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Transfer Processes in Fractal Media

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An irreversible process in fractal media involves coupling relation between the space and the time. The present note displays how the fractional derivation has to be introduced to describe this effect. As a result the law of the chemical diffusion to a fractal is given.

KEY WORDS: Irreversible process; fractal; fractional derivation.

1. HETEROGENEOUS MEDIA AND CHEMICAL KINETICS

Heterogeneous media are used widely in the chemical industry. Well-known examples include the catalytic cracking of petroleum fractions in fluidized or fixed bed reactors,(1-3) the roasting of ores, and the use of porous electrodes(4,5) in electrochemical power sources. The detailed chemical and physical processes that occur at the micro level inside these complex heterogeneous media are not accessible to experimental observation below a certain scale that depends upon the methods of observation. The microkinetics of the local processes must necessarily be inferred from macro-level observations on the operating units and from data obtained in idealized model experiments in conjunction with sets of parameters that characterize the heterogeneous medium and various other assumptions regarding the relationships between these parameters and the physicochemical properties of the chemical system.(1,2)

The traditional descriptions of heterogeneous media rely on the particle size and shape distributions, the pore size distributions, the surface areas, and the tortuosity of the media,(6,7) each of which is defined in terms of unique experimental data and particular model assumptions. A problem with these characteristics is that they are model and experimental method-

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dependent. Thus, they do not represent independent geometric system invariants for any particular material. It is reasonable, therefore, to inquire whether a more representative and a more universally applicable method can be developed to describe the geometry of heterogeneous media.

Mandelbrot has provided suggestive evidence that a wide class of heterogeneous media may be fractal in nature.(8) This conjecture was explored in earlier studies, and it was found, for example, that both porous electrodes and various cathode materials used in electrochemical energy sources could be described as fractals and that the processes occurring in these media could be simply related to the fractal characteristics expressed in terms of the invariant nonintegral dimensions of the media.(9)

The successful descriptions thus obtained stimulated further investigations into the theoretical relationships between the fractal geometries of heterogeneous media and the irreversible processes that may occur in these media.

In approaching such investigations, certain qualitative model considerations appeared to be desirable to delimit the scope of the analysis. The model considerations may be paraphrased in terms of the following questions:

1. In what sense are heterogeneous media to be considered as fractals?
2. What is the proper framework within which to describe the rates of physicochemical processes in fractal media?

It is the purpose of this introductory note to address these questions. The quantitative developments will be presented in the next section. For concreteness, the two questions will be discussed with reference to porous electrodes, such as are used in electrochemical energy storage devices.

Microscopic analyses of the geometric configurations of several different electrode materials spanning a wide range of magnifications revealed that they all possessed internal random self-similarity, or very nearly so.(9,10) Since self-similar configurations constitute an important class of fractals with well-defined nonintegral dimensions, it appeared reasonable to consider the porous electrodes to be fractals in the sense of random self-similarity, at least as a first-order approximation.

The second question requires a little more thought. Again, with reference to porous electrodes and electrochemical processes, we may begin the discussion with a consideration of the irreversible processes at idealized interfaces that can be closely realized in laboratory experiments. The rates of such processes can be fixed over a wide range of values by the deliberate control of the electric system variables (thermodynamic electrochemical potential), and since the reactions are carried out on geometrically well-defined interfaces (integral Euclidean geometries), it is possible to determine the detailed kinetic and transport parameters associated with the physicochemical processes occurring in these geometries. If the rate is controlled by an experimentally accessible thermodynamic driving force located at a well-defined Euclidean interface separating the two media (liquid and solid phases in the case of electrochemical processes), the process is called a "transfer process" in the sense that both chemical species and energy is transferred from one state to another at an interface. Since it occurs at a well-defined interface accurately located in space it will be designated as a δ transfer (Fig. 1). By contrast, the transfer process will be designated as a distributed transfer in systems where the driving force is not so located in terms of the space coordinates (Fig. 2). It is often called transport process. The δ nomenclature is suggested by the process localization that may be described by a Dirac delta function pointing out a discontinuity of the media.[2]

Consider now a particular mechanical transformation of a two-phase system with an initially well-defined interface having an integral Euclidean dimension: the two phases may be separately subdivided and then intermixed in such a manner and to such an extent that the integral dimension of the original Euclidean interface disappears. How can be kinetic–geometric

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[2] This nomenclature was proposed by Dr. Bro in order to release previous technical disturbances involved by the confusion between the sentence transfer and the sentence transport.

