fact mentioned also takes place for the original boundary-value problem (17)-(19), and allows to replace everywhere the dependence $\lambda_2 = \lambda_2(\beta)$ by the limiting value $\lambda_2(\infty) = 3/4$.

In the model equation [6], corresponding to the partial differential equation (17), it is natural to select the available analog limiting properties in the parameters β and Pe of the ordinary differential equation putting in it (20), putting in it $\lambda_2(\beta) = \lambda_2(\infty)$.

The solution of problem (20) is ($\lambda_2 = 3/4$)

$$c = \Lambda(\mathrm{Pe},\ 1+\beta)\int\limits_0^y \exp\left[-\frac{\mathrm{Pe}}{2}\left(\frac{y^2}{1+\beta}+y^3\right)\right]dy, \tag{21}$$

$$\Lambda(\mathrm{Pe},\ 1+\beta) = \left\{\int\limits_0^\infty \exp\left[-\frac{\mathrm{Pe}}{2}\left(\frac{y^2}{1+\beta}+y^3\right)\right]dy\right\}^{-1}.$$

The local diffusion flow at the limiting critical point of the drop, corresponding to the solution (21), is determined by the expression

$$j = \Lambda(\mathrm{Pe},\ 1+\beta). \tag{22}$$

Taking into account that $\mathrm{Pe} \gg 1$, from Eqs. (21), (22) we obtain the following asymptotic:

$$\beta = O(1),\ j \to j_\beta = (2\mathrm{Pe})^{1/2}[\pi(1+\beta)]^{-1/2};$$
$$\beta \to \infty,\ j \to j_\infty = 3\cdot 2^{-1/3}\Gamma^{-1}(1/3)\,\mathrm{Pe}^{1/3}. \tag{23}$$

Here j_β and j_∞ are the local diffusion currents at the limiting critical point of a drop of moderate viscosity and of a solid sphere; it must be noted that $j_\infty \neq \lim\limits_{\beta\to\infty} j_\beta = 0$.

From the asymptotic equations (23) we express the parameters β and Pe in terms of j_β and j_∞, and substitute into Eq. (22). As a result we have

$$j = \Lambda\left(\frac{2}{27}\Gamma^3\left(\frac{1}{3}\right)j_\infty^3,\ \frac{4}{27\pi}\Gamma^3\left(\frac{1}{3}\right)\frac{j_\infty^3}{j_\beta^2}\right). \tag{24}$$

To obtain the true expression for the mean Sherwood number at the surface of the drop we use a similarity principle [6]; more precisely, we assume that the fundamental dependence of the mean Sherwood number Sh on the auxiliary Sherwood numbers (7), determined by the asymptotic solutions of the original boundary-value problem (17)-(19) for $\beta = 0$ (1) and $\beta = \infty$ ($\mathrm{Pe} \gg 1$), is similar to dependence (24) for the local diffusion flows corresponding to the model problem (20), i.e., the following equation (S is the dimensionless area of the particle surface) is valid

$$\mathrm{Sh} = \Lambda\left(\frac{2}{27}\Gamma^3\left(\frac{1}{3}\right)\mathrm{Sh}_\infty^3,\ \frac{4}{27\pi}\Gamma^3\left(\frac{1}{3}\right)\frac{\mathrm{Sh}_\infty^3}{\mathrm{Sh}_\beta^2}\right), \tag{25}$$

$$\left(\mathrm{Sh} = \frac{1}{S}\int\limits_s \frac{\partial c}{\partial n}ds\right).$$

