

UNSTEADY DIFFUSION IN IRREGULAR BODIES

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Received January 10th, 1978

Asymptotic functional models have been formulated and numerically tested of an unsteady diffusion in particles of an arbitrary shape and under arbitrary course of the surface concentration.

Models of transport phenomena in heterogeneous two-phase systems usually cannot work with exact geometry of individual particles of the dispersed phase. It is therefore useful to search for such descriptions of the transport properties of heterogeneous systems in which the geometrical structure is characterized by a limited number of parameters, most conveniently by the (single) equivalent diameter of particles of the dispersed phase. Typical example of this approach is Aris¹ formulation of the generalized description of the effectiveness of catalytic pellets of irregular shape. In other situations the diversity of studied phenomena cannot be adequately expressed by a single geometrical parameter and one has to distinguish between dynamic transport properties of individual particles in dependence on their shape².

In the presented paper, taking a relatively simple problem of an unsteady diffusion without chemical reaction in particles of constant shape, for constant diffusivity and an arbitrary course of the surface concentration, we have studied general dynamic conditions permitting formulation of a generalized description of concentration changes in a particle of an arbitrary shape. It turns out that for an arbitrary course of the surface concentration it suffices to distinguish between individual kinetic regimes by a single dynamic criterion, the diffusional Deborah number, De .

FORMULATION

Consider the case of an unsteady diffusion of an active component (AC) with a concentration field $c(t, \mathbf{r})$ in a permeable particle of volume V and surface area A . Let us confine ourselves to the cases when the original state of the particle at a time $t = 0$ is one of concentration equilibrium

$$c = c_e, \quad (\mathbf{r} \in A, t \leq 0). \quad (1)$$

This state is being disturbed in the ensuing process by concentration changes of AC at particle's surface

$$c = c_A(t) = c_e + f(t), \quad (r \in A, t > 0). \quad (2)$$

The diffusion of AC in the material of the particle is assumed to be governed by the Fickian relations with constant diffusivity, D_s

$$\partial_t c = D_s \nabla^2 c, \quad (r \in V, t \geq 0). \quad (3)$$

For a solution of the problem we shall take transient development of the mean concentration of AC in the particle

$$c_M(t) = V_s^{-1} \int_V c(t, r) dV \quad (4)$$

or the total amount of AC exchanged between the particle and the surroundings

$$q_M(t) = A^{-1} D_s \int_0^t \int_A \mathbf{n} \cdot \nabla c dA dt. \quad (5)$$

The constraint between the parameters c_M , q_M , the former of which is averaged over particle's volume, the latter over its surface, expresses the integral balance of AC

$$c_M(t) - c_e = R_s^{-1} q_M(t), \quad (6)$$

where

$$R_s = V/A \quad (7)$$

is Aris's equivalent particle diameter.

For a given transient development of the surface concentration of AC the set (1)–(3) poses a boundary value problem already studied for a number of particle shapes^{3,4}. In view of the linearity of the problem its general solution for an arbitrary time course of the surface concentration may be expressed explicitly by means of the convolution integral³⁻⁵. These generally known results shall be used to describe the dynamic properties of individual particles in terms of a response (as a time course of the mean concentration of AC) to external disturbances represented by the transient development of the surface concentration of AC.

From a mathematical point of view we shall be interested in what response function $c_M(t)$, $t \geq 0$, is assigned to an influence function $c_A(s)$, $0 \leq s \leq t$, for a par-



particle of an arbitrary shape. This assignment for a particle of given shape may be formally expressed by

$$c_M(t) = \mathfrak{F}[c_A(s)]_0^t \quad (8)$$

The symbol \mathfrak{F} here represents a mathematical object called the response functional⁶.

To the mathematical model (1)–(3) and hence also to the response functional implicitly defined by the model we may apply current methods of the theory of similarity. The similarity analysis indicates that for all geometrically similar particles of various sizes or various diffusivities the response functional may be expressed in a common normalized form containing as a single dimensional constant – the characteristic time. Its explicit definition depends on the choice of the characteristic dimension of the particle. Considering the form of the normalized integral balance (6) we shall select for the characteristic length the parameter R_S from Eq. (7) and define the relaxation time as

$$\lambda_S = R_S^2/D_S \quad (9)$$

On normalizing both time variables t and s in the definition of the response functional (8) by the parameter λ_S as $x = s/\lambda_S$, $\Theta = t/\lambda_S$ we arrive at the formulation of the response functional

$$c_M(t) = \mathfrak{F}^*[c_A(\lambda_S x)]_0^\Theta \quad (10)$$

having identical structure for all geometrically similar particles.

