

1 Atomic diffusion on surfaces

One important reason surface diffusion is of interest is that it is so different from diffusion in bulk solids, and is involved in many important processes – among them crystal and film growth as well as evaporation, chemical surface reactions, catalysis, and condensation. However, before becoming intimately involved in the description of surface events, it will be useful to outline the formalism that describes diffusion on surfaces.

1.1 Diffusivities: an introduction

To describe diffusion on a crystal surface it is convenient to adapt the procedures developed for bulk diffusion [1]. The flux J crossing a line of unit length is given by Fick's first law

$$J = -D \partial c / \partial x, \tag{1.1}$$

where $\partial c / \partial x$ gives the gradient of the concentration c and D is the diffusivity; the diffusivity establishes the magnitude of the flux in relation to the gradient, and is generally given in units of cm^2/sec . Establishing a known gradient of the concentration on a surface, and measuring the flux J are difficult, and it is therefore useful to transform Eq. (1.1). Consider two parallel lines on a surface, shown in Fig. 1.1, a distance of Δx apart, which is comparable with the jump length ℓ executed in diffusion. The flux into line 1 will be different from that into line 2, as material accumulates in the region between the two lines. If the flux is considered per unit length, then

$$J_1 = J_2 - \partial J / \partial x \Delta x. \tag{1.2}$$

The difference in the flux to the two lines can obviously be written as

$$J_1 - J_2 = -\partial J / \partial x \Delta x, \tag{1.3}$$

that is in terms of the amount of material accumulated, so that

$$J_1 - J_2 = -\partial J / \partial x \Delta x = \partial c / \partial t \Delta x. \tag{1.4}$$

However, from Eq. (1.1) we know that

$$\partial J / \partial x = -\partial (D \partial c / \partial x) / \partial x, \tag{1.5}$$

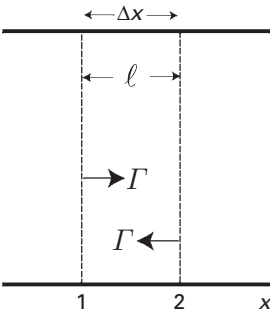


Fig. 1.1 Schematic illustrating atomic jumps at rate Γ per atom in surface diffusion. Jump length = ℓ .

and therefore

$$\partial c/\partial t = \partial(D \partial c/\partial x)/\partial x. \tag{1.6}$$

This is Fick’s second law, more directly applicable to examining surface diffusion. We will generally consider here diffusion of single atoms over a crystal plane, so that the diffusivity D will not be a function of the concentration, and Eq. (1.6) can therefore be written as

$$\partial c/\partial t = D \partial^2 c/\partial x^2. \tag{1.7}$$

Note that we have only considered one-dimensional diffusion, with the flux as well as the gradient along the x -axis, but this will suffice for our problems.

One possible way of looking at diffusion is to deposit a line of m_a atoms on a surface, and to examine how the deposited material spreads out with time. The solution of Eq. (1.7) for this case is

$$c(x, t) = \frac{m_a}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right), \tag{1.8}$$

where x is the distance normal to the initial deposit, and t indicates the length of the diffusion time interval; the solution is shown in Fig. 1.2a. Equation (1.8) can be readily confirmed by differentiating $c(x, t)$ with respect to both x and t . The boundary conditions here are that at $x=0$, $c \rightarrow \infty$ and for $|x| > 0$ as $t \rightarrow 0$, $c \rightarrow 0$.

If instead of just a line, a part of the entire crystal surface can be covered with adsorbed material, as in Fig. 1.2b; boundary conditions now are that with the border of material at $x=0$, $c=c_o$ for $x > 0$, and $c=0$ for $x < 0$, both with $t=0$. The covered region can be considered as an array of adjacent lines at a separation z . We just integrate the answer in Eq. (1.8) to give

$$c(x, t) = \frac{c_o}{\sqrt{4\pi Dt}} \int_0^\infty \exp\left[-\frac{(x-z)^2}{4Dt}\right] dz. \tag{1.9}$$