The approximate expressions (7), (25) reflect well the behavior of the mean Sherwood number in the whole region of variation of the parameter β: $0 \leqslant \beta \leqslant \infty$ In particular, for $\beta = O(1)$ or $\beta \to \infty$ ($\mathrm{Pe} \gg 1$) Eq. (25) transforms to the results of [1], which are given by relationships (7). Moreover, the variable replacement $y' = \mathrm{Sh}_\beta y$ in the integral of (21), (25) shows that there exists a similarity parameter $Q = \mathrm{Sh}_\infty/\mathrm{Sh}_\beta$ (12), generating the following relation between the mean Sherwood numbers:

$$\frac{\mathrm{Sh}(\mathrm{Pe}_1,\ \beta_1)}{\mathrm{Sh}(\mathrm{Pe}_2,\ \beta_2)} = \left[\frac{\mathrm{Pe}_1(1+\beta_2)}{\mathrm{Pe}_2(1+\beta_1)}\right]^{1/2} \text{ for } \frac{\mathrm{Pe}_1^{1/3}}{1+\beta_1} = \frac{\mathrm{Pe}_2^{1/3}}{1+\beta_2}. \tag{26}$$

It is important to stress that despite the fact that relations (26) were obtained from the approximate equation (25), they are an exact consequence of the original boundary-value problem (17)-(19) (with $\lambda_2 \approx \lambda_2(\infty) = 3/4$), with the same similarity parameter Q. The latter is proved by introducing the new variable $y_* = \mathrm{Pe}^{1/2}(1+\beta)^{-1/2}y$ directly into (17)-(19).

The analysis in [10] of the boundary-layer equation was carried out numerically without linearization of the current function. It must be noted, however, that to obtain a given accuracy for large Peclet numbers the grid step must be sensitive to the values of the parameters β and Pe; in this case, according to the discussion above, during a numerical study of the problem (17)-(19) in the case $Pe \gg 1$ and $\beta \gg 1$ the value of the similarity parameter Q must be selected for a choice of the grid step (this should have been done in [10]); in this case Eqs. (26) can serve as a criterion of the accuracy of the calculation.

We note an important feature, which is typical of the use of the method of model equations and similarity: the validity region of the approximate equation (25) is substantially wider than the information contained in the original statement of problem (17)-(19). In particular, the approximate expression (25) can also be used successfully to determine the mean Sherwood number for pure shear flow of a drop in the whole region of variation of the ratio of viscosity of the drop to that of the surrounding liquid $0 \leqslant \beta \leqslant \infty$ for large Peclet numbers. In this case one must use for the parameters Sh_β and Sh_∞ in (25) the corresponding limiting values, obtained in [11]:

$$Sh_\beta = (3/\pi)^{1/2}(1+\beta)^{-1/2}Pe^{1/2},\ Sh_\infty \simeq 1{,}22Pe^{1/3},\ Pe = a^2\alpha D^{-1}. \tag{27}$$

It is interesting to note that here too we have the same similarity parameter Q, and relationship (26) is valid.

In the example above it was shown that in using the method of model equations and similarity [6] the approximate solution of the model equation was substantially improved by means of the exact asymptotics (7).

Comment. We now show how Eq. (11), derived earlier by a different method, can be obtained by approximate solution of the model equation (20) by an integral method with subsequent use of the similarity principle. For this we rewrite Eq. (20) for $c_* = 1 - c$ and integrate it over y from zero to infinity, assuming that the quantity c_* and all its derivatives tend exponentially to zero for $y \to \infty$. As a result, we obtain after several transformations

$$2\int_0^\infty [\lambda_1(\beta) + 2\lambda_2 y](1-c)\,dy = \frac{1}{Pe}\left(\frac{dc}{dy}\right)_{y=0}. \tag{28}$$

Here, as earlier, it is assumed that $\lambda_2 = \lambda_2(\infty) = 3/4$.

As usual, the solution of the integral identity (28) is sought in the form

$$c = \varphi(y/\delta), \tag{29}$$

where the profile $\varphi=\varphi(x)$ is chosen arbitrarily, and the constant δ, corresponding to the width of the diffusion boundary layer at the limiting critical point of the drop, is determined by the solution of the equation

$$j^3 - 2Pe\lambda_1(\beta)\sigma_1 j - 4Pe\lambda_2\sigma_2 = 0,\ j = A\delta^{-1}, \tag{30}$$

$$A = \left(\frac{d\varphi}{dx}\right)_{x=0},\ \sigma_n = A^n\int_0^\infty x^{n-1}[1-\varphi(x)]\,dx \quad (n = 1, 2),$$

which was obtained after several transformations as a result of substituting (29) into identity (28).

