ON THE FLUX OF DIFFUSING MATTER THROUGH BOUNDARIES

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Introduction. Suppose $C(x, t)$, the concentration of a substance diffusing in a slab of homogeneous material of thickness a, is determined by the system

$$\frac{\partial C}{\partial t} = K\frac{\partial^2 C}{\partial x^2}, \qquad 0 < x < a;$$

$C=C_0$ at $x=0$; $C=0$ at $x=a$ for $t>0$; $C=0$ at $t=0$.

The quantity of matter

$$Q(t) = \int_0^t \left[K\frac{\partial C}{\partial x}\right]_{x=a} dt$$

which has passed through the medium in time t approaches an asymptote of slope C_0K/a as t tends to infinity, intercepting the t-axis at a point $t'=a/6K$. This intercept has been used by Daynes [1] and Barrer [2, p. 19] as the basis of a method for obtaining the diffusion constant K. In this note we show how to calculate the slope and intercept of the asymptote in the more general case where

$$Q(t) = \int_0^t \left\{\iint_{S_0} K(u) \operatorname{grad} u\cdot ds\right\} dt \tag{1}$$

is the quantity of diffusing substance which has passed through the part S_0 of the boundary ∂R of a region R in time t and u is determined by the system

$$\operatorname{div}[K(u)\operatorname{grad} u] - \frac{\partial u}{\partial t} = \frac{\partial w}{\partial t} = f(u, w) \tag{2}$$

in R for $t>0$; $u=u_0$, $w=w_0$ in $\bar{R}$, the closure of R, at $t=0$; $u=C(x, y, z, t)$ on ∂R for $t>0$. Such systems govern the diffusion of a substance U of concentration $u(x, y, z, t)$ which diffuses through a medium in accord with Fick's first law and simultaneously interacts with an immobile phase W. If $w(x, y, z, t)$ is the local concentration of W, the principle of conservation of matter requires that u and w satisfy the differential equation

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$$\frac{\partial u}{\partial t} + \frac{\partial w}{\partial t} = \operatorname{div}[K(u) \operatorname{grad} u] \tag{3}$$

throughout the region R defined by the medium. The second equation

$$\frac{\partial w}{\partial t} = f(u, w) \tag{4}$$

describes the local law governing the rate of interchange of matter between the two phases U and W.

Calculation of the asymptote. Let D denote the open region $\{(x, y, z, t): (x, y, z) \in R, t > 0\}$ and $\bar{D}$ its closure. Suppose u and w are continuous in $\bar{D}$, while in D, $\partial w/\partial t$ is continuous, the second order space derivatives and the t-derivative of u are also continuous and these derivatives satisfy the pair of equations (3) and (4). The function $K(u)$ is assumed to be positive and have a continuous derivative for all admissible values of u. In addition, suppose u_∞, w_∞ are defined and continuous in $\bar{R}$ with continuous derivatives satisfying the system

$$\operatorname{div}[K(u_\infty) \operatorname{grad} u_\infty] = 0 = f(u_\infty, w_\infty) \tag{5}$$

in R, while u and w and their derivatives approach the corresponding values of u_∞, w_∞ and their respective derivatives at each point of R.

The flux of U over a part S_0 of the boundary ∂R is

$$F(t) = -\iint_{S_0} [K(u) \operatorname{grad} u] \cdot ds \tag{6}$$

and as t tends to infinity this approaches the constant value

$$F(\infty) = -\iint_{S_0} [K(u_\infty) \operatorname{grad} u_\infty] \cdot ds. \tag{7}$$

The amount of phase U which has passed through S_0 in time t is

$$Q(t) = \int_0^t F(\tau) d\tau = F(\infty)t - \int_0^t [F(\infty) - F(\tau)] d\tau. \tag{8}$$

It will be shown that $\int_0^t [F(\infty) - F(\tau)] d\tau$ tends to a constant A as t tends to infinity.

Let us define $\phi(x, y, z, t)$ as $\int_{u(x,y,z,t)}^{u(x,y,z,\infty)} K(\theta) d\theta$ and $\psi(x, y, z, t)$ as $\int_0^t \phi(x, y, z, \tau) d\tau$ in $\bar{D}$, so that

$$\nabla^2\psi = -\int_0^t \operatorname{div}\{K(u) \operatorname{grad} u - K(u_\infty) \operatorname{grad} u_\infty\} d\tau$$

$$(9) \qquad = -\int_0^t \left[\frac{\partial u}{\partial \tau} + \frac{\partial w}{\partial \tau}\right] d\tau$$

$$= u_0 + w_0 - u(x, y, z, t) - w(x, y, z, t)$$

in R for each value of t, while on the boundary ∂R,

$$\psi = \int_0^t \int_{u(x,y,z,\tau)}^{u(x,y,z,\infty)} K(\theta) d\theta d\tau$$

$$(10) \qquad = \left[\tau \int_{u(x,y,z,\tau)}^{u(x,y,z,\infty)} K(\theta) d\theta\right]_0^t + \int_0^t \tau K(u) \frac{\partial u}{\partial \tau} d\tau.$$

In the limit as t tends to infinity, ψ tends to a function ψ_∞ defined by the system

$$\nabla^2\psi_\infty = u_0 + w_0 - u_\infty - w_\infty \text{ in } R,$$

$$(11) \qquad \psi_\infty = \int_0^\infty \tau K(u) \frac{\partial u}{\partial \tau} d\tau \text{ on } \partial R$$

provided this last integral exists and is continuous at each point of ∂R, and the boundary is sufficiently smooth.