If we let $u = \frac{x-z}{\sqrt{4Dt}}$, then

1.1 Diffusivities: an introduction

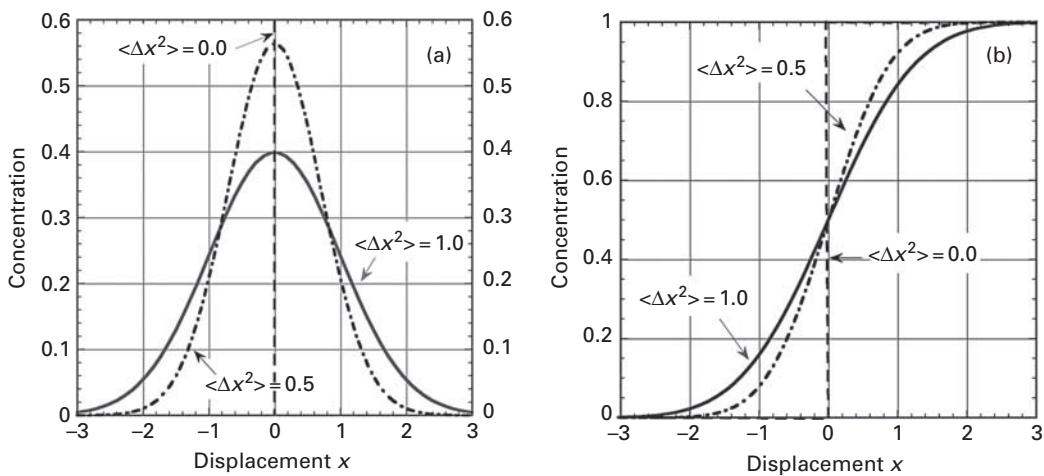


Fig. 1.2 Concentration profiles established in diffusion for different mean-square displacements. (a) Spreading from an initial straight-line deposit. (b) Spreading out of a half-covered surface.

$$c(x, t) = \frac{c_o}{\sqrt{\pi}} \int_{-\infty}^{\frac{x}{\sqrt{4Dt}}} \exp(-u^2) du. \tag{1.10}$$

Inasmuch as the error function is given by

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-u^2) du, \tag{1.11}$$

and $\operatorname{erf}(-\infty) = -1$, the solution can be more simply written as

$$c(x, t) = \frac{c_o}{2} \left[1 + \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right) \right]. \tag{1.12}$$

Spreading will yield a gradually diminishing boundary region, as shown in Fig. 1.2b.

An alternative geometry for observing atomic diffusion is to deposit a circular spot containing m_a atoms and to study spreading from it. The solution to the diffusion equation then is

$$c(R_r, t) = \frac{m_a}{4\pi Dt} \exp\left(-\frac{R_r^2}{4Dt}\right), \tag{1.13}$$

where R_r gives the distance from the center of the original deposit.

As a final example, consider the spreading of a deposit from the front of a ribbon of width d to the initially clean back. In this finite system we have the initial condition that at $t=0$, $c=c_o$ for $0 < x < d$, and $c=0$ for $d < x < w$, where $w > d$. The solution to the diffusion equation under these circumstances, given by Barrer [2], is

$$c(x, t) = c_o \left\{ \frac{d}{w} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi d}{w} \cos \frac{n\pi x}{w} \exp\left(-\frac{n^2 \pi^2}{w^2} Dt\right) \right\}. \tag{1.14}$$

By measuring the spreading as a function of time and position, values of $c(x,t)$ can be established experimentally. The diffusivity is then obtained by fitting the appropriate solution to the measured concentration profile. It is clear that here we have covered only the simplest examples useful in studies of surface diffusion. More complicated ones are described by Crank [1]. It should also be noted that under many conditions these approaches are not at all easy to implement.