For $Pe \to \infty$ we have from the cubic equation (30) the asymptotic

$$\beta = O(1),\ j \to j_\beta = [2Pe\lambda_1(\beta)\sigma_1]^{1/2}; \tag{31}$$

$$\beta \to \infty,\ j \to j_\infty = (4Pe\lambda_2\sigma_2)^{1/3}$$

Using relations (31) to express the parameters β and Pe in terms of j_β and j_∞, and substituting them into (30), we obtain the following equation for the local diffusion flow:

$$j^3 - j_\beta^2 j - j_\infty^3 = 0. \tag{32}$$

Using now for (32) the similarity principle, we reach an approximate equation for the mean Sherwood number, namely Eq. (11).

It must be stressed that the final result (11) (or Eq. (32)) is independent of the specific choice of the concentration profile $\varphi=\varphi(x)$ (29). We also note that the exact relation for the mean Sherwood number (26) follows from the approximate expression (11).

3. "Carryover" Method of Integral Transforms. In solving linear problems, one often uses various integral transforms of the unknown function (for example, the Laplace—Carlson

transform, the Bessel transform, etc.), which can be written tentatively in the form

$$u = \mathbf{L} * c, \tag{33}$$

where c is the unknown function (the inverse image), **L** is some integral operator, and u is the image.

It appears that in a number of cases a transform of shape (33) can also be used for approximate analysis of nonlinear boundary-value problems, a "carryover" transform under the function sign according to the rule

$$\mathbf{L} * f(c) \simeq f(\mathbf{L} * c) = f(u), \tag{34}$$

where f = f(c) is some nonlinear function of the argument c. The validity region of the approximate operation (34) must be established separately in each specific case.

We now illustrate an application of the "carryover" method of integral transforms on a specific example of independent interest.

Consider nonstationary convective diffusion to a reacting (solid or liquid) spherical particle during liquid flow with an arbitrary exchange chemical reaction. In dimensionless variables the corresponding boundary-value problem is formulated as follows:

$$\frac{\partial c}{\partial t} + \mathrm{Pe}\,(\mathbf{v}\cdot\nabla)\,c = \Delta c - kf(c) \quad (f(0) = 0,\ f'_c \geqslant 0,\ k \geqslant 0), \tag{35}$$

$$t = 0,\ c = 0;\ r = 1,\ c = 1;\ r \to \infty,\ c \to 0; \tag{36}$$

$$c = \frac{C}{C_s},\ k = \frac{a^2 k_V F(C_s)}{DC_s},\ f(c) = \frac{F(C)}{F(C_s)},\ t = \frac{Dt_*}{a^2}.$$

Here $C_S \neq 0$ and $k_V F(C)$ is the chemical reaction rate.

We apply to the equation, initial and boundary conditions (35), (36) the Laplace–Carlson transformation. Carrying out the transformation under the sign of the function f according to rule (34), we obtain

$$pu + \mathrm{Pe}\,(\mathbf{v}\cdot\nabla)\,u = \Delta u - kf(u);\ r = 1,\ u = 1;\ r \to \infty,\ u \to 0. \tag{37}$$

To analyze problem (37) we use the method of model equations and similarity [6] (see also Sec. 2). The simplest one-dimensional analog of problem (37) is the model equation

$$u''_{xx} + \mathrm{Pe}\,u'_x - pu = kf(u);\ x = 0,\ u = 1;\ x \to \infty,\ u \to 0, \tag{38}$$

which has been obtained by approximating the coefficients of the original equation (37) by their values at infinity in the case of translational flow ($\mathbf{v} \to -\mathbf{e}_x$, where $\mathbf{e}_x$ is the unit vector along the x axis) with consequent replacement of the curvilinear surface of the sphere r = 1 by the tangent plane x = 1 at the inflow point and the replacement $x \to x - 1$.

