Fractal-Like Behavior Observed for a Mass-Transport Process

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In recent years, the anomalous features of dynamical processes within disordered media have been investigated rather extensively in the field of statistical physics. Typical examples of such processes are: the charge transport in amorphous materials (Scher and Montroll, 1975); the diffusion-controlled chemical reactions within glassy matrices (Plonka, 1986); and those inside porous polymeric membranes and porous glasses (Kopelman, 1986, 1989). The anomalous features, which are often referred to as "fractal-like kinetics," are attributed to the geometric or energetic disorders inherent in the disordered media and cannot be described by the well-established, classical theories. We believe that such new concepts should be introduced in a more complete form to the field of chemical engineering with the reconsideration of conventional models for diffusion or mass-transport processes.

In this work, we report a striking example of the fractal-like behavior observed in a preliminary response experiment for a packed bed and then propose a simple new model for elucidating the behavior.

Experiment

A simple, standard-response experiment was carried out. A column (0.8-cm-dia.) packed with activated charcoal particles (~ 450-μm-dia.) serves as a packed bed (5-cm-long). Most of the experimental equipment is made of teflon and maintained at 25°C by a water bath. First, we let an aqueous solution of $SrCl_2$ (concentration of $Sr^{2+} = 50$ ppm) flow through the bed for about two weeks. Then, we abruptly switched the flow to deionized water (flow rate $= 0.072\ cm^3/min$) containing no Sr^{2+}. The response, the variation of C_{out} (ppm) with t (min), is measured by the inductively-coupled plasma-emission spectroscopy. The result observed for $t \leq 10^4$ min is shown in Figure 1. A striking feature of the response is that C_{out} decreases in accordance with the power law, $C_{out} = C_0 t^{-\alpha}$, for $t \gtrsim 10^2$ min. Applying the method of least squares to the data for 10^2 min $< t < 10^4$ min yields $\alpha = 0.95$. As will be explained later, this "fractal-like" behavior cannot be described by the conventional partial differential equations for a mass-transport process.

Model

Here, we consider a general situation where a fluid flows through disordered media and solute molecules or ions in the fluid move with the flow being trapped on adsorption sites and dead-end pores or spaces and released from these "trappers." It should be noted that the fluid flows through the backbones (for example, fractures) only. The trappers are decomposed into several different classes. The density of the solute molecules at any point in the media at any time is the sum of the density of the solute molecules moving with the fluid flow, plus the density of the solute molecules being trapped in the trappers:

$$n(x, t) = P(x, t) + \sum_i P_i(x, t), \tag{1}$$

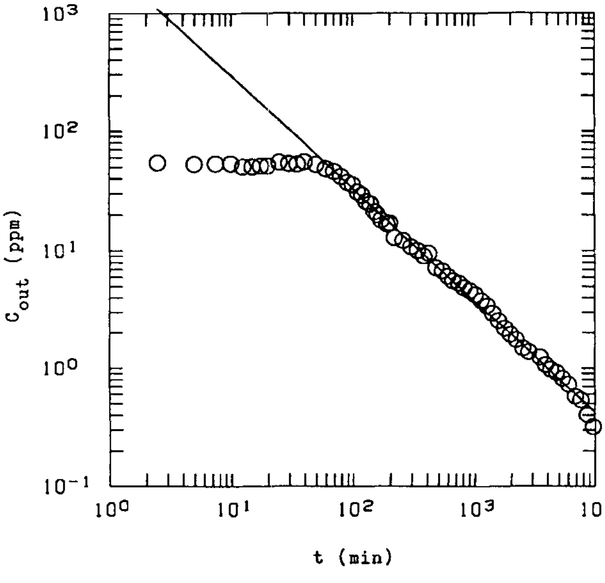

Figure 1. Typical response observed in our preliminary experiment.

The slope of the straight line drawn is -0.95.

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The solute molecules moving with the fluid flow should obey the usual continuity equation:

$$(\partial n/\partial t) = -v(\partial P/\partial x) + D(\partial^2 P/\partial x^2). \qquad (2)$$

Here, we introduce the overall residence-time distribution function, $\Phi_i(t)$, for trappers of the ith class. Denoting the transfer rate constant for solute molecules from the fluid to trappers of the ith class by ω_i, we obtain:

$$\partial \Delta P_i/\partial t = \omega_i \Delta P - \omega_i \int_0^t \Delta P(x, t-\tau)\Phi_i(\tau)d\tau, \qquad (3)$$

where

$$\Delta P_i(x, t) = P_i(x, t) - P_i(x, 0), \qquad (4)$$

$$\Delta P(x, t) = P(x, t) - P(x, 0). \qquad (5)$$

We then study $\Phi_i(t)$ for the adsorption sites ($i=1$) and the dead-end pores or spaces ($i=2$) separately. First, we consider the adsorption sites. The desorption of a solute molecule from a site is an activation process and the desorption rate constant u is given by:

$$u = u_0 \exp[-E/(RT)]. \qquad (6)$$

We note that the residence time of a solute molecule adsorbed on a site whose activation energy is E cannot uniquely be determined because the desorption is a stochastic process: some solute molecules are shortly released to the fluid flow, while others spend a rather long time on that site. Assuming that the desorption occurs in a completely random manner, we can express the distribution of the residence time by an exponential-type one (Feller, 1971):

$$\phi_1(t, u) = u \exp(-ut). \qquad (7)$$

In Eq. 7 the average value of the residence time is $1/u$. For the disordered media, the activation energy E should vary from site to site. Assuming that E obeys a completely random distribution with a finite average value (that is, exponential type), we obtain:

$$q(E) = q_0 \exp[-E/(RT_c)]. \qquad (8)$$

The average value of E corresponds to $1/q_0 = RT_c$, and T_c is a constant depending on the adsorbent and solute molecules. We note, however, that there should be a mininum value $E_{\min}$ and a maximum value $E_{\max}$ for the adsorption sites. Denoting the distribution function for u by $h(u)$ and using the relation, $q(E)dE = -h(u)du$, and Eq. 8, we obtain:

$$h(u) \sim u^{-1+T/T_c}. \qquad (9)$$

The value of u should be in the range from $u_{\min}$ to $u_{\max}$, and $X \sim Y$ means that X is proportional to Y except in the regions of very small Y and very large Y. Regarding $u_{\min}$ and $u_{\max}$ as virtually zero and infinitely large, respectively, we can express the overall residence-time distribution function $\Phi_1(t)$ by:

$$\Phi_1(t) = \int_0^\infty h(u)\phi_1(t, u)du. \qquad (10)$$

Employing Eqs. 7, 9 and 10 yields:

$$\Phi_1(t) \sim \Gamma(T/T_c + 1)t^{-1-T/T_c}, \qquad (11)$$

where Γ denotes the gamma function. $\Phi_1(t)$ is expressed by a power law whose algebraic form is similar to that studied by Pfister and Scher (1978). The exponent is temperature-dependent. It should be noted, however, that there is no fundamental reason that T/T_c should be smaller than unity.

We then proceed with the study of the overall residence-time distribution function for dead-end pores or spaces. The residence time of a solute molecule which stepped inside a dead-end pore or space of volume V is not uniquely determined: some solute molecules are shortly released to the fluid flow, while others spend a rather long time in that pore or space. Thus, the release is a stochastic process, and ϕ_2 is given by:

$$\phi_2(t, V) = \{1/(bV)\}\exp[-t/(bV)], \qquad (12)$$

where b is a constant. Equation 12 is supported by our Monte Carlo simulation whose details are to be published in a subsequent full-length article. If we assume that the self-similarity is inherent in the pores or spaces, the volume distribution function $g(V)$ obeys the following:

$$g(V) \sim V^{-1-\gamma}. \qquad (13)$$

Again, there should be a minimum value $V_{\min}$ and a maximum value $V_{\max}$ for the dead-end pores and spaces. Regarding $V_{\min}$ and $V_{\max}$ as virtually zero and infinitely large, respectively, we obtain:

$$\Phi_2(t) = \int_0^\infty g(V)\phi_2(t, V)dV \sim \Gamma(\gamma+1)t^{-1-\gamma}. \qquad (14)$$

Thus, $\Phi_2(t)$ is expressed by a power law which is similar to the case of adsorption sites. The exponent in this case, however, is independent of temperature.

Although the basic idea of deriving Eqs. 1 and 2 is similar to that of Noolandi (1977) who studied the charge transport in amorphous materials, the introduction of $\Phi_i(t)$ and the derivation of Eqs. 11 and 14 for the two specific classes of trappers are our new developments. In the actual cases, however, the two classes of trappers do not always contribute to the transport process separately, and the effect of their interplay should be investigated further.

Application of the Model to Experimental Result

In our experiment, the disordered media and the solute molecules correspond to the charcoal bed and Sr^{2+} ions, respectively. The Laplace transform of Eqs. 1 through 5 yields the following:

$$\Delta\tilde{P}(L, s) = \tilde{G}(s)\Delta\tilde{P}(0, s), \tag{15}$$

$$\tilde{G}(s) = \exp[\{Lv/(2D)\}\{1-(1+4D\tilde{a}(s)/v^2)^{1/2}\}], \tag{16}$$

$$\tilde{a}(s) = s + \sum_i \omega_i\{1-\tilde{\Phi}_i(s)\}, \tag{17}$$

where $\tilde{G}(s)$ is the transfer function. Our model predicts that:

$$\Phi_i(t) \sim t^{-1-\alpha_i}, \quad \alpha_1 = T/T_c \text{ and } \alpha_2 = \gamma. \tag{18}$$

