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Nonlinear Diffusion of Vacancies in a Crystal

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The correlated motion of vacancies breaks the translational symmetry of the jump probability if the concentraton of the vacancies varies from place to place. This leads to a significant deviation from the result of linear diffusion theory. The problem is treated by using the model of a generalized random walk in which the probabilities of a jump by the walker depend on the position.

The commonly assumed basic equation governing a diffusion is Fick's law,

$$j = -D_0 \frac{\partial c}{\partial x} \tag{1}$$

where j is the flux density and c the concentration; D represents the diffusion coefficient (see Manning, 1968, 1973, and Peterson, 1968). The relation (1) is valid when the concentration c and its gradient $\partial c/\partial x$ are both very small. In certain practical cases, a finite concentration gradient may be maintained in a finite region. For example, let us consider a steady-state diffusion across two parallel boundaries as shown in Figure 1. Two different concentrations are kept at c_1 and c_2 at the outer sides of the two boundaries. The concentration in between may or may not be the straight (dotted) line AB. The phenomenological studies (Barrer, 1946; Ash and Barrer, 1971; see also Crank, 1975) showed that the concentration calculated in terms of Fick's law

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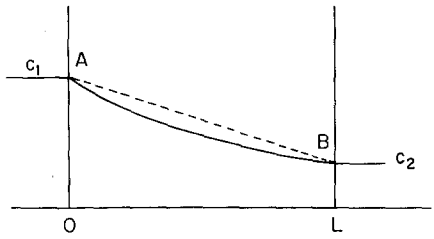

Fig. 1. A steady-state diffusion is maintained across two membranes separated by the distance L. The dotted line AB corresponds to the linear diffusion and deviations from it represent a nonlinear behavior.

must follow the straight line. Any deviations from it should come from nonlinear effects. In the present paper we will report a source of nonlinear effect on a vacancy diffusion in which a deviation from Fick's law is realized.

In Figure 2 three vacant sites are shown in a periodic lattice. The motion of the molecules generates that of the vacancies. If the concentration changes from place to place, the motion of the vacancies will be such that the difference in concentration will become smaller and smaller.

When the concentration of vacancies is large the motion of the vacancies will be correlated. At a higher concentration, the movement of vacancies may become easier, and therefore the rigidity of the lattice may be reduced; we may also say that the probability of a jump by vacancy will become greater. This dependence of the jump probability on the concentration generates the position dependence if the concentration gradient exists in the system. This may best be understood by drawing an energy barrier diagram (LeClair, 1958). If the vacancy concentration is uniform, the energy barrier will be symmetric at each site, as shown in Figure 3a. If the concentration is higher on the left than on the right, the barrier height will be unequal and depend on the site, as indicated in Figure 3b; the probability of a jump toward the right will be less than that toward the left.

In order to treat the problem in a systematic manner, let us introduce an extended model of random walk (Uhlenbeck and Ornstein, 1930; Chandrasekhar, 1943). A walker (vacancy) at the site m may take a step to the right and reach the site $m + 1$ with the probability p_m; it may take a step to the

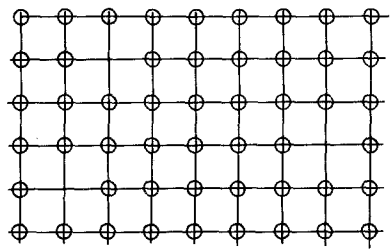

Fig. 2. Three vacancies are shown in a lattice.

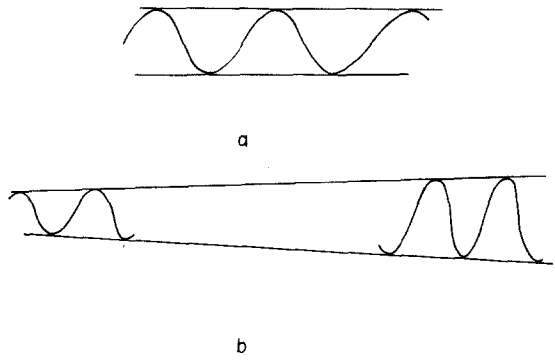

Fig. 3. The energy barriers are shown for a homogeneous (a) and inhomogeneous (b) system.

left with the probability q_m; or it may remain at the same site with the probability r_m. The normalization requires that

$$p_m + q_m + r_m = 1 \tag{2}$$

Here it is noted that the *probabilities depend on site m*, and also that explicit introduction of the *staying probability* r_m is essential in the following discussions.

