
**CERTAIN PROBLEMS WITH THE APPLICATION OF STOCHASTIC
DIFFUSION PROCESSES FOR DESCRIPTION OF CHEMICAL
ENGINEERING PHENOMENA; DIFFUSION EQUATIONS
IN CURVILINEAR COORDINATES**

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Parabolic partial differential equations used in chemical engineering for the description of mass transport and heat transfer and analogous relationships derived in stochastic processes theory are given. A standard transformation procedure is applied, allowing these relations to be generally written in curvilinear coordinates and particular expressions for cylindrical and spherical coordinates to be derived. The relation between the probability density for the position of a discernible particle and the concentration of a set of such particles is discussed.

Previously¹ it was demonstrated that diffusion equations can be written in alternative ways following from the application of the stochastic approach. The differences between the ways of expression have been shown² to follow from the different definitions of the stochastic integral^{3,4}. It has also been suggested¹ that in these forms, unconventional in chemical engineering, the equations can be used to describe some processes where the "classical" diffusion equation fails.

In the present paper, the standard mathematical procedure^{5,6} enabling the relations discussed to be written in curvilinear coordinates will be used. For this, the equations given previously² will be first presented in a simplified form. (References to equations in refs^{1,2} will be denoted as (K . I), where K is the equation number in the corresponding paper and I is the reference number in the list of references appended to the present paper.)

The unifying expression for all the above-mentioned relations can be written in the form of a differential balance of a scalar f which is generally a function of the position vector \mathbf{x} and time t ,

$$\partial f(\mathbf{x}, t) / \partial t + \nabla \cdot \mathbf{q}(\mathbf{x}, t) = 0, \quad (1)$$

where vector \mathbf{q} is the flux intensity of quantity f . The equation does not involve the source term — this is a simplification adopted previously¹. From the chemical engineering point of view, f can be the volume concentration of a substance component,

enthalpy or temperature. From the “probabilistic” aspect, f is the probability density (conditional or unconditional) describing the position of a randomly moving particle in space and time. The definition of the last-mentioned quantity is given by Eq. (13.1); the relations between the other quantities are represented by Eqs (19.1), (20.1) and (24.1). All of them are linear transformations independent of the variables \mathbf{x} and t , so that Eq. (1) and relations that will be given for the general quantity f can readily be written for particular cases.

The relation for the flux intensity \mathbf{q} in principle depends on the way the stochastic integral is defined²; Ito’s definition leads to the form

$$\mathbf{q}(\mathbf{x}, t) = \mathbf{v}^I(\mathbf{x}, t)f(\mathbf{x}, t) - (1/2) \nabla \cdot [\mathbf{B}(\mathbf{x}, t)f(\mathbf{x}, t)], \quad (2)$$

where \mathbf{B} is a second-rank tensor (the diffusion tensor) and \mathbf{v}^I is the so-called drift velocity. The first right-hand term in this equation describes the motion of the scalar quantity with the “environment” by which it is entrained whereas the second term characterizes the relative motion of the quantity f with respect to this environment. We will assume that the \mathbf{B} tensor components do not explicitly depend on function f and that the tensor is symmetric.

The physical meaning of the terms in Eq. (2) as well as the justification of the simplifying assumptions have been discussed^{1,2}. Substitution of Eq. (2) in Eq. (1) leads to the Kolmogorov forward diffusion equation⁴ whose solution is the $f(\mathbf{x}, t)$ function (see Eqs (18.1) and (25.2)). In ref.¹, examples are given of application of this equation in the description of chemical engineering stirring processes^{7,8}.

The “classical” form of the diffusion equation differs in the position of the differential operator ∇ in the diffusion term,

$$\mathbf{q}(\mathbf{x}, t) = \mathbf{v}^T(\mathbf{x}, t)f(\mathbf{x}, t) - (1/2) \mathbf{B}(\mathbf{x}, t) \cdot [\nabla f(\mathbf{x}, t)]. \quad (3)$$

This approach is most widely used in chemical engineering (see, e.g., Eqs (4.1) and (36.2)). The equation emerging from the substitution of Eq. (3) in Eq. (1) is referred to as the transport equation.

(Note: as previously², the notation used is such that operator ∇ acts upon all coefficients standing to the right from it; parentheses indicate the sequence of operations; and the dot denotes the scalar (more precisely: internal) product of the objects between which it stands.)

In order to make it possible to write the relation for the flux intensity of a scalar quantity in Stratonovich’s form^{3,4,9}, we first introduce the tensor $\mathbf{G}(\mathbf{x}, t)$, which can be regarded as the “root” of the diffusion tensor, the two being interrelated by

$$\mathbf{G}(\mathbf{x}, t) \cdot \mathbf{G}^+(\mathbf{x}, t) = \mathbf{B}(\mathbf{x}, t). \quad (4)$$

Here \mathbf{G}^+ is the tensor transposed with respect to \mathbf{G} (see Eq. (26.2)). This tensor occurs in the "randomizing" term of the stochastic differential equations (6.2), (16.2) and (21.2) and can be referred to as the stochastic tensor. Applying the divergence operation to Eq. (4) and rearranging we obtain

$$\nabla \cdot \mathbf{B}(\mathbf{x}, t) = \mathbf{j}(\mathbf{x}, t) + \mathbf{k}(\mathbf{x}, t), \quad (5a)$$

where

$$\mathbf{j}(\mathbf{x}, t) = [\mathbf{G}^+(\mathbf{x}, t) \cdot \nabla] \cdot \mathbf{G}^+(\mathbf{x}, t) \quad (5b)$$

$$\mathbf{k}(\mathbf{x}, t) = \mathbf{G}(\mathbf{x}, t) \cdot [\nabla \cdot \mathbf{G}(\mathbf{x}, t)]. \quad (5c)$$

Vectors \mathbf{j} and \mathbf{k} are introduced for brevity of the expression. The former has been defined by Eq. (15.2) and called the semidiffusion flux.

