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DIFFUSION IN SOLIDS

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A knowledge of diffusion in solids is necessary in order to describe the kinetics of various solid state reactions such as phase transformations, creep, annealing, precipitation, oxidation, corrosion, etc., all fundamental processes in materials science. There are two main approaches to diffusion in solids [1–5]: (i) the atomistic approach, where the atomic nature of the diffusing entities is explicitly considered; and (ii) the continuum approach, where the diffusing entities are treated as a continuous medium and the atomic nature of the diffusion process is ignored. Many useful results and general relations can be obtained within the continuum approach, but a more complete picture is obtained if the atomic motions are considered. Macroscopic quantities, such as diffusion fluxes, can then be related to microscopic quantities, such as atomic jump frequencies. Knowledge of how atoms move in solids is also intimately connected with the study of defects in solids.

1. The Diffusion Equation

In the continuum approach the diffusion coefficient D is introduced through the Fick's law which expresses the flux of particles $\mathbf{j}(\mathbf{r}, t)$ in terms of the gradient of the particle concentration $n(\mathbf{r}, t)$ at the same position \mathbf{r} and time t

$$\mathbf{j}(\mathbf{r}, t) = -D\nabla n(\mathbf{r}, t) \quad (1)$$

To arrive at the standard diffusion equation Fick's law is combined with the equation which describes the conservation of particles,

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0 \quad (2)$$

which implies that

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D\nabla^2 n(\mathbf{r}, t) \quad (3)$$

We have here assumed that D itself is independent on concentration. The solution to this equation is obtained exploiting the Fourier transform method. It can be written on the form

$$n(\mathbf{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} \int n_0(\mathbf{r}') e^{-(\mathbf{r}-\mathbf{r}')^2/4Dt} d\mathbf{r}' \quad (4)$$

where $n_0(\mathbf{r}) = n(\mathbf{r}, t = 0)$ is the initial particle concentration. If boundary conditions have to be specified at finite distances the Fourier series expansion method has to be used.

Several different diffusion coefficients can be defined. The tracer or self-diffusion coefficient D_s describes the diffusive behavior of a given, or tagged, particle. Experimentally, that can be measured using a small amount of radioactive isotopes. The density of the tagged particle is described by the probability $p(\mathbf{r}, t)d\mathbf{r}$ to find the particle at time t in the volume element $d\mathbf{r}$ at \mathbf{r} , and is given by

$$\frac{\partial p(\mathbf{r}, t)}{\partial t} = D_s \nabla^2 p(\mathbf{r}, t) \quad (5)$$

which is identical to Eq. (3) except for that D is replaced by D_s . The probability to find the tagged particle at position \mathbf{r} at time t , given that it was located at $\mathbf{r} = 0$ at time $t = 0$, can be obtained from the general solution (4), i.e.,

$$p(\mathbf{r}, t) = \frac{1}{(4\pi D_s t)^{3/2}} e^{-r^2/4D_s t} \quad (6)$$

This Gaussian function describes the diffusive spreading of the probability distribution. The width is equal to the mean squared displacement of the tagged particle motion, $\langle \mathbf{R}^2(t) \rangle = 6D_s t$, and can be used as a definition of the self-diffusion coefficient.

$$D_s = \frac{1}{6t} \langle \mathbf{R}^2(t) \rangle \quad (7)$$

where the notation $\langle \dots \rangle$ is used for the averaging procedure. Equation (5) is based on the assumption that the motion is diffusive. For short times, the particle motion deviates from purely diffusive behavior and Eq. (7) becomes invalid. Therefore, the definition of D_s should be supplemented with the condition that $t > \tau_0$, where τ_0 is a suitable microscopic time-scale.

The various diffusion coefficients depend on the thermodynamic variables, i.e., temperature, pressure and composition. It is well known that diffusion coefficients in solids generally depend rather strongly on temperature, being very low at low temperatures but appreciable at high temperatures. Empirically, this dependence can often be described by the Arrhenius formula

$$D = D_0 e^{-E_a/k_B T} \quad (8)$$

where D_0 is commonly referred to as the pre-exponential factor and E_a the activation energy for diffusion.

2. The Continuum Approach

In the general case the situation can be quite complicated [1–3]. In a multi-component system one has to introduce material fluxes for each component i ,

$$\mathbf{j}_i(\mathbf{r}, t) = - \sum_j D_{ij} \nabla n_j(\mathbf{r}, t) \quad (9)$$

The gradient in the concentration of one species may contribute to the flux of another species, described by the off-diagonal components of D_{ij} . The diffusion coefficient is a function of composition as well as of temperature and pressure (or more generally stress). If a temperature or pressure gradient is present that may also introduce material fluxes and the Fick's law of diffusion has to be generalized. Thermodynamic equilibrium demands not only that temperature and pressure be the same throughout a system but also that the chemical potential be everywhere the same. Therefore, the gradient of the chemical potential should enter in a more general description of diffusion.