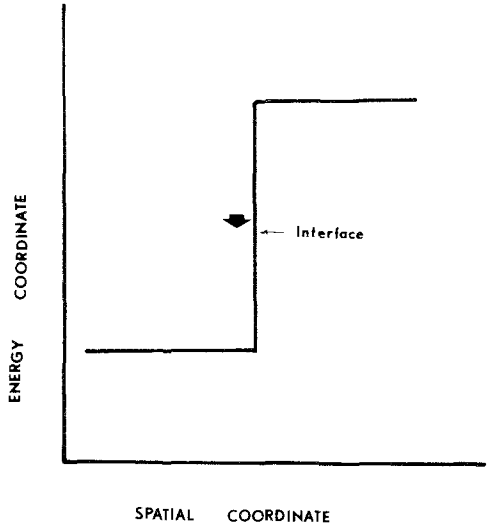

Fig. 1. Schematic view of the spatial energy distribution in the case of "δ-transfer" process. The spatial resolution is limited by the molecular dimensions and the step of energy is controlled by the bulk thermodynamic conditions on both sides of the interface. The arrow points out the thermodynamic direction of the irreversible process.

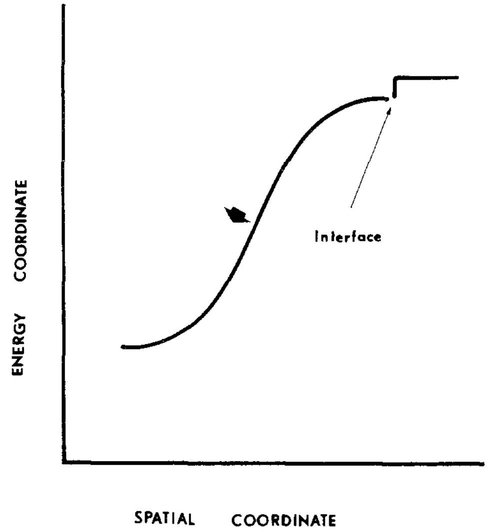

Fig. 2. Schematic view of the spatial energy distribution in the case of "distributed transfer" process. The spatial distribution is here very extensive only on one side of the interface. The arrow points out the thermodynamic direction of the irreversible process. The step of the energy on the interface is small with regard to the spatial distribution of the energy.

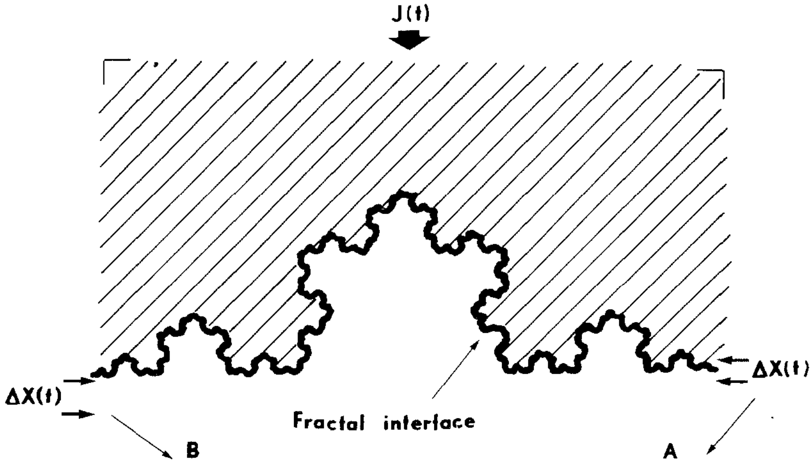

Fig. 3. Schematic view giving the major variables for the irreversible transfer through a fractal interface. $J(t)$ is the macroscopic flow. $\Delta X(t)$ is the related thermodynamic force located either on both sides of the fractal interface A (δ transfer), or essentially distributed in the bulk B (distributed transfer).

relationships obtained on the original Euclidean interface be applied to the dispersed phase system? From an operational point of view, the accessible parameters on the dispersed system are the bulk intensive (= global) thermodynamic parameters, not the extensive parameters obtained at the level of the local (= micro) geometry where the processes actually occur. Since the interface in the dispersed medium is assumed to be a fractal, a hypothesis (Fig. 3) is needed in regard to the transfer process on the fractal interface. At first, it will be assumed that the transfer process at the fractal interface is a δ-transfer process and that the rate of the process is controlled by the homogeneous bulk chemical and thermodynamic factors that are well defined to the extent that the geometric properties of the system allow the definition of any intensive properties. As will be seen in Section 2, this makes it possible to describe the rate of the global process in terms of well-defined, independent geometric and kinetic factors.