The flux intensity of a scalar quantity in Stratonovich's form is then given by the expression

$$\mathbf{q}(\mathbf{x}, t) = \mathbf{v}^S(\mathbf{x}, t) f(\mathbf{x}, t) - (1/2) \mathbf{G}(\mathbf{x}, t) \cdot [\nabla \cdot \mathbf{G}(\mathbf{x}, t) f(\mathbf{x}, t)] \quad (6)$$

which, inserted in Eq. (1), gives the corresponding diffusion equation (see Eq. (29.2)).

The drift velocities in Eqs (2), (3) and (6) are interrelated² through

$$\mathbf{v}^T(\mathbf{x}, t) = \mathbf{v}^I(\mathbf{x}, t) - \mathbf{j}(\mathbf{x}, t) = \mathbf{v}^S(\mathbf{x}, t) - (1/2) \mathbf{j}(\mathbf{x}, t) \quad (7)$$

(see Eq. (22.2)). The second relation can be used to mutually uniquely transform the relations for the flux intensity in Ito's and Stratonovich's approaches, i.e., Eqs (2) and (6). Transformation between the transport equation (3) and the two other expressions is only possible if in addition, the condition

$$\mathbf{j}(\mathbf{x}, t) = \mathbf{k}(\mathbf{x}, t) \quad (8)$$

holds true. If this is not the case, the term $\nabla \cdot \{[\mathbf{j}(\mathbf{x}, t) - \mathbf{k}(\mathbf{x}, t)] f(\mathbf{x}, t)\}$, which does not appear in the "classical" diffusion equation, must be added to the right-hand side of Eq. (3). It can be demonstrated that from the mathematical point of view, all of the equations give then identical solutions (for identical initial and boundary conditions). The chemical engineer's problem is, which of the drift velocities in Eq. (7) to identify with the actual fluid velocity¹⁻³. The answer does not seem straightforward, and so it is convenient to have equations for all the alternatives available.

For the case of orthogonal Cartesian coordinates the relations have been presented in ref.² (Eqs (25a.2), (29a.2) and (31a.2)). With regard to the fact that many chemical engineering equipment components possess the cylindrical symmetry (or, less fre-

quently, spherical symmetry), the corresponding equations will be given in these coordinate systems as well. The transformation procedure suggested, however, enables the relations to be written in curvilinear coordinates of a general type.

THEORETICAL

Diffusion Equations in Curvilinear Coordinates

Mathematical apparatus requisite for the transformation of relations which involve tensors of different ranks (i.e., including scalars and vectors) is available^{5,6,10}. It allows equations to be written in any number of dimensions. Some notations will be first introduced. The Cartesian orthogonal coordinates of the position vector \mathbf{x} in the preceding equations will be denoted x_i ($i = 1, 2, \dots$), the general curvilinear coordinates will be denoted z^l . Basis vectors will be denoted \mathbf{e}_i in the case of Cartesian coordinates and \mathbf{g}_i or \mathbf{g}^i in the general case. Einstein's convention will be adopted, i.e. the summation sign with respect to a subscript or superscript occurring twice in the expression will be omitted. For instance, vector \mathbf{x} in Cartesian or curvilinear coordinates will be written as

$$\mathbf{x} = x_i \mathbf{e}_i = z^i \mathbf{g}_i = z_i \mathbf{g}^i$$

instead of

$$\mathbf{x} = \sum_i x_i \mathbf{e}_i = \sum_i z^i \mathbf{g}_i.$$

(The superscripts denote the so-called contravariant coordinates of the vector, subscripts denote covariant coordinates. In Cartesian coordinates they are identical and we do not distinguish between them.)

Furthermore, assume that transformation equations for expressing Cartesian orthogonal coordinates in curvilinear coordinate terms are given:

$$x_i = x_i(z^1, z^2, \dots) \quad (i = 1, 2, \dots). \quad (9)$$

In this transformation, the basis vectors are functions of the coordinates and thus, they change on differentiation with respect to the coordinates. It can be demonstrated that Eq. (1) for general curvilinear coordinates can be written as

$$(\partial f / \partial t) + (1/\sqrt{g}) [\partial(\sqrt{g}q^l) / \partial z^l] = 0 \quad (\mathbf{q} = g_i q^i), \quad (10)$$

where g is the metric tensor determinant; its root can be calculated directly as the absolute value of the Jacobian of transformation (9):

$$\sqrt{g} = |\det(\partial x_i / \partial z^j)|. \quad (11)$$

(The arguments of functions f and \mathbf{q} are omitted for brevity).

Before going on, it is appropriate to define the metric tensor components. Its covariant coordinates obey the relation

$$g_{ij} = \mathbf{g}_i \cdot \mathbf{g}_j = (\partial x_m / \partial z^i) (\partial x_m / \partial z^j)$$

so that, taking into account Eq. (11), we have

$$g = \det(g_{ij}) = [\det(\partial x_i / \partial z_j)]^2. \quad (12)$$

For so-called mixed coordinates the expressions are simple,

$$g_{\cdot j}^i = \mathbf{g}^i \cdot \mathbf{g}_j = \delta_j^i \quad (\delta_j^i = 1 \text{ for } i = j, \delta_j^i = 0 \text{ for } i \neq j).$$

The contravariant components of the metric tensor can be found by means of the relation

$$g^{ij} = \mathbf{g}^i \cdot \mathbf{g}^j = h_{ij} / g$$

where h_{ij} is the cofactor of element g_{ij} in the metric tensor determinant, i.e. the determinant formed from it by leaving out elements of the i -th row and the j -th column.