Let $W(m, N)$ be the probability that the walker, starting from the origin O, reaches the site m after N unit times. It is easily verified that W's satisfy the following equations:

$$W(m, N) = p_{m-1}W(m-1, N-1) + q_{m+1}W(m+1, N-1) + r_m W(m, N-1) \tag{3}$$

and

$$\begin{aligned} W(0, 0) &= 1 \\ W(m, N) &= 0 \qquad \text{for } N < |m| \end{aligned} \tag{4}$$

Let a be the lattice spacing and t_0 be the unit time interval; $Nt_0 \equiv t$ will denote the elapsed time, and $x \equiv ma$ the displacement after N moves. We now consider the limits in which

$$\begin{aligned} a &\to 0, \qquad t_0 \to 0 \\ m &\to \infty, \qquad N \to \infty \end{aligned} \tag{5}$$

such that

$$\begin{aligned} x = ma &= \text{finite} \\ t = Nt_0 &= \text{finite} \\ a^2/t_0 &= \text{finite} \end{aligned} \tag{6}$$

In these limits, we may introduce continuous functions:

$$W(m, N) \to w(x, t)$$
$$p_m \to p(x), \qquad q_m \to q(x), \qquad r_m \to r(x) \tag{7}$$

We obtain from (3) and (4)

$$\frac{\partial w(x, t)}{\partial t} = -\frac{\partial}{\partial x}[M_1(x)w(x, t)] + \frac{\partial^2}{\partial x^2}[M_2(x)w(x, t)] \tag{8}$$

$$M_1(x) \equiv \frac{a}{t_0}[p(x) - q(x)]$$
$$M_2(x) \equiv \frac{a^2}{t_0}[p(x) + q(x)] \tag{9}$$

$$w(x, 0) = \delta(x)$$
$$w(\infty, t) = 0 \tag{10}$$

Equation (8) is a generalized Fokker–Planck equation with the position dependence of M_1 and M_2 arising from the position dependence of the jump probabilities.

In the absence of a concentration gradient, the probabilities of jumps are given by

$$p = q = \text{const.} \times \exp(-Q/kT) \tag{11}$$

where Q is the activation energy for a jump (see, e.g., Manning, 1968). For a finite (constant) gradient the activation energy will have a term linear in the position, as seen from Figure 3b. Thus, the energy to be overcome by a vacancy moving right and left may be represented by $Q - bx$ and $Q + bx$, respectively, where b may be taken as a constant proportional to the concentration gradient

$$b \propto \frac{\partial c}{\partial x} \tag{12}$$

The linear correction term tends to zero as the gradient disappears (as it should). We may therefore assume that

$$p(x) = \text{const.} \times \exp[(-Q + bx)/kT]$$
$$q(x) = \text{const.} \times \exp[(-Q - bx)/kT] \tag{13}$$

That is, due to the correlation of the vacancy movement, the probabilities of jumping toward the right and toward the left are no longer equal to each other.

It is well known that the concentration $c(x, t + \Delta t)$ of vacancies at

position x and time $t + \Delta t$ is related to that at position $x - \Delta x$ and time t by (see Manning, 1968)

$$c(x, t + \Delta t) = \int P(x; \Delta x, \Delta t) c(x - \Delta x, t) d(\Delta x) \tag{14}$$

where $P(x; \Delta x, \Delta t)$ is the probability of the transition from $(x - \Delta x, t)$ to $(x, t + \Delta t)$. Expanding both sides of equation (14) around $\Delta x = 0$ $\Delta t = 0$, and retaining the lowest order term in Δt, we obtain

$$\frac{\partial c(x, t)}{\partial t} = \sum_{s=1} \frac{1}{s!} \left(-\frac{\partial}{\partial x} \right)^s [K_s(x) c(x, t)]$$