Afterward, it will also be assumed (Section 3) that δ transfer at the fractal interface is kinetically controlled by distributed chemical and thermodynamic factors in the fractal bulk. In that case, the analysis requires a more advanced point of view and the physical meaning of the concept of separability for the kinetic and geometric factors becomes more complex. Meanwhile, the fractal assumptions lead to the analytical solutions of the transport properties in the fractal media, to the fractal interface.

Based on the preceding qualitative model considerations we can now proceed to the quantitative analysis of the transfer and transport processes that may occur in fractal media.

2. LINEAR δ TRANSFER (TEISI MODEL)

We consider any linear δ transfer (see Section 1) on a planar interface $[A]$ separating the space into two distinct regions. The linear δ-transfer hypothesis means that the following:

(i) The transfer kinetics of any extensive quantity m through $[A]$ is controlled by a step change of the free energy $\Delta X(t)$ (intensive thermodynamics variable) at the interface $[A]$. It assumes the existence of a statistical average energy related to a Poisson distribution of the energy.(12,13)

(ii) We consider the case where the relationship between the driving force $\Delta X(t)$ and the density of flow $\phi(t)$ is linear(14):

$$\phi(t) = \frac{1}{\tau} \Delta X(t) \tag{2.1}$$

where $1/\tau$ is a kinetic constant derivated from the molecular properties that govern the transfer. The rate of entropy production is given by the quadratic form(14):

$$\sigma(t) = \phi(t)\, \Delta X(t) = \frac{1}{\tau} \Delta X^2(t)$$

If the area of the planar interface is A, the total macroscopic flow of m, $J(t)$, which crosses the interface $[A]$, is given by

$$J(t) = \frac{1}{\tau} A\, \Delta X(t) \tag{2.2}$$

The TEISI model(15) concerns the case where the interface $[A]$ is a fractal characterized by a nonintegral Hausdorff–Mandelbrot dimension d.(8) Each of the two regions is assumed to remain at a constant potential in term of the free energy. As the result, the driving force across the fractal interface may be controlled just as in the case of a planar interface. The relationship between the input $J(t)$ and the output $\phi(t)$ of the fractal system may be described with reference to an equation derived from systems theory(16):

$$J(t) = A(t) * \phi(t) \tag{2.3}$$

where $*$ signifies the convolution(17) between the unknown geometric factor $A(t)$ and the density of flow $\phi(t)$ that is controlled by the intensive thermodynamics properties alone. The Laplace transform of (2.3) is

$$\overline{J(s)} = \overline{A(s)}\, \overline{\phi(s)} \tag{2.4}$$

Where the bars signify the Laplace transform, s being the Laplace variable. A comparison between (2.2) and (2.4) shows that $\overline{A(s)}$ is no more than the measure of the interface of exchange in the space of Laplace variables.

In addition, the d-fractal metric of $[A]$ suggests(8)

$$\overline{A(s)} = \gamma(D_T)\, \overline{N(s)}\, \overline{\eta^{D_T}(s)} \tag{2.5}$$

D_T is the topological dimension of the space of the exchange of energy. $\gamma(D_T) = (1/2)^{D_T}\, \Gamma(1/2)^{D_T}/\Gamma(1 + D_T/2)$, $\Gamma(\ )$ being the gamma function. $\overline{\eta(s)}$ is the "gauge" used to characterize the interface $[A]$. $\overline{N(s)}$ is the result of the measure of the fractal $[A]$ using the "gauge" $\overline{\eta(s)}$ [from Ref. 8 $\overline{N(s)}\, \overline{\eta^{d}(s)} = l_0^d$; l_0 is a macroscopic characteritic length; d is the fractal dimension.]