In the description of the transient course of the surface concentration one can always introduce a characteristic time interval t_0 possessing *e.g.* the meaning of the overall duration time of the process, period of the process, *etc.* On expressing the course of the function $c_A(t)$ in the normalized form with two adjustable dimensional parameters, c_0 , t_0

$$c_A(t) = c_e + c_0 F(t/t_0), \quad (11)$$

we arrive at the dimensionless form of the response functional

$$(c_M(t) - c_e)/c_0 \equiv C_M = \mathfrak{F}^*[F(De x)]_0^\Theta \quad (12)$$

with a dimensionless dynamic criterion, the diffusional Deborah number

$$De = \lambda_S/t_0 \quad (13)$$

For a given type of time variations of the surface concentration of AC, represented by the function $F(T) = \text{idem}$, and for given particle geometry, represented by the

normalized response functional \mathfrak{F}^* , De becomes a quantitative measure of the rate of concentration changes taking place within the particle. For $De \rightarrow 0$ changes are very slow; for $De \rightarrow \infty$, on the contrary, they are very fast.

We shall show now that for $De \rightarrow 0$ and for $De \rightarrow \infty$ the response functionals \mathfrak{F}^* taken on an identical asymptotic structure for particles of an arbitrary shape. This offers the advantage of an *a priori* choice of the normalizing parameter λ_s in the form (9). Further we shall show that, spare for the region of medium rate concentration changes (usually for $0.1 < De < 10$), the course of the mean concentration may be approximated by means of simple functional models of integro-differential type⁷. These contain a single shape factor each: β_0 (for $De \ll 1$) and β_∞ (for $De \gg 1$).

Note: From the general theory of unsteady diffusion³⁻⁵ it follows that the response functional \mathfrak{F} for a given particle shape may be characterized by a real function $H(\Theta)$ appearing in the convolution representation of the response functional*)

$$\mathfrak{F}^*[F(De x)]_0^\Theta = \int_0^\Theta \frac{dH(\Theta - x)}{d\Theta} F(De x) dx. \quad (14)$$

The function H takes the physical meaning of the time course of the mean concentration following a step change of the surface concentration, $F(0) = 0$, $F(\Theta) = 1$ for $\Theta > 0$. Fig. 1 plots the function H for three bodies of considerably different geometry: a sphere, a cylinder and a slab. From the figure it is apparent that individual courses do not differ appreciably and that for $\Theta \rightarrow 0$ or $\Theta \rightarrow \infty$ they coincide. This conclusion is a heuristic starting point of all subsequent considerations aimed at quantification of the mentioned analogy in structures of the response functionals of particles of different shape.

SLOW AND FAST PROCESSES

Intuitively it is felt that at sufficiently slow changes of the surface concentration the concentration differences between the surface and the core tend to fade out. Under such conditions we may write approximately

$$c_M(t) \approx c_e + f(t). \quad (15)$$

This approximate description, adequate for sufficiently slow processes, shall be termed the equilibrium asymptote.

Intuitively it seems also acceptable that the disturbances in the original equilibrium concentration field in the particle, $c = c_e$, following very swift changes

* See also the explicit representation in Table I.

of the surface concentration in an early stage of the process, shall be felt only within a very thin shell adhering to the surface. As long as the thickness of this layer is much smaller than the radius of curvature of the particle as well as the diameter of the particle, the curvature of the surface may be neglected and the shell of the material below the surface may be looked upon as part of an infinite semi-space confined by a plane surface.

This concept leads to an approximate undimensional model of penetration of AC into the material given according to Eqs (1)–(3) by the following set of equation

$$\begin{aligned} \partial_t c &= D_S \partial_{xx}^2 c \quad ; \quad x \geq 0, t \geq 0 \\ c &= c_e \quad ; \quad x \geq 0, t \leq 0 \\ c &= f(t) + c_e \quad ; \quad x = 0, t > 0. \end{aligned} \quad (16)$$

The general solution of this set is known^{3,4} and leads to the following expression for the net flux of AC across a unit interfacial surface

$$q_M(t) = D_S^{1/2} d_t^{-1/2} f(t), \quad (17)$$

where $d_t^{-\alpha}$ is an integro-differential operator^{7,8} of the order $(-\alpha)$, see the Appendix I.

