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ANOMALOUS DIFFUSION-CONTROLLED EVAPORATION*

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ABSTRACT

Diffusion-controlled, steady-state evaporation through certain membranes has been reported to proceed anomalously faster into a humid than into a dry atmosphere. The diffusion coefficient of such a membrane depends explicitly on both concentration and location within the membrane. Moreover, the membrane has a skin at its evaporating surface, the non-zero thickness of which is independent of atmospheric concentration. The inner surface of the skin is characterised by the steady-state diffusion coefficient becoming zero or infinite there. Examples are given of hypothetical diffusion coefficients that yield the anomalous evaporative behavior considered.

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Consider a diffusion process that controls evaporation by delivering to the surface of a membrane a substance that evaporates therefrom into an atmosphere. Some authors, cited by Jost (1960, p. 297) and Crank (1950), report that for certain materials the steady-state rate of diffusive flow to the surface is increased by increasing the atmospheric concentration of the evaporating substance. That is, the evaporation is reported to proceed faster into a humid than into a dry atmosphere. Such diffusion behavior has defied explanation by the ordinary methods of diffusion analysis (for example, Crank 1950). This note derives necessary, qualitative conditions for the diffusion process and gives examples of hypothetical diffusion coefficients that yield anomalous diffusion behavior.

The situation may be described with reference to a membrane extending in thickness from $x = 0$ to $x = 1$. Suppose the evaporation to occur from the surface $x = 1$. Denote by $c_1(x)$ and $c_2(x)$ the continuous steady-state concentrations of the diffusing substance in the membrane with

$$c_1(0) = c_2(0) = a > c_1(1) = b_1 > c_2(1) = b_2.$$

These are the simplest boundary conditions. With the non-negative diffusion coefficient $D = D(x,c)$, c_1 and c_2 satisfy

$$D(x,c_1)\ \frac{dc_1}{dx} = -P_1 \tag{1}$$

$$D(x,c_2)\ \frac{dc_2}{dx} = -P_2\ , \tag{2}$$

where P_1 and P_2 are the respective non-negative rates of diffusive flow. The reported behavior requires $P_1 > P_2$.

Following Hartley's (1948) method for asymmetrical membranes, suppose $D(x,c) = f(x)g(c)$. Then from eq. (2) follows

$$\int_{b_2}^{a} g(c)dc \left[\int_{0}^{1} \frac{dx}{f(x)}\right]^{-1} = P_2, \qquad (3)$$

provided that both integrals exist. Increasing b_2 cannot increase the left-hand side of eq. (3), and this implies $P_1 \leq P_2$. Therefore, a diffusion coefficient yielding $P_1 > P_2$ cannot be multiplicatively separable into appropriately integrable factors of a single variable each. In particular, D cannot be a function of c alone, already shown by Crank (1950), or of x alone.

Let y be any point for which $c_1(y) = c_2(y)$. One such point is $y = 0$. Suppose that the common value $D[y,c_1(y)] = D[y,c_2(y)]$ is finite and not zero. Then, since $P_1 > P_2$, eqs. (1) and (2) show that $\frac{dc_1(y)}{dx} < \frac{dc_2(y)}{dx}$. This implies that $c_1(x) \leq c_2(x)$ for $0 \leq x \leq 1$ and contradicts the relation $b_1 > b_2$. Therefore, at some point of coincidence of c_1 and c_2, necessarily away from the evaporating surface, the diffusion coefficient is zero or infinite.

Thus, for the diffusion process here considered there is inside the membrane or on its entry surface a characteristic singular surface where the steady-state diffusion coefficient is zero or infinite. The location of this singular surface is independent of concentration at the evaporating surface within the range evoking the anomalous behavior. It follows that the membrane may correctly be considered to have a fixed skin of some thickness at the evaporating surface.

Examples: Denote by $c(x)$ the steady-state concentration and by P the corresponding rate of flow. Let $c(0) = 1$ and $c(1) = 1 - h$. Suppose $D(x,c) = 2x^{3/2}(1 - c)^{-2}$. Then $c(x) = 1 - hx^{1/2}$, and $P = h^{-1}$. For this c, $D(x,c) = 2x^{1/2}h^{-2}$, and $D(0,1) = 0$, while $\frac{dc(0)}{dx}$ is infinite. Next, suppose $D(x,c) = 2^{-1}x^{3/2}(1-c)^{-5/4}$. Then $c(x) = 1 - hx^2$, and $P = h^{-4}$. For this c, $D(x,c) = h^{-5/4}x^{-1}$, and $D(0,1)$ is infinite, while $\frac{dc(0)}{dx} = 0$. In both examples $D(x,c)$ is multiplicatively separable, but the factors are not appropriately integrable. In both examples P increases as $c(1)$ increases, imitating the reported anomaly.

The diffusion of water through a rubber membrane is anomalous in the present sense (Jost 1960, p. 298). The water-content data shown by Barrer (1951, p. 435) suggest that the steady-state diffusion coefficient of the rubber membrane is zero on the entry surface, while the steady-state concentration in the membrane resembles that of the first foregoing example.

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