The changes in the basis vectors during their differentiation with respect to the curvilinear coordinates can be expressed by means of Christoffel's symbols, which can be calculated by using the formulas

$$\Gamma_{ij}^n = (g^{mk}/2) [(\partial g_{kj} / \partial z^i) + (\partial g_{ik} / \partial z^j) - (\partial g_{ij} / \partial z^k)];$$

these quantities obey the relations

$$\Gamma_{ij}^n = \Gamma_{ji}^n; \quad \Gamma_{ik}^i = (\partial \ln \sqrt{g} / \partial z^k). \quad (13)$$

Now, we are ready to write the flux intensity vector in all the variants. Before this, however, we rewrite Eq. (4) in the components:

$$\mathbf{B} = B_{\cdot k}^i \mathbf{g}_i \mathbf{g}^k = G^{ij} G_{jk}^+ \mathbf{g}_i \mathbf{g}^k = G^{ij} G_{kj} \mathbf{g}_i \mathbf{g}^k; \quad (14)$$

hence, it is convenient to regard the \mathbf{B} tensor components as mixed. It can be demonstrated that this relation also holds for coordinates $B_{k\cdot}^i$, i.e., that tensor \mathbf{B} is symmetric.

The flux intensity vector in Ito's form can be written as

$$\mathbf{q} = \left\{ v_k^1 f - \frac{1}{2} \left[\frac{1}{\sqrt{g}} \frac{\partial(\sqrt{g} B_{\cdot k}^i f)}{\partial z^i} - B_{\cdot j}^i \Gamma_{ki}^j f \right] \right\} \mathbf{g}^k = q_k \mathbf{g}^k \quad (15)$$

In the "transport" form, this same vector can be written in a considerably simpler manner:

$$\mathbf{q} = [v_k^T f - (1/2) B_{\cdot k}^i (\partial f / \partial z^i)] \mathbf{g}^k = q_k \mathbf{g}^k ; \quad (16)$$

this, however, is only valid if condition (8) is met. This condition can be presented in curvilinear coordinates if vectors \mathbf{j} and \mathbf{k} defined by Eqs (5) are expressed in these coordinates.

$$\mathbf{j} = j_k \mathbf{g}^k = G^{ij} [(\partial G_{kj} / \partial z^i) - G_{mj} \Gamma_{ki}^m - G_{km} \Gamma_{ji}^m] \mathbf{g}^k \quad (17a)$$

$$\mathbf{k} = k_k \mathbf{g}^k = G_{kj} [(\partial G^{ij} / \partial z^i) + G^{mj} \Gamma_{mi}^i + G^{im} \Gamma_{im}^j] \mathbf{g}^k \quad (17b)$$

and one is subtracted from the other; on rearrangement we obtain

$$(j - k)_k = (G^{ij})^2 [\partial(G_{kj} / G^{ij}) / \partial z^i] - 2G_{kj} G^{im} \Gamma_{im}^j - B_{\cdot m}^i \Gamma_{ki}^m - B_{\cdot k}^m \Gamma_{mi}^i = 0 \quad (k = 1, 2, \dots) \quad (18)$$

In this rearrangement, the first of Eqs (13) and Eq. (14) were taken into account.

In the Stratonovich form, \mathbf{G} tensor components must be employed:

$$\mathbf{q} = \left\{ v_k^S f - \frac{1}{2} G_{kj} \left[\frac{\partial(\sqrt{g} G^{ij} f)}{\sqrt{g} \partial z^i} + G^{im} \Gamma_{im}^j f \right] \right\} \mathbf{g}^k = q_k \mathbf{g}^k . \quad (19)$$

To make it possible to substitute from these relations in Eq. (10), the rule $q^l = g^{lk} q_k$ must be applied. So, for instance, the diffusion equation is finally obtained in the transport form

$$\frac{\partial f}{\partial t} + \frac{1}{\sqrt{g}} \frac{\partial}{\partial z^i} \left[\sqrt{g} g^{lk} \left(v_k^T f - \frac{1}{2} B_{\cdot k}^i \frac{\partial f}{\partial z^i} \right) \right] = 0 . \quad (20)$$

The two remaining relations can be written likewise.

One important fact must be drawn attention to. If the function $f(\mathbf{x}, t)$ has the meaning of volume concentration, enthalpy or temperature, it is an absolute scalar, which does not change during the transformation¹⁰. If $f(\mathbf{x}, t) = p(\mathbf{x}, t)$ is the probability density, then the transformation

$$p_z(z^1, z^2, \dots; t) = p(x_1, x_2, \dots; t) \sqrt{g} = f(z^1, z^2, \dots; t) \sqrt{g} \quad (21)$$

holds true¹¹; here \sqrt{g} is the Jacobian of the transformation (Eq. (11)) and p_z is the probability density in the curvilinear coordinates. For instance, substituting p_z/\sqrt{g} for function f in Eq. (15) and also inserting this term in Eq. (10) and rearranging, we obtain

$$\frac{\partial p_z}{\partial t} + \frac{\partial}{\partial z^i} \left\{ g^{ik} \left[2v_k^1 p_z + B_{,j}^i \Gamma_{ki}^j p_z - \frac{\partial(B_{,k}^i p_z)}{\partial z^i} \right] \right\} = 0. \quad (22)$$

The alternative equations can be rearranged likewise.

The Use of Orthogonal Coordinates

Orthogonal coordinates of a metric tensor are defined by the relations⁵

$$g_{ij} = \mathbf{g}_i \cdot \mathbf{g}_j = 0 \quad (i \neq j)$$

stating that elements of the metric tensor matrix save the diagonal ones are zeroes. The use of orthogonal coordinates simplifies the above relations considerably while it does not detract seriously from their practical value. All coordinate systems employed in chemical engineering are orthogonal.