For particles of a finite volume V and an infinite surface A one can obtain from Eqs (6) and (17) an approximate expression for the transient development of the mean concentration

$$c_M(t) \approx c_e + \lambda_S^{-1/2} d_t^{-1/2} f(t) \quad (18)$$

where

$$\lambda_S^{-1/2} = D_S^{1/2} A/V \quad \text{resp.} \quad \lambda_S = R_S^2/D_S.$$

This asymptotic relation, whose validity is limited to sufficiently fast or sufficiently short-lived processes, shall be termed the penetration asymptote.

ASYMPTOTIC REPRESENTATION OF THE RESPONSE FUNCTIONAL

In the adopted and already dimensionless notation, Eqs (15) and (18) may be expressed in the form

$$C_M = \mathfrak{F}^*[F(\text{De } c)]_0^{\infty} \approx \begin{cases} F(\text{De } \Theta); & \text{De} \rightarrow 0 \\ d_{\Theta}^{-1/2} F(\text{De } \Theta); & \text{De} \rightarrow \infty. \end{cases} \quad (19a)$$

$$(19b)$$

From the results pertaining to a step change of the surface concentration of AC

in Fig. 1 it is apparent that the asymptotic representation (19a,b) of the response functional may have a rather broad interval of validity. For other types of time variations of the surface concentration, however, the region of applicability may be substantially reduced. It is therefore necessary to examine the formal structure of the response functional for $De \rightarrow 0$ or $De \rightarrow \infty$ in more detail.

The application of the Laplace transforms to mathematical model (1)–(3), or, directly to the convolution representation of the response functional from Eq. (14), can yield the general expression for the \mathcal{L} -transform of the normalized mean concentration

$$\bar{C}_M(P) = \mathcal{L}C_M(\theta) = \int_0^\infty \exp(-P\theta) C_M(\theta) d\theta \quad (20)$$

in the form

$$\bar{C}_M(P) = De^{-1}P \bar{H}(P) \bar{F}(De^{-1}P), \quad (21)$$

where

$$\bar{F}(P) = \mathcal{L}F(\theta) \quad \text{and} \quad \bar{H}(P) = \mathcal{L}H(\theta).$$

For some particle shapes one can find explicit forms of the function $\bar{H}(P)$ in terms of the elementary functions, series, etc.^{3,4}. Especially simple expressions of $H(P)$ may be found for particles with so many symmetries that the problem (1)–(3) becomes from the geometrical point of view a unidimensional one. Typical examples are^{3,4} spherical particles

$$P \bar{H}(P) = P^{-1/2} (\coth \sqrt{3P} - \sqrt{3P}), \quad (22a)$$

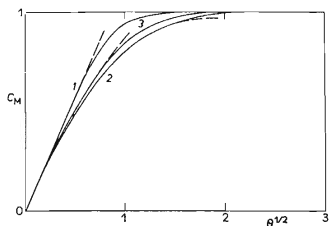
cylindrical particles

$$P \bar{H}(P) = P^{-1/2} I_1(2\sqrt{P})/I_0(2\sqrt{P}) \quad (22b)$$

FIG. 1

Transient Course of the Normalized Mean Concentration $C_M = H(\theta)$ after a Step Change of Surface Concentration

1 Slab, 2 sphere, 3 cylinder. Solid lines represent exact courses of $C_M(\theta)$, broken lines the "fast" asymptotes in Eq. (24a) and dash-and-dot lines the equilibrium asymptotes in Eq. (19a).



or slabs

$$P \bar{H}(P) = P^{-1/2} \tanh(P^{1/2}). \quad (22c)$$

The functions (22a,b,c) for $P \rightarrow \infty$ or $P \rightarrow 0$ may be expanded into power series of similar structure

$$P \bar{H}(P) \approx P^{-1/2} - \beta_{\infty} P^{-1} + 0(P^{-3/2}), \quad P \rightarrow \infty \quad (23a)$$

or

$$P \bar{H}(P) \approx 1 - \beta_0 P + 0(P^2), \quad P \rightarrow 0 \quad (23b)$$

with the shape coefficients β_{∞}, β_0 given in Table I. Substituting the expansions (23a,b) back into Eq. (21) one obtains by formal inverse term-by-term transformation the asymptotic representations of the response functional $\bar{\mathfrak{F}}^*$ in the form

$$\bar{\mathfrak{F}}^*[F(\text{De } x)]_0^{\Theta} = \begin{cases} d_{\Theta}^{-1/2} - \beta_{\infty} d_{\Theta}^{-1} F(\text{De } \Theta) + \varepsilon_{\infty}, & \text{De} \rightarrow \infty \\ (1 - \beta_0 d_{\Theta}^1) F(\text{De } \Theta) + \varepsilon_0, & \text{De} \rightarrow 0. \end{cases} \quad (24a,b)$$