As a result

$$\overline{J(s)} = \overline{N(s)}\, \overline{j(s)} \tag{2.6}$$

where

$$\overline{j(s)} = \frac{1}{\tau} \gamma(D_T)\, \overline{\eta^{D_T}(s)}\, \overline{\Delta X(s)} \tag{2.7}$$

is the "gauge" of the flow in the space of the Laplace variable. The scaling properties in the Laplace space shall be distinguished from the scaling properties in the space of the time.(18,19)

In order to arrive at the relevant macroscopic kinetic expression, we conjecture that(15)

$$\overline{N(s)} = \frac{s}{\varepsilon_0}, \qquad \text{where} \quad \varepsilon_0^{1/d} = \frac{\lambda_0}{l_0} \tag{2.8}$$

l_0 being a characteristic length.

The validity of this conjecture is supported by the observed agreement between experimental results and prediction based on this conjecture. The conjecture signifies that $\overline{\eta(s)} = \lambda_0/s^{1/d}$, that is to say, (i) the Haussdorff content is related to a Laplace variable, and (ii) the "gauge" of uncertainty in the space-time $\eta(t)^{*d}$, the inverse Laplace transform of $\overline{\eta^d(s)}$, is a geometrical invariant λ_0, which means that the geometry is stationnary in the time.

As a result

$$s^{(D_T/d)-1}\, \overline{J(s)} = K_0\, \overline{\Delta X(s)} \tag{2.9}$$

where

$$K_0 = \frac{\gamma(D_T)\, \lambda_0^{D_T}}{\tau \varepsilon_0}$$

Introducing the nonintegral differential operator(20) $d^{(D_T/d)-1}/dt^{(D_T/d)-1}$ as the inverse Laplace transform of $s^{(D_T/d)-1}$, (2.9) may be written in space-time as

$$\frac{d^{(D_T/d)-1}}{dt^{(D_T/d)-1}} J(t) = K_0\, \Delta X(t) \tag{2.10}$$

which is a generalization of the fractional differential equation previously given in the elementary TEISI model ($D_T = 1$, $0 < d < 2$).(15) This is the kinetic equation linking the only two macroscopic variables needed to describe the irreversible phenomenon under consideration.

In contrast with other models which suggests a time dependance of the local kinetic constant in the fractal media,(21,22) the present proposal stresses the fundamental aspects involved by incorporating the interfacial characteristics into the fractional derivative in space-time.

The fractional derivative arises from the mathematical analysis and the model assumptions and it may be observed that it leads to a general input–output transfer function of the form

$$\frac{\overline{\Delta X(s)}}{\overline{J(s)}} = \frac{1}{K_0} \frac{1}{s^{1-(D_T/d)}} \tag{2.11}$$

which involves a Curie–von Schweilder type of time relaxation mode(23) according in the space time to a t^{-n} function with $n = D_T/d$.

If the interface of exchange is considered as a constant one, that form might indeed be though of as a modification of the kinetics constant.(21)

The major role played by the geometry, however, has been and will be emphasized in the literature with reference to a variety of experimental results.(15,24–26) Particularly it may be noticed that when the driving force is of the form $\Delta X(t) = X_\infty(t) - X(t)$, also called a marginal form, and when the linear δ transfer is a first-order δ transfer: $J(t) = c\, dX(t)/dt$(14,27); the transfer function $X(s)/X_\infty(s)$ takes the form

$$\frac{\overline{X(s)}}{\overline{X_\infty(s)}} = \frac{1}{1 + (\tau_0 s)^{D_T/d}} \tag{2.12}$$

called the "Cole and Cole" form(28) $\tau_0 = (c/K_0)^{d/D_T}$. This result is especially important since, under these conditions, experimental data provide detailed information of the local irreversible events via τ_0 even if the kinetics are carried out in complex media.(25,26)

The kinetic and thermodynamic consequences of such experiments are currently under investigation in order to obtain more comprehensive characterizations of the kinetics in the heterogeneous random media (electrodes, composite materials, catalysts...).(25)

The preceding schematic analysis suggests an extension of the concept and formulation of the energy dissipation. The use of $\Sigma_1(t) = J(t) * \Delta X(t)$ has been suggested elsewhere(15); however, this functional is only related to the spectral density of energy and to the correlation function of the forces. A more comprehensive description of the dissipation would be $\Sigma_2(t) = A(t) * \sigma(t)$, that is to say,

$$\Sigma_2(t) \propto \frac{d^{1-(D_T/d)}}{dt^{1-(D_T/d)}} \sigma(t)$$

where $\sigma(t)$ is the traditional rate of the production of entropy.(14) The total process might then be a nondissipative one, depending on the value of D_T with respect to the fractal dimension, that is to say, depending on the topology of the space of dissipation with respect to the metric of the space of transfer.