In place of the metric tensor coordinates and determinant it is convenient to introduce the quantities

$$e_i = \sqrt{g_{ii}} = 1/e^i \quad (i = 1, 2, \dots), \quad e = \sqrt{g} = \prod_i e_i \quad (23)$$

where \prod_i is the multiplication symbol. In these and the following relations, the summation convention will no more be adhered to and all summations will be fully indicated.

Furthermore, instead of the covariant and contravariant coordinates of vectors and tensors, so-called physical coordinates can be introduced by the relations

$$\hat{a} = a_i/e_i = a^i e_i \quad (i = 1, 2, \dots)$$

$$\hat{A}_{ij} = A_{ij}/(e_i e_j) = A^{ij} e_i e_j = A_{,j}^i e_i/e_j \quad (i, j = 1, 2, \dots).$$

Christoffel's symbols are also simplified considerably:

$$\Gamma_{jk}^i = 0 \quad (i \neq j \neq k \neq i); \quad \Gamma_{ii}^j = -(e_i/e_j^2)(\partial e_i/\partial z^j) \quad (j \neq i)$$

$$\Gamma_{ki}^i = \Gamma_{ik}^i = \partial \ln e_i/\partial z^k \quad (i \neq k); \quad \Gamma_{ii}^i = \partial \ln e_i/\partial z^i.$$

For a simplification of the notation, we introduce the symbol

$$\partial s^i \equiv e_i \partial z^i \quad (i = 1, 2, \dots).$$

Using these simplifications, Eq. (1) takes the form

$$\partial f / \partial t + \sum_k (e_k / e) \partial [\hat{q}_k(e/e_k)] / \partial s^k = 0 \quad (24)$$

The corresponding flux intensity vector components in Ito's, transport, and Stratonovich's approaches are

$$\hat{q}_k = \hat{v}_k^I f - \frac{1}{2} \sum_i \left[\frac{e_i}{e e_k} \frac{\partial}{\partial s^i} \left(\hat{B}_{ik} \frac{e e_k}{e_i} f \right) - \hat{B}_{iif} \frac{\partial \ln e_i}{\partial s^k} \right] \quad (25)$$

$$\hat{q}_k = \hat{v}_k^T f - \frac{1}{2} \sum_i \hat{B}_{ik} \frac{\partial f}{\partial s^i} \quad (26)$$

$$\begin{aligned} \hat{q}_k = \hat{v}_k^S - \frac{1}{2} \sum_j \hat{G}_{kj} \left\{ \sum_i \left[\frac{e_i e_j}{e} \frac{\partial}{\partial s^i} \left(\hat{G}_{ij} \frac{e f}{e_i e_j} \right) + \right. \right. \\ \left. \left. + (\hat{G}_{ij} + \hat{G}_{ji}) f \frac{\partial \ln e_j}{\partial s^i} - \hat{G}_{iif} \frac{\partial \ln e_i}{\partial s^j} \right] \right\}, \quad (27) \end{aligned}$$

respectively.

For Eq. (26) to be valid, condition (8) must be met; this condition will be written in the form

$$\begin{aligned} \hat{j}_k - \hat{k}_k = d_k - 2 \sum_j \sum_{i \neq j} \hat{G}_{kj} \left(\hat{G}_{ji} \frac{\partial \ln e_j}{\partial s^i} - \hat{G}_{ii} \frac{\partial \ln e_i}{\partial s^j} \right) - \\ - \sum_i \left[\hat{B}_{ii} \frac{\partial \ln e_i}{\partial s^k} + \hat{B}_{ik} \frac{\partial}{\partial s^i} \ln (e/e_i e_k) \right] = 0. \quad (28) \end{aligned}$$

The term d_k involves derivatives of the \mathbf{G} tensor coordinates; apparently, it can be expressed in various ways:

$$d_k = \sum_{i \neq k} \sum_j (\hat{G}_{ij} \partial \hat{G}_{kj} / \partial s^i - \hat{G}_{kj} \partial \hat{G}_{ij} / \partial s^i) \quad (29a)$$

$$d_k = \sum_{i \neq k} \sum_j \hat{G}_{kj} \hat{G}_{ij} \partial \ln (\hat{G}_{kj} / \hat{G}_{ij}) / \partial s^i \quad (29b)$$

$$d_k = \sum_{i \neq k} \sum_j \hat{G}_{ij}^2 \partial (\hat{G}_{kj} / \hat{G}_{ij}) / \partial s^i \quad (29c)$$

Now we shall show some examples of substitution of the flux intensity vector in Eq. (24). For the "transport" equation we obtain

$$\frac{\partial f}{\partial t} + \sum_k \frac{e_k}{e} \frac{\partial}{\partial s^k} \left(\hat{v}_k^T \frac{ef}{e_k} - \frac{e}{2e_k} \sum_i \hat{B}_{ik} \frac{\partial f}{\partial s^i} \right) = 0. \quad (30)$$

The corresponding relation for the probability density p_z in Ito's approach, taking into account Eqs (21) and (23), is

$$\begin{aligned} \frac{\partial p_z}{\partial t} + \sum_k \frac{\partial}{\partial z^k} \left\{ v_k^I \frac{p_z}{e_k} + \frac{1}{2} \sum_i \left[\hat{B}_{ii} \frac{p_z}{e_k^2} \frac{\partial \ln e_i}{\partial z^k} - \right. \right. \\ \left. \left. - \hat{B}_{ik} \frac{p_z}{e_i e_k} \left(\frac{\partial \ln e_k}{\partial z^i} + \frac{\partial \ln e_i}{\partial z^k} \right) - \frac{\partial}{\partial z^i} \left(\hat{B}_{ik} \frac{p_z}{e_i e_k} \right) \right] \right\} = 0. \quad (31) \end{aligned}$$