TABLE I

Parameters of Exact^a and Asymptotic Representations of the Response Functional in Eq. (24a,b)

Values	Sphere 2R in diameter	Cylinder ^b 2R in diameter	Slab 2R thick
R_S	$R/3$	$R/2$	R
a	$2/3$	1	2
b_k	$(k\pi/3)^2$	$(\alpha_k/2)^2$	$((k - 1/2)\pi)^2$
β_{∞}	$1/8$	$1/4$	0
β_0	$3/5$	$1/2$	$1/3$

^a a, b are parameters of the exact representation^{3,4} of the kernel of the response functional (14) in the form

$$\frac{dH(\Theta - x)}{d\Theta} = a \sum_{k=1}^{\infty} \exp(b_k(\Theta - x)).$$

^b α_k are roots of the equation $J_0(\alpha_k) = 0$ where J_0 is the Bessel function of the zero-th order, first kind.

The errors ε_∞ or ε_0 of these representations may be expressed generally in the form

$$\varepsilon_\infty = 0(d_\Theta^{-3/2} F(\text{De } \Theta)) = (d_T^{-3/2} F(T)) 0(\text{De}^{-3/2}),$$

or

$$\varepsilon_0 = 0(d_\Theta^2 F(\text{De } \Theta)) = d_T^2 F(T) 0(\text{De}^2). \quad (25a,b)$$

For a given function $F(T)$ thus $\varepsilon_\infty = 0(\text{De}^{-3/2})$, $\varepsilon_0 = 0(\text{De}^2)$, as the expressions $d_T^2 F(T)$ are independent of the time variable $T = t/t_0 = \text{De } \Theta$.

If for a given $F(T)$ the function $C_M(\Theta, \text{De})$ can be expanded into a power series with respect to De at $\text{De} \rightarrow 0$ and $\text{De} \rightarrow \infty$, the first terms of this series, according to the theorems of the Laplace transform, shall be identical with the corresponding terms of the asymptotic functional expansions in Eqs (24a,b). If the asymptotic expansions of the function $C_M(\Theta, \text{De})$ take a different form, e.g. $C_M = \text{De}^{-1/2} \Phi_0(T) + \text{De}^{-1} \Phi_1(\exp(-\text{De } T))$ for $\text{De} \rightarrow \infty$ or $C_M = \psi_0(T) + \text{De } \psi_1(\exp(1/\text{De } T))$ for $\text{De} \rightarrow 0$, the formal asymptotic expansions fail in the sense that all but the first terms vanish for the rest of the series converges to zero for $\text{De} \rightarrow \infty$ or $\text{De} \rightarrow 0$ more rapidly than any power of De .

With the above stipulation, Eqs (24a,b) may be regarded to be general asymptotic representations of the response functional for particles of an arbitrary shape. Values of the shape coefficients β_0, β_∞ for spherical and slab particles may be regarded as limits for β_0 and β_∞ for a particle of an arbitrary shape.

For the power-law type course of the surface concentration

$$f(s) = Ks^n, \quad 0 \leq s \leq t, \quad (26)$$

one can introduce as the only characteristic time scale the time of duration of the process, $t_0 = t$, i.e. $t/\lambda_S = \Theta = \text{De}^{-1}$. In addition, it is convenient to introduce a characteristic concentration by $c_0 = K\lambda_S^n$, leading to the expression of $C_M = (c_M - c_0)/(K\lambda_S^n)$ in the form

$$C_M = \Theta^n \mathfrak{F}^*[(\Theta^{-1} x)^n]_0^\Theta = \Theta^n C_M^*(\Theta). \quad (27)$$

