DIFFUSION ALONG INTERFACES UNDER EXTERNAL FORCES

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A solution is given for an equation of parabolic type describing diffusion along interfaces under external forces, one of the coefficients being a function of time. A particular case of this solution is considered in which diffusion occurs along grain boundaries in response to external forces.

Fisher's model [1] is used for diffusion in a semiinfinite crystal with grain boundaries of width 2δ, which are perpendicular to the surface of the specimen; then

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - w\frac{\partial c}{\partial x} - \frac{2D_v}{\delta}\left(\frac{\partial c_v}{\partial y}\right)_{y=0},$$
$$\frac{\partial c_v}{\partial t} = D_v\frac{\partial^2 c_v}{\partial y^2} \qquad (D \gg D_v). \tag{1}$$

Here D and D_v are the diffusion coefficients at the boundary and in the volume, c(x, t) and $c_v(y, t)$ are the concentrations in those places, and w is the rate of transfer of the diffusing particles produced by the external forces.

The first equation in (1) describes the distribution at the boundary, the third term representing withdrawal of the material from the boundary into the volume, which is described by the second equation in (1). The boundary conditions for (1) are

$$c(0, t) = c_0, \qquad c(\infty, t) = 0, \qquad c(x, 0) = 0, \tag{2}$$
$$c_v(0, t) = c(x, t), \qquad c_v(\infty, t) = 0, \qquad c_v(y, 0) = 0. \tag{3}$$

Then, if that withdrawal occurs in accordance with the law for a fixed source [1, 2], we may put

$$\frac{2D_v}{\delta}\left(\frac{\partial c_v}{\partial y}\right)_{y=0} = f(t)\,c(x, t). \tag{4}$$

Then the first equation in (1) becomes

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - w\frac{\partial c}{\partial x} - f(t)\,c \tag{5}$$

and is solved subject to Eq. (2).

A solution to this problem has been sought [1, 2] on the assumption that dc/dt = 0 for t large, which restricts the range of application of the solution. The substitution [3]

$$c(x, t) = u(x, t)\exp\left(\frac{wx}{2D} - \frac{w^2 t}{4D}\right) \tag{6}$$

reduces Eq. (5) to

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2} - f(t)\,u \tag{7}$$

subject to the boundary and initial conditions

$$u(0, t) = c_0\exp(w^2 t/4D),$$
$$u(\infty, t) = 0, \qquad u(x, 0) = 0. \tag{8}$$

We solve Eq. (7) subject to Eq. (8) via a Fourier sine transformation [4]:

$$\Phi_s(\xi, t) = \left(\frac{2}{\pi}\right)^{1/2}\int_0^\infty u(x, t)\sin\xi x\,dx,$$
$$u(x, t) = \left(\frac{2}{\pi}\right)^{1/2}\int_0^\infty \Phi_s(\xi, t)\sin\xi x\,d\xi. \tag{9}$$

Then Eq. (7) becomes

$$\frac{\partial\Phi_s}{\partial t} = \left(\frac{2}{\pi}\right)^{1/2} Dc_0\xi\exp\frac{w^2 t}{4D} - \xi^2 D\Phi_s - f(t)\,\Phi_s. \tag{10}$$

The solution to this inhomogeneous differential equation is

$$\Phi_s(\xi, t) = \left(\frac{2}{\pi}\right)^{1/2} Dc_0\xi\exp\left[-\xi^2 Dt - \int_0^t f(\lambda)\,d\lambda\right]\int_0^\infty \times$$
$$\times\exp\left[\frac{w^2\lambda}{4D} + \xi^2 DA + \int_0^\lambda f(\alpha)\,d\alpha\right]d\lambda. \tag{11}$$

We apply to Eq. (11) the reverse Fourier transformation of Eq. (9) to get

$$u(x, t) = \frac{c_0 x}{2\sqrt{\pi D}}\exp\left[-\int_0^t f(\lambda)\,d\lambda\right]\int_0^\infty \times$$
$$\times\exp\left[\frac{w^2\lambda}{4D} + \int_0^\lambda f(\alpha)\,d\alpha - \frac{x^2}{4D(t-\lambda)}\right]\frac{d\lambda}{(t-\lambda)^{3/2}}. \tag{12}$$

Use of Eqs. (12) and (6) gives

$$c(x, t) = \frac{c_0 x}{2\sqrt{\pi D}}\exp\left[-\int_0^t f(\lambda)\,d\lambda + \right.$$
$$\left. + \frac{wx}{2D}\right]\int_0^t \exp\left[-\frac{w^2(t-\lambda)}{4D} - \right.$$
$$\left. - \frac{x^2}{4D(t-\lambda)} + \int_0^\lambda f(\alpha)\,d\alpha\right]\frac{d\lambda}{(t-\lambda)^{3/2}}. \tag{13}$$

We make the change of variable $\xi = {}^1/_2\, x / \sqrt{D(t-\lambda)}$ to get

$$c(x, t) = \frac{2c_0}{\sqrt{\pi}}\int_{x/2\sqrt{Dt}}^\infty \times$$
$$\times\exp\left[-\int_{t-x^2/4D\xi^2}^t f(\lambda)\,d\lambda - \left(\xi - \frac{wx}{4D\xi}\right)^2\right]d\xi. \tag{14}$$

This solution satisfies the conditions of Eq. (2); it takes no account of the effects of the external field on the diffusion in the volume, since the transport rate in the volume is less than that at the boundary by several orders of magnitude.

The complexity of Eq. (14) is due to the general form of $f(t)$, which takes account of boundary geometry, diffusion from the boundary into the volume, etc. The solution may be simplified considerably for particular cases. For instance, for diffusion at a plane boundary [2] we have $f(t) = \sqrt{D_v / y^2 t}$, and Eq. (14) becomes

$$c(x, t) = \frac{2c_0}{\sqrt{\pi}}\int_{x/2\sqrt{Dt}}^\infty \exp\left[-\frac{2\sqrt{D_v t}}{\delta} + \right.$$
$$\left. + \frac{2}{\delta}\left(D_v t - \frac{x^2 D_v}{4D\xi^2}\right)^{1/2} - \left(\xi - \frac{wx}{4D\xi}\right)^2\right]d\xi. \tag{15}$$

Usually, D_v is determined independently, so D and w may be determined by the method of standard curves, which are constructed by computer methods.

REFERENCES

1. J. C. Fisher, "Calculation of diffusion penetration curves for surface and grain boundary diffusion," J. Appl. Phys., vol. 22, no. 1, 1951.

2. S. M. Klotsman, A. N. Timofeev, and I. Sh. Trakhtenberg, "Intercrystallite self-diffusion of silver in an electric field," Fiz. tverd. tela, 5, no. 11, 1963.

3. A. Einstein and M. Smoluchowski, Brownian Motion [Russian translation], ONTI, 1963.

4. E. C. Titchmarsh, Introduction to the Theory of Fourier Integrals [Russian translation], Gostekhizdat, 1948.

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