Now, the relations derived will be employed for setting up equations in the concrete coordinates.

a) *Cartesian coordinates.* In this simplest type of coordinates, the transformation relations $z^i = x_i$ ($i = 1, 2, 3$) are formally valid; from these we have $e_i = e = 1$, $\partial s^i = \partial x_i$, $\Gamma_{jk}^i = 0$ for all i, j, k . The diffusion equations for coordinates of this type have been presented previously² (Eqs (25a.2), (29a.2), (31a.2)). Condition (28) takes on the form

$$\hat{j}_k - \hat{k}_k = d_k = \sum_{i,j=1}^3 \left(\hat{G}_{ij} \frac{\partial \hat{G}_{kj}}{\partial x_i} - \hat{G}_{kj} \frac{\partial \hat{G}_{ij}}{\partial x_i} \right) = 0 \quad (i \neq k; k = 1, 2, 3) \quad (32)$$

This condition can be, naturally, expressed in any form following from Eq. (29).

b) *Cylindrical coordinates.* Cylindrical coordinates are given by the transformation equations

$$x_1 = z^1 \cos z^2; \quad x_2 = z^1 \sin z^2; \quad x_3 = z^3$$

and we have

$$\begin{aligned} e_1 = e_3 = 1; \quad e_2 = e = z^1; \\ \partial s^1 = \partial z^1; \quad \partial s^2 = z^1 \partial z^2; \quad \partial s^3 = \partial z^3. \end{aligned}$$

Here, polar coordinates are labelled by using superscripts, which contributes to brevity; the conventional symbols are r ($= z^1$), ϑ ($= z^2$) and z ($= z^3$). Similarly, the physical vector or tensor coordinates will be written as \hat{v}_1 ($= v_r$), \hat{v}_3 ($= v_z$), \hat{G}_{12} ($= G_{r\vartheta}$) etc.

In these coordinates, Eq. (1) is

$$\partial f / \partial t + \hat{q}_1 / z^1 + \sum_{i=1}^3 \partial \hat{q}_i / \partial s^i = 0. \quad (33)$$

In this equation, expressions for the flux intensity vector coordinates can be inserted; these are given by the system of equations for all the approaches considered,

$$\begin{aligned} \hat{q}_1 &= \hat{v}_1^1 f - \frac{1}{2} [m_1^1 + (\hat{B}_{11} - \hat{B}_{22}) f / z^1] = \hat{v}_1^T f - \frac{1}{2} m_1^T = \\ &= \hat{v}_1^S f - \frac{1}{2} \{ m_1^S + [\hat{B}_{11} - (\hat{G}_{11} \hat{G}_{22} - \hat{G}_{12} \hat{G}_{21})] f / z^1 \} \end{aligned} \quad (34a)$$

$$\begin{aligned} \hat{q}_2 &= \hat{v}_2^1 f - (1/2) (m_2^1 + 2\hat{B}_{12} f / z^1) = \hat{v}_2^T f - (1/2) m_2^T = \\ &= \hat{v}_2^S f - (1/2) (m_2^S + \hat{B}_{12} f / z^1) \end{aligned} \quad (34b)$$

$$\begin{aligned} \hat{q}_3 &= \hat{v}_3^1 f - (1/2) (m_3^1 + \hat{B}_{13} f / z^1) = \hat{v}_3^T f - (1/2) m_3^T = \\ &= \hat{v}_3^S f - (1/2) \{ m_3^S + [\hat{B}_{13} - (\hat{G}_{22} \hat{G}_{31} - \hat{G}_{32} \hat{G}_{21})] f / z^1 \}. \end{aligned} \quad (34c)$$

The following symbols were used in these equations:

$$\begin{aligned} m_k^1 &= \sum_{i=1}^3 \frac{\partial}{\partial s^i} (\hat{B}_{ik} f); \quad m_k^T = \sum_{i=1}^3 \hat{B}_{ik} \frac{\partial f}{\partial s^i}; \\ m_k^S &= \sum_{i,j=1}^3 \hat{G}_{kj} \frac{\partial}{\partial s^i} (\hat{G}_{ij} f). \end{aligned} \quad (35)$$

As an example, the transport equation in the conventional notation is

$$\begin{aligned} \frac{\partial f}{\partial t} + v_r^T \frac{f}{r} + \frac{\partial}{\partial r} (v_r^T f) + \frac{1}{r} \frac{\partial}{\partial \vartheta} (v_\vartheta^T f) + \frac{\partial}{\partial z} (v_z^T f) - \frac{1}{2} \left[\frac{B_{rr}}{r} \frac{\partial f}{\partial r} + \frac{B_{r\vartheta}}{r^2} \frac{\partial f}{\partial \vartheta} + \frac{B_{rz}}{r} \frac{\partial f}{\partial z} + \right. \\ \left. + \frac{\partial}{\partial r} \left(B_{rr} \frac{\partial f}{\partial r} + \frac{B_{r\vartheta}}{r} \frac{\partial f}{\partial \vartheta} + B_{rz} \frac{\partial f}{\partial z} \right) + \frac{\partial}{\partial \vartheta} \left(B_{r\vartheta} \frac{\partial f}{\partial r} + \frac{B_{\vartheta\vartheta}}{r} \frac{\partial f}{\partial \vartheta} + B_{\vartheta z} \frac{\partial f}{\partial z} \right) + \right. \\ \left. + \frac{\partial}{\partial z} \left(B_{rz} \frac{\partial f}{\partial r} + \frac{B_{\vartheta z}}{r} \frac{\partial f}{\partial \vartheta} + B_{zz} \frac{\partial f}{\partial z} \right) \right] = 0. \end{aligned} \quad (36)$$