3. DISTRIBUTED δ TRANSFER

In contrast with the δ transfer [linear (Section 2) or not], the distributed transfer is characterized by a spatial distribution of the driving forces. The best-known example of such behavior is observed in diffusion processes.$^{(29)}$ The case of semi-infinite diffusion has already been treated elsewhere$^{(30)}$ using the semiderivation which leads to the following equation$^{(31)}$:

$$\frac{d^{-1/2}}{dt^{-1/2}} J(t) = \sqrt{D}\, \Delta X(t) \tag{3.1}$$

where D is the diffusion coefficient. This equation is exactly the same as Eq. (2.10) with $d = 2$ (Peano interface) and $D_T = 1$. This point of view may be generalized by considering some of distributed transfers in Euclidean space as equivalent to δ transfers on a d_f-fractal interface, i.e.,

$$\begin{bmatrix} \text{distributed transfer} \\ + \\ \text{Euclidean space} \end{bmatrix} \approx \begin{bmatrix} \delta \text{ transfer} \\ + \\ d_f\text{-fractal space} \end{bmatrix}$$

where [according to Eq. (2.10)] d_f is the fractal dimension of the kinetic limitation of a δ transfer. d_f is not only a useful formalism artifice but may have an accurate geometrical meaning.$^{(32)}$

Thus the linear elementary event on the above d-fractal interface may be extended to a distributed process by using the linear δ transfer and by letting these be distributed by the d_f-fractal interface. According to the linear TEISI model equation,

$$\frac{d^{(D_T/d_f)-1}}{dt^{(D_T/d_f)-1}} \phi(t) = \frac{1}{\tau} \Delta X(t) \tag{3.2}$$

using $\phi(t)$, which is the local density of flow[3]; $\Delta X(t)$, the related macroscopic driving force; τ, a constant originated in the molecular elementary event; d_f, the fractal dimension of the local kinetic limitation; and D_T, which is always the topological dimension of the space of the exchange of energy.

Then, the reasoning of Section 2 may be employed without any change of the assumptions to give the following distributed TEISI model equation of the macroscopic through the d-fractal interface:

$$\frac{d^{(1/\theta)-1}}{dt^{(1/\theta)-1}} J(t) = K_0 \Delta X(t) \tag{3.3}$$

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[3] We emphasize that in this case the fractional derivation is applied over the density of flow, which means (i) the limiting event is not the transfer through the d-fractal interface but a lower-rate one, and (ii) the dissipative factor is located in the bulk and not on the d-fractal interface.

where $J(t)$ is the macroscopic flow; $\Delta X(t)$ is the thermodynamic driving force; K_0 a constant, and θ is now a (d, d_f) function given by

$$\theta = \frac{dd_f}{D_T(d + d_f) - dd_f} \tag{3.4}$$

Equations (3.3) and (3.4) signify "Transfer through a d-fractal interface is driven by a complex process which is controlled by a d_f-fractal geometry imbedded in a d-fractal media."

If $D_T = 1$ and $d_f = 2$, that is to say, if the δ transfer through the d-fractal interface is driven by a diffusion process then $\theta = 2d/(2 - d)$. This result was tested experimentally and found to give an accurate description of the diffusion of the "reactive species" to a d-fractal interface [chemical species diffusion,(33) phonons diffusion(18,19)]. In addition,

If $d_f = 1$, the simple δ-transfer equation is recovered.

The general case where $2 > d_f > 1$ is found, for example, to give an accurate description of the kinetic control of the electrochemical transfer of the ionic species into a fractal solid state lattice when the electrolyte is partially crystallized.(34) As a result the distributed TEISI model is very useful in order to understand the laws of the behavior of any fractal composite structure.

In addition the distributed TEISI model may be further generalized to cases where the topological dimension D_T of the energy transfer depends on the fractal dimension, i.e., $D_T = f(d)$.

Although the extended TEISI model presents a unified treatment of a variety of interfacial energy dissipation processes within a general kinetic-geometric framework, several problems remain to be examined for example the bulk dissipation of energy in nonreactive walls media (electrolyte in porous fractal media, amorphous phase in crystalline structure, etc....). As an approach to their solution it may be useful to postulate the validity of the distributed TEISI model. This point of view is currently tested in our laboratory in the case of solid state ionic percolation.

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