With a value of the diffusivity in hand, the question arises immediately how to interpret the diffusivity D in terms of the atomic jump processes. We follow here the approach pioneered by Einstein [3]. Consider a surface of unit width, with a uniform concentration gradient in the x direction. Atoms jump in the x direction at the rate Γ per atom, and in the $-x$ direction at the same rate. We now draw two lines perpendicular to the x -axis as was done in Fig. 1.1; the second is separated from the first by a distance equal to the jump length ℓ executed by an atom in diffusion. The rate at which atoms cross line 1 is $m_1\Gamma$, and line 2 is $m_2\Gamma$ where m_1 and m_2 are the number of atoms per unit length. The net rate at which atoms are transferred to the right will be given by

$$m_1\Gamma - m_2\Gamma = \Gamma(m_1 - m_2); \tag{1.15}$$

that is, the flow to the right from line 1 is compensated to some extent by the flow to the left from line 2. The number of atoms m_a can be related to the surface concentration by $m_a = c\ell$, so that the net flux J becomes

$$J = (c_1 - c_2)\ell\Gamma. \tag{1.16}$$

Now $c_1 = c_2 - \ell\partial c/\partial x$, so that

$$J = -\ell^2\Gamma\partial c/\partial x. \tag{1.17}$$

From Eq. (1.1) it follows that

$$D = \Gamma\ell^2, \tag{1.18}$$

and we see that the diffusivity is just given by the product of the jump rate Γ per atom in one direction times the square of the jump length. For a more realistic view of diffusion, ℓ should of course be taken as the square root of the average of the squares of the individual displacements.

For the jump rate Γ per atom that has entered here we can write the expression available from transition state theory for the rate of overcoming a potential barrier of height W [4],

$$\Gamma = \nu \exp\left(-\frac{W}{kT}\right), \tag{1.19}$$

where ν accounts for the vibrational frequencies of the system, known also as attempt frequency. The diffusivity D can therefore be written as

$$D = \nu\ell^2 \exp\left(-\frac{W}{kT}\right). \tag{1.20}$$

Here W is really a free energy change ΔF between the top of the potential and the atom in its equilibrium position, but confined to a plane perpendicular to the diffusion path. Since $\Delta F = \Delta E - T\Delta S$, the diffusivity becomes

$$D = v\ell^2 \exp\left(\frac{\Delta S_D}{k}\right) \exp\left(-\frac{\Delta E_D}{kT}\right). \tag{1.21}$$

The usual approximation is that v , ℓ , and ΔS_D are not strongly dependent upon the temperature T , so that a plot of $\ln(D)$ versus $1/T$ will provide us with ΔE_D , the activation energy for diffusion, as the slope and the logarithm of $v\ell^2 \exp\left(\frac{\Delta S_D}{k}\right)$ as the y -intercept of the diffusivity D , with ΔS_D as the change in the entropy in diffusion. It is customary to write

$$v \exp\left(\frac{\Delta S_D}{k}\right) = v_0 \tag{1.22}$$

as we often have some idea about the expected jump length ℓ , and D can be more briefly written as

$$D = D_o \exp\left(-\frac{\Delta E_D}{kT}\right), \text{ with } D_o = v_0 \ell^2. \tag{1.23}$$

where D_o is known as the prefactor for the diffusivity.

A somewhat different formulation has been offered by Kürpick *et al.* [5], who considered the transfer of an otherwise unconstrained atom from a normal site to the top of the barrier peak, where the degree of freedom in the direction of diffusion is withdrawn from the free energy. She arrived at an expression for the diffusivity as

$$D = D_o \exp\left(-\frac{\Delta\Phi}{kT}\right), \tag{1.24}$$

where $\Delta\Phi$ is the difference in the structural energy of the system between the barrier peak and the normal minimum. The prefactor, itself a function of the temperature T , is given by

$$D_o = \frac{kT}{h} \ell^2 \exp\left(\frac{\Delta S_{vib}}{k}\right) \exp\left(-\frac{\Delta E_{vib}}{kT}\right). \tag{1.25}$$

Here ΔS_{vib} and ΔE_{vib} give the difference between the peak maximum and the minimum in vibrational contributions to the entropy and the internal energy, which have been evaluated by Kürpick [6].