The equation for the probability density p_c in cylindrical coordinates is obtained by substituting for function f from the relation $p_c = fr$.

c) *Spherical coordinates*. In these coordinates, the following transformations hold true:

$$x_1 = z^1 \sin z^2 \cos z^3; \quad x_2 = z^1 \sin z^2 \sin z^3; \quad x_3 = z^1 \cos z^2,$$

wherefrom the relations

$$e_1 = 1, e_2 = z^1, e_3 = z^1 \sin z^2, e = (z^1)^2 \sin z^2 ;$$

$$\partial s^1 = \partial z^1, \partial s^2 = z^1 \partial z^2, \partial s^3 = z^1 \sin z^2 \partial z^3$$

follow. The conventional symbols for spherical coordinates are $r (= z^1)$, $\vartheta (= z^2)$ and $\varphi (= z^3)$.

Eq. (1) in spherical coordinates is

$$\partial f / \partial t + (1/z^1)(2\hat{q}_1 + \cotg z^2 \hat{q}_2) + \sum_{i=1}^3 \partial \hat{q}_i / \partial s^i = 0. \quad (37)$$

and the \mathbf{q} vector coordinates are

$$\hat{q}_1 = \hat{v}_1^1 f - (1/2) [m_1^1 + (2\hat{B}_{11} - \hat{B}_{22} - \hat{B}_{33} + \hat{B}_{12} \cotg z^2) f / z^1] =$$

$$= \hat{v}_1^T f - (1/2) m_1^T \quad (38a)$$

$$\hat{q}_2 = \hat{v}_2^1 f - (1/2) \{m_2^1 + [3\hat{B}_{12} + \cotg z^2 (\hat{B}_{22} - \hat{B}_{33})] f / z^1\} =$$

$$= \hat{v}_2^T f - (1/2) m_2^T \quad (38b)$$

$$\hat{q}_3 = \hat{v}_3^1 f - (1/2) [m_3^1 + (3\hat{B}_{13} + 2\hat{B}_{23} \cotg z^2) f / z^1] =$$

$$= \hat{v}_3^T f - (1/2) m_3^T \quad (38c)$$

(expressions for m^1 and m^T are given by Eqs (35)). Explicit relations in Stratonovich's approach are very complex in this case.

Finally, the transport equation in spherical coordinates is

$$\frac{\partial f}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r^T f) + \frac{1}{r \sin \vartheta} \left[\frac{\partial}{\partial \vartheta} (\sin \vartheta v_\vartheta^T f) + \frac{\partial}{\partial \varphi} (v_\varphi^T f) \right] -$$

$$- \frac{1}{2} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \left(B_{rr} \frac{\partial f}{\partial r} + \frac{B_{r\vartheta}}{r} \frac{\partial f}{\partial \vartheta} + \frac{B_{r\varphi}}{r \sin \vartheta} \frac{\partial f}{\partial \varphi} \right) \right] + \right.$$

$$+ \frac{1}{r \sin \vartheta} \frac{\partial}{\partial \vartheta} \left[\sin \vartheta \left(B_{r\vartheta} \frac{\partial f}{\partial r} + \frac{B_{\vartheta\vartheta}}{r} \frac{\partial f}{\partial \vartheta} + \frac{B_{\vartheta\varphi}}{r \sin \vartheta} \frac{\partial f}{\partial \varphi} \right) \right] +$$

$$\left. + \frac{1}{r \sin \vartheta} \left[\frac{\partial}{\partial \varphi} \left(B_{r\varphi} \frac{\partial f}{\partial r} + \frac{B_{\vartheta\varphi}}{r} \frac{\partial f}{\partial \vartheta} + \frac{B_{\varphi\varphi}}{r \sin \vartheta} \frac{\partial f}{\partial \varphi} \right) \right] \right\} = 0. \quad (39)$$

The probability density in spherical coordinates is given by the equation $p_s = f r^2 \cdot \sin \vartheta$.

DISCUSSION

Expressing diffusion equations in curvilinear coordinates requires some conclusions made in the previous papers to be refined or generalized. This concerns particularly the validity of condition (32.2),

$$G_{ij}(\partial G_{kj}/\partial x_i) = G_{kj}(\partial G_{ij}/\partial x_i)$$

(no summation!), which is a prerequisite for the conventional transport diffusion equation form. This condition was used in an attempt at finding the analytical solution for the \mathbf{G} tensor coordinates. This condition is correct in Cartesian coordinates but it is not general even in this case. General relations are given in the present paper. The vector form of the condition enabling the classical diffusion equation (3) to be written is given by relation (8). Furthermore, this condition is expressed by Eq. (18) for curvilinear coordinates, Eq. (28) for orthogonal curvilinear coordinates, and Eq. (32) for Cartesian coordinates. Attempts at finding the general analytical solution of these relations, however, failed.

Additional refinement concerns the relation between the substance component concentration and the probability density for the position of a particle of this component, or the temperature and the probability density (see Eqs (20.1) and (24.1)). The two relations can be formally described by the equation $f(\mathbf{x}, t) = kp(\mathbf{x}, t)$, where f is the concentration or temperature and k is a proportionality constant. These equations are only valid in Cartesian coordinates.