Asymptotic representations of thus introduced mean concentration $C_M = C_M(\Theta, n)$ may be expressed (see the Appendix) as

$$C_M^*(\Theta) \approx \begin{cases} \frac{\Gamma(n+1)}{\Gamma(n+3/2)} \Theta^{1/2} - \frac{\beta_\infty}{1+n} \Theta + 0(\Theta^{3/2}), & \Theta \rightarrow 0 \\ 1 - \beta_0 n \Theta^{-1} + 0(\Theta^2), & \Theta \rightarrow \infty \end{cases} \quad (28a)$$

$$C_M^*(\Theta) \approx \begin{cases} \frac{\Gamma(n+1)}{\Gamma(n+3/2)} \Theta^{1/2} - \frac{\beta_\infty}{1+n} \Theta + 0(\Theta^{3/2}), & \Theta \rightarrow 0 \\ 1 - \beta_0 n \Theta^{-1} + 0(\Theta^2), & \Theta \rightarrow \infty \end{cases} \quad (28b)$$

Fig. 2 shows the exact³ and approximate courses of C_M^* for $n = 1$, i.e. for the linear increase of the surface concentration. The case $n = 0$, i.e. the step change of the surface concentration has been examined earlier, see Fig. 1.

As the second example we took exponential transition of the surface concentration from an equilibrium value, c_e , to another equilibrium value, $c_e + c_0$, i.e. $c_A = c_e + c_0(1 - \exp(-t/t_0))$, or

$$F(T) = 1 - \exp(-T). \quad (29)$$

Exact solution to this case can be also found in the literature^{3,4}. Asymptotic representation of the concentration response from (24a,b) can be found for $De \rightarrow 0$ in the form

$$C_M \approx 1 - (1 + \beta_0 De) \exp(-T) \quad (30a)$$

and for $De \rightarrow \infty$ in the form

$$C_M \approx 2^{-1/2}(\theta^{1/2} - De^{-1/2} \exp(-T)) - \int_0^{T^{1/2}} \exp z^2 dz - \beta_\infty De^{-1}(T - 1 + \exp(-T)). \quad (30b)$$

The exact and asymptotic courses of C_M for De equal 0.1, 1.0 and 10 are shown in Figs 3–5 for a sphere and a slab. The case of a long cylinder falls always between corresponding courses for the slab and the sphere; these, however, are not shown.

As the third example we shall consider a periodic stationary concentration process $C_A(t) = c_0 \sin(\omega t)$, i.e.

$$F(T) = \sin(T) \quad (31)$$

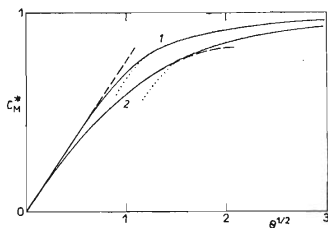


FIG. 2

Transient Course of the Normalized Mean Concentration $C_M^* = (c_M - c_e)/(Kt)^n$ after a Linear Change of Surface Concentration, $n = 1$.

1 Slab, 2 sphere. Solid lines represent exact courses³ of C_M^* ; broken lines "fast" asymptotes in Eq. (24a), dotted line the "slow" asymptote in Eq. (24b). Penetration asymptote in Eq. (19a) is identical with the slow asymptote for slab particles.

Due to the linearity of the response functional the resulting periodic course of the mean concentration may be generally expressed in the form

$$C_M = A \sin(T) - B \cos(T) = C^0 \sin(T - T^0), \quad (32)$$

where A , B and C^0 , T^0 are some functions of the parameter De and it holds that $C^0 = (A^2 + B^2)^{1/2}$, $T^0 = \text{arctg}(B/A)$.

For slab bodies the exact solutions of this problem may be found in the form $A = (\sinh a \cosh a + \sin a \cos a)/C$, $B = (\sinh a \cosh a - \sin a \cos a)/C$, where $C = 2a(\sinh^2 a + \cosh^2 a)$, $a = (De/2)^{1/2}$, and for spherical bodies the exact solution takes the form $A = (\sinh a \cosh a - \sin a \cos a)/C$, $B = (\sinh a \cosh a + \sin a \cos a)/C - 3/2a^{-2}$, where $C = 2a(\sinh^2 a + \cosh^2 a)$, $a = 3(De/2)^{1/2}$.

Asymptotic solutions to this problem can be found (see the Appendix) using methods of integro-differential calculus in the form

$$A \approx \begin{cases} (2 De)^{-1/2} + 0(De^{-3/2}), & De \rightarrow \infty \\ 1 + 0(De^2) & De \rightarrow 0 \end{cases}, \quad B \approx \begin{cases} (2 De)^{-1/2} - \beta_\infty De^{-1}, & De \rightarrow \infty \\ \beta_0 De + 0(De^2), & De \rightarrow 0 \end{cases} \quad (33)$$

The most important characteristics of periodic concentration changes is the amplitude of the mean concentration, C^0 . Its courses in dependence on De following from the exact and asymptotic solutions for the slab and the sphere are shown in Fig. 6.