It is useful to establish another connection between diffusivity and jump length, as the standard approaches for evaluating diffusivities are often difficult to carry out. We therefore evaluate the distance covered by a long sequence of N transitions, where $N = 2\Gamma t$. If transition i gives a vector displacement x_i , then the overall displacement $x(N)$ will be

$$x(N) = x_1 + x_2 + x_3 + \cdots + x_N = \sum_{i=1}^N x_i. \tag{1.26}$$

On squaring the above we get

$$x^2(N) = \sum_{i=1}^N x_i^2 + 2 \sum_{i=1}^{N-j} \sum_{j=1}^{N-1} x_i x_{i+j}. \quad (1.27)$$

Averaging $x^2(N)$ causes the second term on the right to disappear: in a random displacement there is no relation between one jump and the next, so positive and negative transitions are equally probable. The mean-square displacement therefore becomes

$$\langle x^2(N) \rangle = \sum_{i=1}^N x_i^2 = N\ell^2, \quad (1.28)$$

where the mean-square jump length ℓ^2 is given by

$$\ell^2 = \frac{1}{N} \sum_{i=1}^N x_i^2. \quad (1.29)$$

That is, the mean-square displacement is just equal to the total number of jumps times the square of the jump length.

The same result can be obtained in a slightly different way given by Berg [7] for a system of M particles. Consider the x -displacement after n jumps, $x(n)$; this is related to the displacement that has occurred previously by

$$x_i(n) = x_i(n-1) \pm \ell, \quad (1.30)$$

where ℓ is the length of the displacement. For the mean value of $x(n)$ we obtain

$$\langle x(n) \rangle = \frac{1}{M} \sum_{i=1}^M [x_i(n-1) \pm \ell] = \frac{1}{M} \sum_{i=1}^M x_i(n-1) = \langle x(n-1) \rangle. \quad (1.31)$$

The mean location does not change as the number of steps changes, so that a particle starting at $x = 0$ will remain there. The mean value $\langle x(n) \rangle$ is therefore zero. For the square of the displacement we find

$$x_i^2(n) = x_i^2(n-1) \pm 2\ell x_i(n-1) + \ell^2, \quad (1.32)$$

and the mean-square displacement is given by

$$\langle x^2(n) \rangle = \frac{1}{M} \sum_{j=1}^N x_j^2(n) = \frac{1}{M} \sum_{j=1}^N [x_j^2(n-1) \pm 2\ell x_j(n-1) + \ell^2]. \quad (1.33)$$

However, the second term under the brackets at right disappears, as positive and negative terms balance out, so that

$$\langle x^2(n) \rangle = \langle x^2(n-1) \rangle + \ell^2. \quad (1.34)$$

When $n=0$, $x(n)=0$, so that $x^2(1) = \ell^2$, $x^2(2) = 2\ell^2$, and $x^2(n) = n\ell^2$. Therefore,

$$\langle x^2(n) \rangle = n\ell^2, \quad (1.35)$$

as has already been demonstrated. We have previously shown in Eq. (1.18) that $D = \Gamma\ell^2$; but $\langle x(n) \rangle = 0$ and it follows from Eq. (1.28) that $\Gamma\ell^2 = \langle x^2 \rangle / 2t$, so that

$$\langle \Delta x^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 = 2Dt, \quad (1.36)$$

the Einstein relation. In other words, the diffusivity can be derived directly from measurements of the displacement fluctuation or dispersion $\langle \Delta x^2 \rangle$.

We are also going to be interested in the atomic jump processes participating in diffusion. To learn more about these involves just a slight extension – looking in detail at the distribution of atomic displacements. This will be done in various ways in what follows.

1.2 Distribution of atomic displacements

With diffusivities known from measured displacement fluctuations, what can we learn about the atomic jumps contributing to diffusion over a crystal surface? To pursue this question, we will adopt a more detailed view, and explicitly consider diffusion as arising from the movement of atoms or particles; this will involve us in a little more elementary mathematics.

1.2.1 Binomial distributions

Assume that a particle makes a total of N independent, uncorrelated steps, each of length ℓ along an infinite straight line [8]. All jumps take place at the same time interval. We seek the probability p_x that the particle, having started at the origin, will end at position $x = s\ell$, but for the sake of simplicity we will assume the nearest-neighbor jump length to be unity. If the probability of a jump to the right is p and that for a jump to the left is q , then the likelihood of one configuration of n_1 jumps to the right and $N - n_1$ to the left is $p^{n_1} q^{N-n_1}$. Note that $p + q = 1$. How many different independent configurations are there for reaching the endpoint $s\ell$?