The theory of non-equilibrium thermodynamics is used to derive the general formalism for diffusion [3]. The theory put different phenomenological diffusion treatments together into a coherent structure. It is a linear theory and expresses the *fluxes* of the different species J_i in terms of suitable defined *forces* X_j acting on these species, according to

$$J_i = \sum_j L_{ij} X_j \quad (10)$$

where the phenomenological coefficients L_{ij} are the basic kinetic parameters in the theory. In general, they will be functions of the usual thermodynamic variables, but they are independent on the forces X_j . An important theorem, the Onsager reciprocity theorem, states that the matrix L is symmetric, i.e., $L_{ij} = L_{ji}$. This relation derives from the underlying atomic dynamics of the system and ultimately from the principle of detailed balance in statistical mechanics. In an isothermal, isobaric system the appropriate force is the gradient of the chemical potential $X_j = -\nabla \mu_j$, and the corresponding transport coefficient L_{ij} is related, but not equal, to the diffusion coefficient D_{ij} . For instance, although by Onsager's theorem $L_{ij} = L_{ji}$, it does not follow that $D_{ij} = D_{ji}$. In a non-isothermal system the equations must also include the heat flow J_q and a corresponding thermal force $X_q = -\nabla T/T$.

The corresponding set of coupled diffusion equations are derived by supplementing Eq. (10) with the particle conservation law. Numerical software packages for solution of multi-component diffusion equations have been developed [6]. An important application is the simulation of diffusion controlled transformations in alloys of practical importance. Necessary input is kinetic and thermodynamic data. These are derived by collecting and selecting

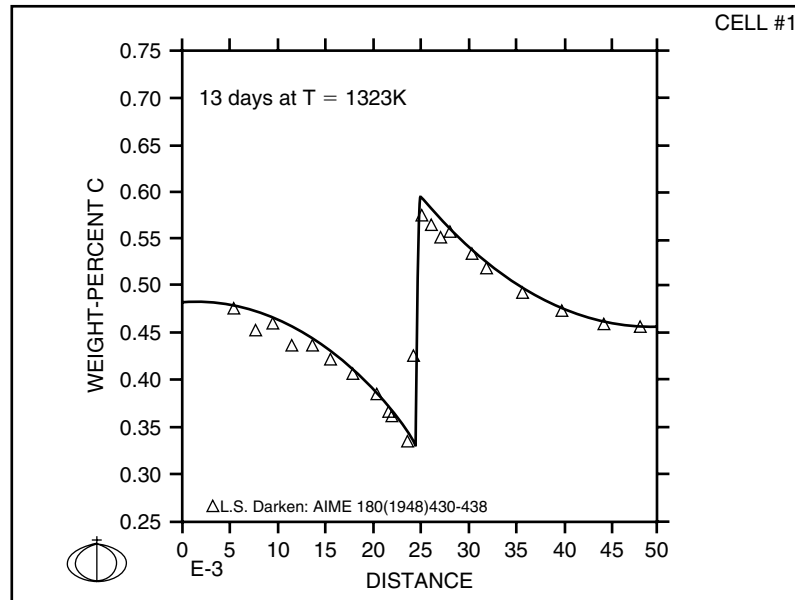


Figure 1. Simulated carbon concentration profile in a weld between two steels with initially similar carbon but different silicon contents see (<http://www.thermocalc.com/Products/Dictra.html>).

experimental data from the literature. The progress of various solid state phase transformations can then be simulated. In Fig. 1 a result from a diffusion simulation is shown produced by the software package DICTRA [6].

3. The Atomic Mechanism of Diffusion

The continuum approach is phenomenological. It does not give information on the nature of the diffusive motion. In order to describe the diffusion phenomena properly a knowledge of the underlying atomic mechanisms is required. Atoms in a solid vibrate around their equilibrium positions. Occasionally these oscillations become large enough to allow an atom to change site. It is these jumps from one site to another which gives rise to diffusion in a solid. The atomic jumps in a solid are rare on a microscopic time scale. The self-diffusion coefficient is about 10^{-8} cm²/s near the melting point in most closed packed metals. The lattice spacing is of the order 10^{-8} cm which implies, using Eq. (7), that the atoms change site about 10^7 times/s. This should be compared with the vibrational frequency which is 10^{13} – 10^{14} per second. Thus even near the melting point the great majority of the time the atom is oscillating about its equilibrium position in the crystal. It changes site only on one oscillation in 10^4 or 10^5 .

There are two common mechanisms by which atoms can diffuse through a crystalline solid, the vacancy and the interstitial mechanism. These are schematically illustrated in Fig. 2.