To construct the unknown functional relation between local currents, we use an approximate method of integrating Eq. (38). For this we introduce the new variable $w = u'_x$ and we write Eq. (38) in the form $dw^2 + 2\mathrm{Pe}\,w du = 2[pu + kf(u)]du$. We further integrate it from zero to u with account of the fact that for $x \to \infty$ $w = u'_x \to 0$. Similarly to [6], the solution of the integral equation thus obtained is sought by an iteration method according to the equation

$$w_n = -\left\{-2\mathrm{Pe}\int_0^u w_{n-1}du + 2k\int_0^u f(u)\,du + pu^2\right\}^{1/2};\ n = 1,\ 2,\ \ldots, \tag{39}$$

where any function can be chosen following the initial profile $w_0 = w_0(u)$.

Restricting ourselves to a single iteration and putting in (39) x = 0, by account of the equalities u(0) = 1 and $\bar{j} = -w(1)$ we reach an expression for the shape of the local diffusion current $\bar{j}$. Putting further k = 0 and p = 0, we obtain the value of the local diffusion current $j_0 = j_0(\mathrm{Pe})$, corresponding to the stationary solution ($t \to \infty$) without exchange chemical reactions. Expressing the Peclet number in terms of j_0: $\mathrm{Pe} = \mathrm{Pe}(j_0)$, and substituting it into the equation for the shape of the local flow $\bar{j}$, we have

$$\bar{j} = \left(j_0^2 + 2k\int_0^1 f(c)\,dc + p\right)^{1/2} \quad \left(j_0^2 = -2\mathrm{Pe}\int_0^1 w_0(u)du\right). \tag{40}$$

According to the similarity principle [6], to obtain the Laplace transform of the mean Sherwood number in (40) one must replace j by Sh. Further carrying out the inverse Laplace–Carlson transform, we find the following expression for the mean Sherwood number:

$$\mathrm{Sh}=\frac{e^{-\xi t}}{\sqrt{\pi t}}+\sqrt{\xi}\,\mathrm{erf}\left(\sqrt{\xi t}\right),\ \xi=\mathrm{Sh}_0^2+2k\int_0^1 f(c)\,dc. \qquad (41)$$

Here Sh_0 is the mean Sherwood number corresponding to the solution of the stationary problem without volume chemical reactions k = 0.

Equation (41) guarantees a correct asymptotic result for small and large t values. The stationary analog of this equation $\mathrm{Sh}=\sqrt{\xi}$, corresponding to the limiting transition $t \to \infty$ in (41), was obtained in [6]. For k = 0 the approximate expression (41) determines the time dependence of the mean Sherwood number in the absence of chemical reactions. For translational Stokes flow of a spherical drop or a solid particle the parameter Sh_0 appearing in (41) is given by the equations $\mathrm{Sh}_0 = \mathrm{Sh}_\beta$ and $\mathrm{Sh}_0 = \mathrm{Sh}_\infty$, where Sh_β and Sh_∞ are given in (7).

NOTATION

a, radius of a spherical drop or a solid particle; C, flow concentration; C_s, concentration at the particle surface; C_∞, undisturbed concentration at infinity; c, dimensionless concentration; D, diffusion coefficient; j, local diffusion flow; k, dimensionless rate constant of volumetric chemical reactions; k_V, rate constant of volumetric chemical reactions; n, order of the reaction; Pe, Peclet number; p, complex parameter of the Laplace–Carlson transform; Q, similarity parameter;, r, θ, spherical coordinate system fixed at the drop; Sh = <j>, mean Sherwood number; t_*, time; U_∞, undisturbed velocity of incoming flow; α, shear coefficient; β, dynamic viscosity ratio of a drop to that of the surrounding liquid (the value β = ∞ corresponds to a solid particle); Γ = Γ(x), gamma function; ψ, stream function; and $u = p\int_0^\infty e^{-pt}c\,dt$.

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