The first jump can be assigned in N ways on an empty line, the second in $N - 1$, and so on. In total we therefore have $N!$ different choices. However, the selections for the n_1 steps to the right all lead to the same result, and there are $n_1!$ different arrangements for such steps. The same can be said about the $N - n_1$ steps to the left, which can be picked in $(N - n_1)!$ different ways giving the same effect. The total number of different configurations is therefore

$$\frac{N!}{n_1!(N - n_1)!} \tag{1.37}$$

The probability of reaching the point s after n_1 steps to the right becomes

$$p_{n_1} = \frac{N!}{n_1!(N - n_1)!} p^{n_1} q^{N-n_1} \tag{1.38}$$

From the binomial theorem we know that

$$(p + q)^N = \sum_{n_1=0}^N \frac{N!}{n_1!(N - n_1)!} p^{n_1} q^{N-n_1} \tag{1.39}$$

Since $p + q = 1$, it is clear that the normalization condition

$$\sum_{n_1=0}^N p_{n_1} = 1 \tag{1.40}$$

is satisfied. The average number $\langle n_1 \rangle$ of jumps to the right is given by

$$\langle n_1 \rangle = \sum_{n_1=0}^N n_1 p^{n_1} \frac{N!}{n_1!(N-n_1)!} q^{N-n_1}. \quad (1.41)$$

This is easy to evaluate if we remember that

$$n_1 p^{n_1} = p \frac{\partial}{\partial p} p^{n_1}, \quad (1.42)$$

so that

$$\langle n_1 \rangle = \sum_{n_1=0}^N p \frac{\partial}{\partial p} p^{n_1} \frac{N!}{n_1!(N-n_1)!} q^{N-n_1}. \quad (1.43)$$

On interchanging the order of summation and differentiation, we have

$$\langle n_1 \rangle = p \frac{\partial}{\partial p} \sum_{n_1=0}^N p^{n_1} \frac{N!}{n_1!(N-n_1)!} q^{N-n_1}. \quad (1.44)$$

Taking advantage of the binomial theorem we find that

$$\langle n_1 \rangle = p \frac{\partial}{\partial p} (p+q)^N = Np(p+q)^{N-1} = Np, \quad (1.45)$$

and for the average number $\langle n_2 \rangle$ of jumps to the left

$$\langle n_2 \rangle = N - \langle n_1 \rangle = N(1-p) = Nq. \quad (1.46)$$

For the mean of the second power of the number of jumps to the right, $\langle n_1^2 \rangle$, we proceed in an analogous fashion.

$$\langle n_1^2 \rangle = p \frac{\partial}{\partial p} pN(p+q)^{N-1} = p \left[N(p+q)^{N-1} + pN(N-1)(p+q)^{N-2} \right] \quad (1.47)$$

and

$$\langle n_1^2 \rangle = Np(q+np). \quad (1.48)$$

For the fluctuation of n_1 we therefore find

$$\langle \Delta n_1^2 \rangle = \langle (n_1 - \langle n_1 \rangle)^2 \rangle = Np(q+np) - N^2 p^2 = Npq. \quad (1.49)$$

We now have many of the interesting quantities for the number of steps n_1 to the right. The value of the position x with ℓ_o unity is given by

$$x = n_1 - n_2 = n_1 - (N - n_1) = 2n_1 - N. \quad (1.50)$$

If the number of steps n_1 to the right is known we also know the position x . The distribution p_x of the position x is therefore the same as for jumps to the right, given by Eq. (1.38). The mean value of x becomes

$$\langle x \rangle = \langle n_1 \rangle - \langle n_2 \rangle = N(p - q). \tag{1.51}$$

For the displacement we have

$$\Delta x = x - \langle x \rangle = 2n_1 - N - (2\langle n_1 \rangle - N) = 2(n - \langle n_1 \rangle) = 2\Delta n_1 \tag{1.52}$$

so that for the displacement fluctuation

$$\langle \Delta x^2 \rangle = 4Npq. \tag{1.53}$$

The distribution can also be written more clearly in terms of the displacement x by taking advantage of Eq. (1.50). This gives

$$p_x = \frac{N!}{\left(\frac{N+x}{2}\right)! \left(\frac{N-x}{2}\right)!} p^{\left(\frac{N+x}{2}\right)} q^{\left(\frac{N-x}{2}\right)}. \tag{1.54}$$

When jumps to the right occur with the same probability as to the left this reduces to

$$p_x = \frac{N!}{\left(\frac{N+x}{2}\right)! \left(\frac{N-x}{2}\right)!} \left(\frac{1}{2}\right)^N. \tag{1.55}$$

We now have an expression that gives us the number of jumps N in terms of the measured displacements, and from Eq. (1.54) we can also find out the jump rates to the left and right.