Now

$$\int_0^t [F(\infty) - F(\tau)] d\tau$$

$$= -\iint_{S_0} \left\{ \int_0^t [K(u_\infty) \operatorname{grad} u_\infty - K(u) \operatorname{grad} u] d\tau \right\} \cdot ds$$

$$= -\iint_{S_0} \left\{ \int_0^t \operatorname{grad} \phi d\tau \right\} \cdot ds$$

$$= -\iint_{S_0} \operatorname{grad} \psi \cdot ds$$

and as t tends to infinity, the right hand side approaches the value $-\iint_{S_0} \operatorname{grad} \psi_\infty \cdot ds$.

Summarizing these results, we see that

$$Q(t) \sim F(\infty)t - A$$

where

$$F(\infty) = -\iint_{S_0} [K(u_\infty) \operatorname{grad} u_\infty]\cdot ds$$

and

$$A = -\iint_{S_0} \operatorname{grad} \psi_\infty \cdot ds.$$

The function u_∞ is determined by the system

$$\operatorname{div}[K(u_\infty) \operatorname{grad} u_\infty] = 0 = f(u_\infty, w_\infty) \text{ in } R,$$

where on ∂R,

$$u_\infty = \lim_{t\to\infty} u(x, y, z, t) = \lim_{t\to\infty} C(x, y, z, t),$$

while the function ψ_∞ satisfies

$$\nabla^2\psi_\infty = u_0 + w_0 - u_\infty - w_\infty \text{ in } R,$$

and the boundary conditions

$$\psi_\infty = \int_0^\infty \int_{u(x,y,z,\tau)}^{u(x,y,z,\infty)} K(\theta)d\theta d\tau = \int_0^\infty \tau K(u) \frac{\partial u}{\partial \tau} d\tau$$

on ∂R.

In the case where S_0 coincides with the whole surface ∂R, an application of the divergence theorem shows that

$$A = \iiint_R [u_\infty - u_0 + w_\infty - w_0]dV,$$

as one would expect from the conservation principle. If $u_\infty = w_\infty = 0$, ψ_∞ is determined by the initial values of u and w and the boundary values of u, so that the total quantity of diffusing matter which flows over any part S_0 of the boundary ∂R is independent of the function $K(u)$. In particular, if a hollow cylinder is saturated under a boundary concentration C_0 and then removed from the saturating environment, the proportion of its contents which flow through the internal cylindrical boundary is independent of $K(u)$ and the function $f(u, w)$ describing the interaction between the phases u and w.

As an example of this method, suppose

$$\frac{\partial}{\partial x}\left[K(u) \frac{\partial u}{\partial x}\right] = \frac{\partial u}{\partial t}, \qquad 0 < x < a,$$

and u satisfies the boundary conditions $u = 0$ at $t = 0$ on $(0, a)$, while

$u = C_0$ at $x = a$ and $u = 0$ at $x = 0$ for all $t > 0$. The time integral of the flux through unit area of the face at $x = 0$ is asymptotic to $F(\infty)t - A$. Since

$$\frac{\partial}{\partial x}\left[K(u_\infty)\frac{\partial u_\infty}{\partial x}\right] = 0,$$

we see that

$$\int_0^{u_\infty} K(\theta)d\theta = \frac{b}{a}x \quad \text{where} \quad b = \int_0^{C_0} K(\theta)d\theta,$$

and hence

$$F(\infty) = \left[K(u_\infty)\frac{\partial u_\infty}{\partial x}\right]_0 = \frac{b}{a} = \int_0^{C_0}\frac{K(\theta)}{a}\,d\theta.$$

Again,

$$\frac{\partial^2 \psi_\infty}{\partial x^2} = -u_\infty, \text{ in } (0, a),$$

while $\psi_\infty = 0$ at $x = 0$ and $x = a$ and therefore

$$\psi_\infty = -\int_0^x (x - z)u_\infty(z)dz + \frac{x}{a}\int_0^a (a - z)u_\infty(z)dz,$$

$$A = \left[\frac{\partial \psi_\infty}{\partial x}\right]_0 = \frac{1}{a}\int_0^a (a - z)u_\infty(z)dz = \frac{1}{2a}\int_0^{C_0} (a - z)^2 du_\infty$$

$$= \frac{a}{2}\int_0^{C_0}\left[1 - \left(\int_0^{u_\infty} K(\theta)d\theta \Big/ \int_0^{C_0} K(\theta)d\theta\right)\right]^2 du_\infty.$$

Evidently $C_0 a/2 > A > 0$.

Let us finally note that the method depends on the fact that u satisfies a conservation law of the form $\nabla^2\phi = \partial q/\partial t$ where ϕ is a known function of u, while q is given initially and at $t = \infty$ and u has known values on ∂R.

References

1. H. Daynes, *Process of diffusion through a rubber membrane*, Proc. Roy. Soc. 97A (1920), 286.

2. R. M. Barrer, *Diffusion in and through solids*, Chapter 1, Cambridge Univ. Press, New York, 1941.

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