The probability density p_z in curvilinear coordinates is generally defined by the relation

$$p_z(z^1, z^2, z^3; t) = \partial^3 F(z^1, z^2, z^3; t) / \partial z^1 \partial z^2 \partial z^3$$

where $F \equiv P\{Z^1(t) \leq z^1; Z^2(t) \leq z^2; Z^3(t) \leq z^3\}$ is the corresponding distribution function and $Z^i(t)$ is the coordinate of the random motion of the particle at time t (compare Eq. (13.1)). On the other hand, for instance, the substance component concentration in a small volume ΔV can be regarded as a quantity proportional to the probability that at time t the particle will occur in this volume, i.e.

$$\varrho_A(\Delta V, t) = M_A \int_{\Delta V} p_{\mathbf{z}}(z^1, z^2, z^3; t) \prod dz^i / \Delta V$$

where M_A is the total mass of the substance component; the volume in curvilinear coordinates is⁵

$$\Delta V = \int_{\Delta V} \sqrt{g} \prod dz^i.$$

We assume that the centre of gravity of the volume considered is a point whose

coordinates are $\{z^1, z^2, z^3\}$, and in the limit we obtain

$$\lim_{\Delta V \rightarrow 0} \varrho_A(\Delta V, t) = M_A p_z(z^1, z^2, z^3; t) \prod dz^i / (\sqrt{g} \prod dz^i) = M_A p_z / \sqrt{g}$$

which — except for the multiplicative constant — is identical with Eq. (21). According to Eq. (11), \sqrt{g} is the Jacobian of the transformation; only in the case of orthogonal Cartesian coordinates it equals unity. The constant M_A vanishes from the diffusion equations by reduction.

The diffusion equations for intensive quantities, used in chemical engineering, thus in curvilinear coordinates have a form different from that of the “probabilistic” diffusion equations also for this reason.

In conclusion let us make some remarks on the backward Kolmogorov equations. These relations describe the development of the stochastic process in “the past”, i.e. at time preceding the given time moment, in contrast to the forward equations describing the process development in the “future”, i.e. starting from the given time moment (see, e.g., refs^{3,4}). Backward equations are not very frequent in chemical engineering. Problems associated with the fluid residence time distribution may be an exception. The Kolmogorov equations are usually written for transitive probability densities

$$f_i(\mathbf{z}; t | \mathbf{y}; \tau) = \frac{\partial^3}{\partial z^1 \partial z^2 \partial z^3} P\{Z^1(t) \leq z^1; Z^2(t) \leq z^2; Z^3(t) \leq z^3 | Z^1(\tau) = y^1; Z^2(\tau) = y^2; Z^3(\tau) = y^3\}, \quad (40)$$

where P is the probability related with the position of the randomly moving particle at time t if at some preceding time τ this particle occurred in a point whose coordinates are (y^1, y^2, y^3) (see Eq. (13.1)).

The backward Kolmogorov equation can be written as^{3,4}

$$\partial f_i / \partial t + \mathbf{v}^1(\mathbf{y}, \tau) \cdot \nabla_y f_i + (1/2) \mathbf{B}(\mathbf{y}, \tau) : \nabla_y^2 f_i = 0 \quad (41)$$

where the operator $\nabla^2 = \nabla \nabla$ is the dyadic product of two differential operators and the column denotes double scalar product. The operator subscript y indicates that function f_i is differentiated with respect to coordinates y . The forward Kolmogorov equation is adjoined to Eq. (41); it is obtained by substituting in Eq. (1) from Eq. (3) taking into account Eq. (21):

$$\partial f_i / \partial t + \nabla_z \cdot [\mathbf{v}^1(\mathbf{z}, t) f_i / \sqrt{g}] - (1/2) \nabla_z \cdot [\nabla_z \cdot \mathbf{B}(\mathbf{z}, t) f_i / \sqrt{g}] = 0. \quad (42)$$

In this case, the coefficients of the equations are functions of the variables z^i , and

the differentiation is with respect to these variables. The fundamental solutions of the two relations are identical¹².

Equation (41) is in Ito's form. Taking into account Eqs (7) and (5) and rearranging, the backward equation can be obtained in Stratonovich's form as³

$$\partial f_t / \partial \tau + \mathbf{v}^S(\mathbf{y}, \tau) \cdot \nabla_{\mathbf{y}} f_t + (1/2) [(\mathbf{G}^+(\mathbf{y}, \tau) \cdot \nabla_{\mathbf{y}}) \cdot \mathbf{G}^+(\mathbf{y}, \tau)] \cdot (\nabla_{\mathbf{y}} f_t) = 0. \quad (43)$$

The transport equation can be analogously written as

$$\partial f_t / \partial \tau + \mathbf{v}^T(\mathbf{y}, \tau) \cdot \nabla_{\mathbf{y}} f_t + (1/2) (\mathbf{j} - \mathbf{k}) \cdot \nabla_{\mathbf{y}} f_t + (1/2) \nabla_{\mathbf{y}} \cdot [\mathbf{B}(\mathbf{y}, \tau) \cdot \nabla_{\mathbf{y}} f_t] = 0. \quad (44)$$

This equation also simplifies if condition (8) is valid. Equations (41), (43) and (44) hold for a general scalar function $f(\mathbf{y}, \tau)$ as discussed at the beginning of the present treatment, because – as follows from Eq. (40) – function f_t does not change on transformation of vector \mathbf{y} .