1.2.2 Approximation for large values of N

When the total number of jumps N becomes large, evaluation of the probability p_{n_1} given by Eq. (1.38) requires more work, but an approximation can be reached readily. For large values of N , the probability p_{n_1} at the maximum becomes large and n_1 also assumes quite a large value. The condition for the maximum is readily derived by operating on the logarithm of the probability, which is less sensitive to n_1 ,

$$\ln(p_{n_1}) = \ln(N!) - \ln(n_1!) - \ln(N - n_1)! + n_1 \ln(p) + (N - n_1) \ln(q). \tag{1.56}$$

The necessary condition for the maximum is

$$\frac{d\ln(p_{n_1})}{dn_1} = 0. \tag{1.57}$$

For large values of N , we can resort to Stirlings approximation $\ln(N)! \approx N \ln(N) - N$, so that

$$\frac{d\ln(N)!}{dN} = \ln(N) \tag{1.58}$$

and from Eq. (1.54) we find

$$\frac{d\ln(p_{n_1})}{dn_1} = -\ln(n_1) + \ln(N - n_1) + \ln(p) - \ln(q) = 0. \tag{1.59}$$

It follows that

$$\ln\left(\frac{[(N - \langle n_1 \rangle)p]}{\langle n_1 \rangle q}\right) = 0, \tag{1.60}$$

where $\langle n_1 \rangle$ is the value of n_1 at the maximum. Now

$$(N - \langle n_1 \rangle)p = \langle n_1 \rangle q \tag{1.61}$$

so that

$$Np = \langle n_1 \rangle(p + q) \tag{1.62}$$

and, since $p + q = 1$,

$$\langle n_1 \rangle = Np, \tag{1.63}$$

which agrees with the result already obtained for the binomial distribution in Eq. (1.45).

We can expand the logarithm of the probability p_{n_1} around the maximum as

$$\ln(p_{n_1}) = \ln(p_{\langle n_1 \rangle}) + \frac{d \ln(p)}{dn_1} \Delta n_1 + \frac{1}{2} \frac{d^2 \ln(p)}{dn_1^2} \Delta n_1^2 + \dots \tag{1.64}$$

The derivatives are all evaluated at the maximum so that the first derivative vanishes, and for the second we get from Eq. (1.59)

$$\frac{d^2 \ln(p)}{dn_1^2} = -\frac{1}{n_1} - \frac{1}{N - n_1} = -\frac{N}{n_1(N - n_1)}. \tag{1.65}$$

At the peak, $\langle n_1 \rangle = Np$ and $N - \langle n_1 \rangle = N(1 - p) = Nq$, so that

$$\frac{d^2 \ln(p)}{dn_1^2} = -\frac{N}{NpNq} = -\frac{1}{Npq}. \tag{1.66}$$

Note that the second derivative is negative as it must be at a maximum. Inserting the above result into Eq. (1.64) we obtain

$$\ln(p_{n_1}) = \ln(p_{\langle n_1 \rangle}) - \frac{1}{2} \frac{\Delta n_1^2}{Npq} \tag{1.67}$$

and

$$p_{n_1} = B \exp\left(-\frac{\Delta n_1^2}{2Npq}\right), \tag{1.68}$$

where $B = p_{\langle n_1 \rangle}$ is just a constant of proportionality. Now the normalization requires that

$$\int_{-\infty}^{\infty} p_{n_1} dn_1 = 1 \tag{1.69}$$

so we obtain

$$B \int_{-\infty}^{\infty} \exp\left(-\frac{\Delta n_1^2}{2Npq}\right) dn_1 = 1. \tag{1.70}$$