We have examined three considerably different transient developments of the surface concentration. From Figs 1–6, showing the exact courses of the normalized

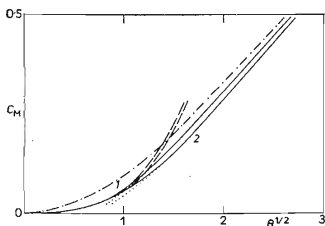


FIG. 3

Transient Course of the Normalized Mean Concentration C_M after an Exponential Change of Surface Concentration, $De = 0.1$

Same caption as for Fig. 2.

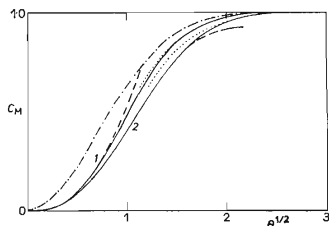


FIG. 4

Transient Course of the Normalized Mean Concentration C_M after an Exponential Change of Surface Concentration, $De = 1$

Same caption as for Fig. 2.

mean concentration, c_M , in comparison with individual types of asymptotic approximations, though it is apparent that the concentration responses have in all cases certain identical features. The results plotted in Figs 1–6 may be summarized as follows:

a) Exact courses of the concentration responses, $C_M(\theta)$, for particles of various shapes but identical λ_s mutually differ by at most 10 to 20% of the instantaneous value and so only in region of medium rate processes, $De \approx 1$. With this accuracy the generalized descriptions of unsteady diffusion, based on the characteristic particle diameter, R_s , or corresponding relaxation time $\lambda_s = R_s^2/D_s$, are generally applicable.

b) In region of asymptotically fast phenomena, $De \gg 10$ or asymptotically slow phenomena, $De \ll 0.1$ the concentration responses of particles of different shape and identical λ_s do not differ significantly and may be approximated to a usually sufficient accuracy by the equilibrium asymptote from Eq. (19a,b).

c) Concentration responses for particles of individual shapes are approximated with an accuracy better than 2% by the appropriate fast or slow asymptote from Eq. (24a,b) over very wide intervals of De which partly overlap in the neighbourhood of $De = 1$. To an accuracy better than 2% one can obtain approximations according to the slow or the fast asymptote for $De \ll 0.5$ or $De \gg 2$.

CONCLUSION

The dynamics has been studied of unsteady diffusion in individual particles of various shapes under conditions when the concentration of the transported active component

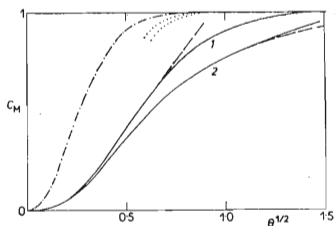


FIG. 5

Transient Course of the Normalized Mean Concentration C_M after an Exponential Change of Surface Concentration, $De = 10$
Same caption as for Fig. 2.

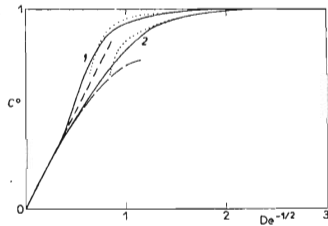


FIG. 6

Amplitude of the Mean Concentration C^0 as a Function of the Rate of Periodic Changes of the Surface Concentration
Same caption as for Fig. 2.

(AC) on particle's surface is uniform but varies with time. The dynamic properties of particles are characterized by the linear response functional, \mathfrak{F} , assigning to a given transient development of the surface concentration $c_A(t)$ corresponding course of the mean concentration $c_M(t) = \mathfrak{F}[c_A(s)]_0^t$.

The principal result of this work is thought to be the formulation and the test of the approximate representations (19) and (24) of the response functional for asymptotically fast and slow processes. Based on this test it may be taken for proven that in region of asymptotically fast or slow processes the concentration response is entirely independent of particle shape. A quantitative measure of whether a given process is asymptotically fast or slow is the value of the diffusional Deborah number, $De = \lambda_s/t_0$. t_0 is a characteristic time scale of the process. For processes with a monotonous and sufficiently smooth course of the surface concentration, with the power-law type course as a typical example, t_0 represents the total duration of the process, for periodic processes their period.