Equation (41) written in curvilinear coordinates (adhering again to the Einstein convention concerning the omitting of the summation signs) is

$$\frac{\partial f_t}{\partial \tau} + g^{lk} \left[v_k^l \frac{\partial f_t}{\partial y^l} + \frac{1}{2} B_{*k}^{i*} \left(\frac{\partial^2 f_t}{\partial y^l \partial y^i} - \Gamma_{il}^m \frac{\partial f_t}{\partial y^m} \right) \right] = 0. \quad (45)$$

All coefficients in this equation, i.e. g^{lk} , v_k^l , B_k^i and Γ_{il}^m are generally functions of coordinates y^i and time τ . The adjointed forward equation is simply obtained by writing f_t instead of p_z in Eq. (22). Furthermore, using the product differentiation rule we express the last term of that equation as

$$\frac{\partial}{\partial z^l} \left[g^{lk} \frac{\partial}{\partial z^i} (B_{*k}^{i*} f_t) \right] = \frac{\partial^2}{\partial z^l \partial z^i} (g^{lk} B_{*k}^{i*} f_t) - \frac{\partial}{\partial z^l} \left[(B_{*k}^{i*} f_t) \frac{\partial}{\partial z^i} g^{lk} \right]$$

and make use of the Ricci proposition concerning the differentiation of metric tensor coordinates¹⁰,

$$\partial g^{lk} / \partial z^i + g^{mk} \Gamma_{mi}^l + g^{lm} \Gamma_{mi}^k = 0.$$

In this manner we arrive at the final relation

$$\frac{\partial f_t}{\partial t} + \frac{\partial}{\partial z^l} (g^{lk} v_k^l f_t) - \frac{1}{2} \frac{\partial}{\partial z^m} (g^{lk} B_{*k}^{i*} \Gamma_{il}^m f_t) - \frac{1}{2} \frac{\partial^2}{\partial z^l \partial z^i} (g^{lk} B_{*k}^{i*} f_t) = 0. \quad (46)$$

All coefficients in this equation are identical with those in Eq. (45) but they are functions of coordinates z^i and time t . It is clear that the equations are adjointed¹². This

will not be true if the solution of the equations is concentration, or temperature, hence, an absolute scalar.

Relations for the probability density have been obtained⁹; general expressions for the transport equation, however, are not commonly given in chemical engineering monographs^{6,13}. They generally enable the propagation of a substance component in nonhomogeneous anisotropic media to be described. They can also be used to obtain simpler relations in a straightforward manner. For instance, for unmoving medium with a constant scalar diffusion coefficient D ($\mathbf{v}^T = \mathbf{0}$, $\mathbf{B} = 2D\mathbf{I}$ where \mathbf{I} is the identity tensor) the well-known "transport" equation in polar coordinates holds true (the axial coordinate is not considered):

$$\frac{\partial f}{\partial t} - D \left(\frac{\partial^2 f}{\partial r^2} + \frac{1}{r} \frac{\partial f}{\partial r} + \frac{1}{r^2} \frac{\partial^2 f}{\partial \vartheta^2} \right) = 0. \quad (47)$$

The analogous forward equation in Ito's form for the transitive probability density is

$$\frac{\partial f_t}{\partial t} - D \left[\frac{\partial^2 f_t}{\partial r^2} + \frac{\partial}{\partial r} (f_t/r) + \frac{1}{r^2} \frac{\partial^2 f_t}{\partial \vartheta^2} \right] = 0 \quad (48)$$

and the adjoined backward equation is

$$\frac{\partial f_t}{\partial \tau} + D \left(\frac{\partial^2 f_t}{\partial \varrho^2} + \frac{1}{\varrho} \frac{\partial f_t}{\partial \varrho} + \frac{1}{\varrho^2} \frac{\partial^2 f_t}{\partial \alpha^2} \right) = 0 \quad (49)$$

where $f_t = f_t(r, \vartheta; t \mid \varrho, \alpha; \tau) = fr$.

Thus the "transport" equation (47) is not identical with the backward diffusion equation (49) — in this respect Feller in his monograph¹⁴ is wrong.

CONCLUSIONS

From the considerations, assumptions and relationships, written in this paper one can draw the following conclusions:

1. Diffusion equations in Ito, Stratonovich and transport form previously² written are expressed in curvilinear coordinates. General expressions for transport equation in cylindrical and spherical coordinates are presented.
2. The formulation of general conditions (8) enabled us to write the transport equation in a form common in chemical engineering literature.
3. We succeeded to point out that a difference exists between coordinate transformation of component concentration or temperature and coordinate transformation of probability density.

SYMBOLS

B	diffusion tensor
<i>D</i>	diffusivity
e	basis vector in Cartesian coordinates
e_i	transformation coefficient ($e_i = \sqrt{g_{ii}}$)
<i>f</i>	scalar quantity (function)
f_t	transitive probability density
G	stochastic tensor
<i>g</i>	metric tensor determinant
g	basis vector in curvilinear coordinates
g_{ij}	metric tensor coordinate
<i>j</i>	vector defined by Eq. (5) ("semidiffusion" flux)
k	vector defined by Eq. (5)
M_A	mass of component A
p_z	probability density
q	flux intensity of scalar quantity <i>f</i>
<i>r</i>	radial coordinate
<i>t</i>	time
<i>V</i>	volume
v	medium velocity
x	position vector
x_i	Cartesian coordinate of vector x
y	position vector (with respect to moment τ)
y^i	curvilinear coordinate of vector y
Z^i	curvilinear position coordinate (random function of time)
<i>z</i>	axial coordinate
z	position vector (with respect to time <i>t</i>)
z^i	curvilinear coordinate of vector z (or x)
α	angular coordinate (with respect to time τ)
Γ	Christoffel's symbol
ϑ	angular coordinate (with respect to time <i>t</i>)
ϱ	radial coordinate (with respect to time τ)
ϱ_A	density of component A
τ	time moment preceding time <i>t</i>
φ	spherical coordinate

Subscripts and superscripts

\mathbf{v}^I	related to Ito's approach
\mathbf{v}^S	related to Stratonovich's approach
\mathbf{v}^T	related to the "transport" approach
v^i	contravariant coordinate of vector v
v_i	covariant coordinate of vector v
\hat{v}_i	physical coordinate of vector v
A^{ij}	contravariant coordinate of tensor A
A_{ij}	covariant coordinate of tensor A
A^i_j	mixed coordinate of tensor A
\hat{A}_{ij}	physical coordinate of tensor A
\mathbf{A}^+	tensor transposed to tensor A

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