$$\equiv -\frac{\partial}{\partial x} J(x, t) \tag{15}$$

where

$$K_s(x) \equiv \langle (\Delta x)^s \rangle \equiv \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int (\Delta x)^s P(x; \Delta x, \Delta t) d(\Delta x) \tag{16}$$

$$J(x, t) = -A(x) c(x, t) - D(x) \frac{\partial c(x, t)}{\partial x} \tag{17}$$

$$A(x) = K_1(x) - \frac{1}{2'} \frac{\partial K_2(x)}{\partial x} + 0\left(\frac{\partial^2 K_3}{\partial x^2} \right) \tag{18}$$

$$D(x) = -\tfrac{1}{2} K_2(x) + 0\left(\frac{\partial K_3}{\partial x} \right) \tag{19}$$

We note that part of the flux generated by the density gradient $\partial c / \partial x$, that is, the second term in (17), is given by

$$-D(x) \frac{\partial c}{\partial x} \equiv \tilde{J}(x, t) \tag{20}$$

This takes the form of a generalized Fick's law with a position-dependent "apparent" diffusion factor $D(x)$.

For the vacancy motion, we may assume that

$$P(x; \Delta x, \Delta t) = W(\Delta x, \Delta t) \tag{21}$$

Then, by using the formal solution of (8):

$$W(x, t) = e^{-\hat{L}t} \delta(x) \tag{22}$$

$$\hat{L} = \frac{\partial}{\partial x} M_1(x) + \frac{\partial^2}{\partial x^2} M_2(x) \tag{23}$$

we can evaluate the moments K_s in (16), and obtain

$$K_1 = M_1, \qquad K_2 = -2M_2 \tag{24}$$
$$K_n = 0, \qquad n \geqslant 3$$

The expression $D(x)$ can be expressed as

$$D(x) = D_0[1 + f(x)] \tag{25}$$

where

$$D_0 = \frac{1}{2}\frac{a^2}{t_0} \tag{26}$$

$$f(x) = \frac{1/2(e^{bx/kT} + e^{-bx/kT})}{1 + e^{bx/kT} + e^{-bx/kT}} \tag{27}$$

where $f(x)$ is chosen so that D is reduced to

$$D_0 \text{ at } x = 0 \qquad \text{(point A in Figure 1)}$$

Following Barrer's treatment (Barrer, 1946), we can now study the steady-state diffusion. The steady-state concentration is found to be depressed, as indicated by the full line, the degree of depression depending on the value of b. Figure 4 shows concentration $c(x)$ for steady state which is obtained from the equation specified by (25).

It is emphasized that since b is proportional to the gradient $\partial c/\partial x$, $D(x)$ describes a situation that is highly nonlinear. In fact, D contains terms of

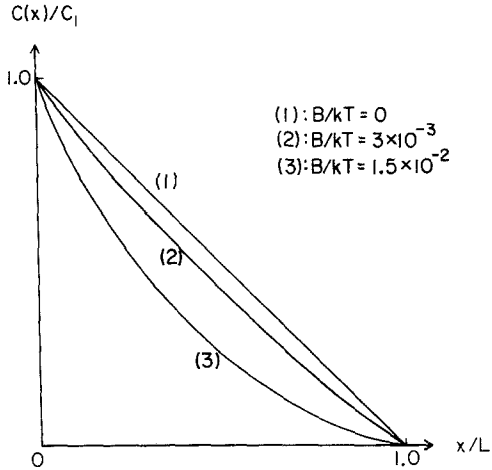

Fig. 4. Steady-state concentration. Here for simplicity we put $c_2 = 0$ and $B = bL$. Note that $B/kT = 0$ represents the simple Fick's law.

indefinite orders in $\partial c/\partial x$ since $b(\propto \partial c/\partial x)$ enters in the exponential in (27). The nonlinearity itself, however, simply arises from the assumed correlation of the vacancy motion characterized by the single parameter b.

Unfortunately, experimental data directly comparable with the present theory are not available at the present time. However, our theory clearly points out a source of possible nonlinearities arising from the correlated motion of the vacancies.

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