The dependence of the concentration response on particle shape is sufficiently accurately characterized by two shape coefficients, namely β_0 in region of slow and β_∞ in region of fast processes. The kinetic regime region, where the shape coefficient in the approximate description of the concentration processes markedly improves the accuracy of the approximation, however, is much too narrow and amounts to less than an order of magnitude in the neighbourhood of $De = 1$.

An example of the generalized description of an unsteady concentration process for particles of different shape, including irregular particles, has been presented in Aris' work² on the dynamics of axial dispersion of a concentration pulse in a column packed by nonspherical particles. The conditions considered in the work (Gaussian axial profile of concentration of AC in the carrier fluid) implicitly restrict the kinetic regime to slow processes, where, according to our concept, the factor β_0 should become effective. Indeed, Aris' shape factor κ is related to our parameter β_0 by $\kappa = 3\beta_0$. Ref.² tabulates values of κ for particles of different shape. The difficulties with the definition of the shape factor, mentioned by Aris in the concluding part of his work², however, are not so much associated with the problem of alternative definition of the shape factor as with the problem whether we are justified to model additional diffusional resistances within the ambient liquid by means of empirical "film" transfer coefficients.

APPENDIX

The asymptotic representations of the response functional discussed in the paper make use of the so-called fractional calculus or the "differentegrals of noninteger order"⁷. These operators may be introduced through the Riemann-Liouville integral

$$d_t^{-\alpha} f(t) = \frac{1}{\Gamma(\alpha)} \int_0^t (t-s)^{\alpha-1} f(s) ds, \quad 0 < \alpha \leq 1 \quad (D1)$$

and extended to all real values of α by

$$d_t^0 f(t) = f(t), \quad (D2)$$

$$d_t^1 f(t) = \frac{d}{dt} f(t), \quad (D3)$$

$$d_t^{a+b} f(t) = d_t^a(d_t^b f(t)) = d_t^b(d_t^a f(t)), \quad (D4)$$

for all a, b or $(a + b)$ times differintegrable functions.

In the construction of asymptotic approximations of the concentration responses we have used primarily the following results⁷ of the differintegral calculus:

The substitution rule for changes of independent variable

$$(x = ay, F(y) = f(ax)) \Rightarrow d_x^{-\alpha} f(ax) = a^{-\alpha} dy^{-\alpha} F(y). \quad (D5)$$

The expression of the differintegral of a power function

$$d_t^{-1/2} t^n = t^{n+1/2} \pi^{-1/2} \int_0^1 (1-x)^{-1/2} x^n dx = \frac{\Gamma(n+1)}{\Gamma(n+3/2)} t^{n+1/2}. \quad (D6)$$

Asymptotic expression for the differintegral of the $\sin(\omega t)$:

$$d_t^{-1/2} \sin(\omega t) \approx \omega^{-1/2} (\sin(\omega t - \pi/4) + O((\omega t)^{-1/2})), \quad t \rightarrow \infty. \quad (D7)$$

LIST OF SYMBOLS

A	particle surface area
c_e	equilibrium concentration of AC, (1)
c_0	characteristic concentration of AC, (11)
c_M	mean concentration of AC in particle, (4)
c_A	particle surface concentration of AC, (2)
$C_M = (c_M - c_e)/c_0$	normalized mean concentration
C_M^*	normalized mean concentration, (27)
C^0	amplitude of periodically variable mean concentration
$d_t^{-1/2}$	integrodifferential $(-1/2)$ order, see Appendix
D_S	diffusivity of AC in material of particle
$De = \lambda_S/t_0$	diffusional Deborah number
$f(t)$	function determining the course of c_A , (2)
$F(T)$	normalized function (11)
$H(\theta)$	course of C_M after a step change of surface concentration
I_0, I_1	modified Bessel functions
q_M	overall flux of AC through a unit surface, (5)
$R_S = V/A$	Aris' characteristic particle size
s	auxiliary time variable, $0 \leq s \leq t$
t	time
t_0	characteristic time interval, (11)
V	particle volume

β_0 shape factor, defined by Eq. (23a)

β_∞ shape factor, defined by Eq. (23b)

$$\theta = t/\lambda_S$$

$$\lambda_S = R_S^2/D_S$$

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Translated by V. Staněk.