Feller (1971) has shown that for $0<\alpha_i<1$ and $s\rightarrow 0$,

$$\tilde{\Phi}_i(s) \sim 1 - A_i s^{-\alpha_i}. \tag{19}$$

In our experiment,

$$\Delta\tilde{P}(0, s) = -C/s, \tag{20}$$

where C is a constant. From Eqs. 15, 16, 17, 19 and 20, we reach the following result:

$$P(L, t) \sim \sum_i (A_i C L \omega_i/v) t^{-\alpha_i}, \; t\rightarrow\infty. \tag{21}$$

In cases of $\alpha_i \geqq 1$, Eq. 21 cannot be mathematically derived from Eq. 18 via the Laplace transform. Even for such cases, however, we have verified that Eq. 21 is reached from Eq. 18 by detailed numerical analyses. Thus, Eq. 21 is valid for all positive values of the exponents, for $\alpha_i > 0$.

The activated charcoal can be characterized by the great adsorption capacity. Also, the operating temperature is relatively low. Thus, it is probable that each Sr^{2+} ion spends most of time on adsorption sites until it leaves the bed. Therefore, the power law observed in the experiment can be interpreted as:

$$C_{\text{out}} \sim P(L, t) \sim t^{-\alpha_1} = t^{-T/T_c}. \tag{22}$$

It follows that in our preliminary experiment $T/T_c \sim 1$. We note that our further experiments performed at 25°C and 5°C showed that the exponent was temperature-dependent and approximately proportional to T. The details of the result will be reported in a subsequent article. A remarkable feature of the power form, $\Phi_1(t) \sim t^{-1-\alpha_1}$ $(m-1<\alpha_1<m;\ m=1, 2, 3, \ldots)$, is the divergence of the nth moment,

$$\overline{t^n} = \int_0^\infty t^n \Phi_1(t)dt, \tag{23}$$

for $n \geqq m$. This feature cannot be described by the conventional theory employing the partial differential equations. Particularly, when $m=1$ and even the first moment diverges, the power form gives rise to an anomalous behavior which is surprisingly different from that described by the conventional theory (Scher and Montroll, 1975). It is not definite in our preliminary experiment that α_1 is significantly smaller than unity. We believe, however, that cases where α_1 is definitely smaller than unity do exist, and we are now pursuing such cases.

Concluding Remarks

A striking experimental result of a "fractal-like behavior" has been reported for a mass-transport process. A new model that can elucidate the behavior has also been proposed. Although the substance described here is still of preliminary nature and should therefore be investigated in further studies, we believe that it covers some pioneering aspects in the field of chemical engineering. We are now performing a series of experiments that are systematically organized and could improve our model. The key parameters varied in the experiments are the bed length, water flow rate, initial concentration of Sr^{2+}, and operating temperature. Tests of other solute species are also undertaken. A lower temperature and solute molecules which are more strongly adsorbed on the sites (that is, a higher value of T_c) may lead to cases of $\alpha_1 < 1$. It is worthwhile to measure the response for a much longer time ($>10^4$ min). We expect that our model can be applied to such subjects as the transport phenomena inside the porous polymeric membranes and porous glasses, the migration of radioactive nuclides through the geologic media, and the regeneration of the adsorbents. We are to investigate these applications. The details of these results will be reported later.

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Notation

C_{out} = concentration of Sr^{2+} at the outlet of the bed, ppm
D = mixing diffusion coefficient, m^2/s
E = activation energy for the desorption defined for a site, J/mol
$g(V)$ = distribution function for volume defined for dead-end pores or spaces, $1/m^3$
$h(u)$ = distribution function for desorption rate constant defined for adsorption sites, s
L = length of the media, m
$n(x, t)$ = total solute molecule density at point x in the media at time t, mol/m^3
$P(x, t)$ = density of solute molecules moving with the fluid flow at point x in the media at time t, mol/m^3
$P_i(x, t)$ = density of solute molecules being trapped in trappers of the ith class at point x in the media at time t, mol/m^3
$q(E)$ = distribution function for activation energy defined for adsorption sites, mol/J
R = gas constant, J/(mol·K)
T = absolute temperature, K
T_c = constant in $q(E)$, K
t = time after the abrupt switch to deionized water, min
u = desorption rate constant for a solute molecule adsorbed on a site, 1/s
V = volume of a dead-end pore or space, m^3
v = drift velocity of the fluid in the backbones, m/s

Greek letters

Φ_i = overall residence-time distribution function defined for trappers of the ith class, 1/s

ϕ_1 = residence-time distribution function for a solute molecule adsorbed on a site, 1/s

ϕ_2 = residence-time distribution function for a solute molecule which stepped inside a dead-end pore or space, 1/s

ω_i = transfer rate constant for solute molecules from the fluid to trappers of the ith class, 1/s

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