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Author
Nooney, Grove C.

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ANOMALOUS DESORPTION*

Grove C. Nooney

Lawrence Berkeley Laboratory
University of California
Berkeley, California

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ABSTRACT

Diffusive desorption from certain films and fibers has been reported to proceed anomalously faster with increased external surface concentration. Such desorption requires a singular surface within the medium where the diffusion coefficient becomes zero or infinite over a certain range of concentration. This surface is located independently of external concentration and may be interpreted as delimiting a fixed skin with singular diffusion properties.

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*Work done under the auspices of the U. S. Atomic Energy Commission.

ANOMALOUS DESORPTION

Grove C. Nooney

The diffusive removal of a substance from a medium under the condition of constant exterior concentration of the substance ordinarily proceeds faster with a lower exterior concentration. Contrary behaviour has been reported[1], in which the rate of removal is anomalously increased with increased exterior concentration. This note shows that such anomalous desorption from a planar sheet requires the existence of a singular surface within the sheet where the diffusion coefficient of the sheet becomes zero or infinite over a certain range of concentration. The location of this surface in the sheet is independent of exterior concentration within the range evoking the anomalous desorption. The singular surface may be taken as the interior limit of a superficial skin on the sheet, confirming earlier intuitive conjectures about the anomaly.[1]

Consider diffusive desorption from a planar sheet extending in thickness from $x = 0$ to $x = 1$, and let $c_1(x, t)$ and $c_2(x, t)$ be the respective concentrations of diffusing substance within the sheet at point x and time t, continuous for $t > 0$, with the initial condition $c_1(x, 0) = c_2(x, 0) = 1$ for $0 \le x < 1$ and the boundary conditions of no flow through the point $x = 0$ and $c_1(1, t) = a_1 > c_2(1, t) = a_2$ for $t \ge 0$. These are the simplest boundary conditions, and they describe one-half of a sheet that is symmetrical about $x = 0$ with surfaces maintained at the same constant concentration. Suppose c_1 and c_2 to be piecewise twice continuously differentiable and to depend continuously on their boundary values.

The amount of diffusing substance remaining in the sheet between $x = 0$ and $x = y$ at time t is proportional to

$$M_i(y,t) = \int_0^y c_i(x,t)dx, \qquad i = 1, 2.$$

The assertion of anomalous desorption is that

$$M_1(1,t) < M_2(1,t) \tag{1}$$

during some period of time. This implies that there is an $x = x(t)$ for which $c_1(x,t) = c_2(x,t)$. Let $x' = x'(t)$ be the greatest such x. Necessarily $0 < x' < 1$,

$$c_1(x,t) > c_2(x,t) \quad \text{for } x' < x \leq 1, \tag{2}$$

and

$$\frac{\partial c_1(x',t)}{\partial x} \geq \frac{\partial c_2(x',t)}{\partial x} \quad . \tag{3}$$

Here and in the sequel functions are defined by continuity from the right-hand side.

Relations (1) and (2) imply

$$M_1(x',t) < M_2(x',t) . \tag{4}$$

Let $\hat{t}$ be the greatest lower bound of those t for which relation (4) holds, and let $\hat{x}$ be the limiting value of $x'(t)$ as t tends to $\hat{t}$. Then

$$M_1(\hat{x},\hat{t}) = M_2(\hat{x},\hat{t}) . \tag{5}$$

The concentrations c_i satisfy the diffusion equation,

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c_i}{\partial x}\right) , \qquad i = 1, 2 ,$$

where $D = D(x, c)$ is the non-negative diffusion coefficient, assumed piece-wise continuous in x. Then the rate of change of $M_i(x', t)$ with respect to t is

$$\frac{dM_i(x', t)}{dt} = c_i(x', t) \frac{dx'}{dt} + D[x', c_i(x', t)] \frac{\partial c_i(x', t)}{\partial x} , \quad i = 1, 2.$$

This yields

$$\frac{dM_1(x', t)}{dt} - \frac{dM_2(x', t)}{dt} = D(t) \frac{\partial c_1(x', t)}{\partial x} - D(t) \frac{\partial c_2(x', t)}{\partial x} ,$$

where $D(t) = D[x', c_1(x', t)] = D[x', c_2(x', t)]$. If $D(t)$ were neither zero nor infinite, then relation (3) would allow the conclusion,

$$\frac{dM_1(x', t)}{dt} \geq \frac{dM_2(x', t)}{dt} . \qquad (6)$$

However, relations (5) and (6) are incompatible with relation (4), and it follows that $D(t)$ is zero or infinite over some interval in t beginning at t: $t \leq t < t_o$, say. Both $\hat{t}$ and t_o depend on a_1 and a_2.

To show x' constant in that time period, apply the foregoing argument to $c_1(x, t)$ and $c_2(x, t + \Delta t)$ with the positive Δt chosen small enough so that $M_1(1, t) < M_2(1, t + \Delta t)$. The argument then proceeds virtually unchanged to the conclusion that the common value, $D[z, c_1(z, t)] = D[z, c_2(z, t + \Delta t)]$, is zero or infinite, with $z = x' + \Delta x'$, say, standing for the new value of x'. Since D is piece-wise continuous and $\Delta x'$ may be made arbitrarily small by small enough Δt, it follows that $D[x, c_1(x,t)]$ is zero or infinite over some interval $\hat{x} \le x \le \hat{x} + \Delta\hat{x}$. Since the flow, $-D\frac{\partial c_1}{\partial x}$, through $\hat{x}$ must be positive and finite, the piecewise continuity of both $\frac{\partial c_1}{\partial x}$ and D implies that $\Delta\hat{x} = 0$. Therefore, $x'(t) = \hat{x}$, and x' is constant over a time interval that may be extended to the interval $\hat{t} \le t < t_o$ by repeating the argument with successively increased values of Δt. Independence of $\hat{x}$ from the boundary values may be obtained in a similar way, by applying the original argument to the concentrations with boundary values a_1 and $a_2 + \Delta a_2$ and then repetitively extending the conclusion of independence to all boundary values within the range evoking the anomaly.

The temporal constancy means that $D(\hat{x}, c)$ is zero or infinite over some (perhaps degenerate) interval in c, $\max c_1(\hat{x}, \hat{t}) \ge c \ge \min c_1(\hat{x}, t_o)$, where the extrema are determined with respect to all a_1 and a_2 that evoke the anomalous desorption.

Thus is established as a necessary condition for anomalous desorption from a sheet that the diffusion coefficient $D(x, c)$ become zero or infinite for c within a certain interval and a fixed x. This result extends to time-dependent diffusion the existence of a singular surface in steady-state anomalous flow.[2] The same necessary condition holds for anomalous sorption, analogously defined, and for anomalous sorption and desorption from a circular cylinder (the case of filaments or fibres). Finally, the immediate extension to heat conduction allows conclusions about the anomalous effects of insulating layers.

REFERENCES

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720