For bulk diffusion in closed packed metals the vacancy mechanism is most important. Near the melting point the vacancy concentration is about 10^{-3} – 10^{-4} site fraction in most metals. These vacancies allow the atoms to move, and this mechanism is operating in most cases with jumps to nearest neighbor sites or also to next nearest neighbor sites in bcc crystals. At high temperatures vacancy aggregates as divacancies may be present and influence the diffusivity. Curvature in the Arrhenius plot of self-diffusion is commonly interpreted as resulting from a monovacancy jump process at low temperatures with an increasing contribution from a divacancy jump process at higher temperatures [1]. That interpretation has recently been questioned based on computer simulations and it is argued that the curvature could be equally well interpreted by a single vacancy mechanism with a temperature-dependent activation energy [7]. At high temperatures interstitials may also be present but due to the high formation energy these defects are in most cases assumed to give no contribution at equilibrium.

Substitutional atoms usually also diffuse by the vacancy mechanism. Other mechanisms as various exchange mechanisms have been suggested [1]. At the present there is no experimental support for any such mechanisms in crystallized metals and alloys. However, in disordered solids these more cooperative motions are more likely operating.

In the interstitial mechanism the atoms move from interstitial site to interstitial site. Usually small interstitial atoms, like hydrogen or carbon atoms in metals, diffuse through the lattice by this mechanism. The surrounding solvent atoms are not greatly displaced from the normal lattice sites. If the interstitial atom is nearly equal in size to the lattice atoms diffusion is more likely to occur by the interstitialcy mechanism [1]. Here the interstitial atom does not move directly to another interstitial site. Instead it moves into a normal lattice site and the atom that was originally at the lattice site is pushed into a neighboring interstitial site.

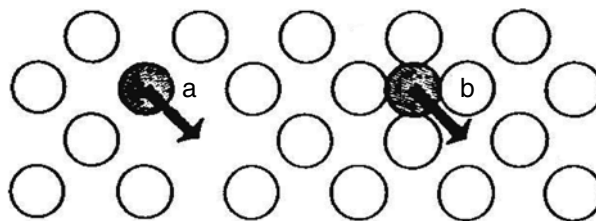


Figure 2. Mechanisms of diffusion in crystals: (a) the vacancy mechanism (b) the interstitial mechanism.

4. The Random Walk Model

The aim of the random walk model is to describe the observed macroscopic diffusion in terms of the atomic jumps which are the elementary processes in diffusion. It has been noted that the atomic jumps in a solid are rare on a microscopic time scale. The actual duration of an atomic jump is, however, short and can be neglected compared with the mean residence time at a site. This justifies an assumption of randomness of the atomic jumps. On the other hand, the total number of jumps over the period of hours or days is immense, about 10^8 each second, and a statistical treatment becomes justified. In the random walk models these aspects of the diffusive motion are taken into account.

Consider a random walk on a simple cubic lattice with lattice spacing a . We assume that all sites are equally available and that the diffusing entities perform a series of uncorrelated jumps, i.e., we assume that interaction between diffusing entities and correlation effects can be neglected. If the jump vector for the i th jump is denoted by \mathbf{s}_i , the total displacement after N jumps can be written as

$$\mathbf{R}_N = \sum_{i=1}^N \mathbf{s}_i \quad (11)$$

From symmetry considerations the mean displacement will be zero, $\langle \mathbf{R}_N \rangle = 0$, while the mean-squared displacement is proportional to the number of jumps

$$\langle \mathbf{R}_N^2 \rangle = \sum_{i=1}^N \sum_{j=1}^N \langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle = \sum_i \langle \mathbf{s}_i \cdot \mathbf{s}_i \rangle + \sum_{i \neq j} \langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle = Na^2 \quad (12)$$

where the last equality follows from the fact that we have assumed the jumps to be uncorrelated, $\sum_{i \neq j} \langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle = 0$. In many situations this is not the case and the analysis becomes much more complicated [5]. We can also write this in terms of the jump rate k between two neighboring sites

$$\langle \mathbf{R}_N^2 \rangle = ka^2t \quad (13)$$

The jump rate is related to the mean residence time τ at a site according to $1/\tau = nk$, where n is the number of nearest neighboring sites. Furthermore, it can be related to the self-diffusion coefficient by comparing with Eq. (7), i.e.,

$$D_s = \frac{a^2}{6}k \quad (14)$$

This very simple random walk model can be extended in many different directions [8] and the more complicated models are most often solved using the numerical Monte Carlo (MC) simulation technique.

The random walk modeling can also be generalized by writing down the equation for the rate of change of the probability distribution directly. We obtain the following rate equation, or Master equation

$$\frac{\partial}{\partial t} p(\mathbf{r}_i, t) = \sum_j [k_{j \rightarrow i} p(\mathbf{r}_j, t) - k_{i \rightarrow j} p(\mathbf{r}_i, t)] \quad (15)$$

with $k_{i \rightarrow j}$ equal to the transition rate from i to j . If nearest neighboring jumps are assumed with the same jump rate it simplifies to

$$\frac{\partial}{\partial t} p(\mathbf{r}, t) = \frac{1}{n\tau} \sum_k [p(\mathbf{r} + \mathbf{a}_k, t) - p(\mathbf{r}, t)] \quad (16)$$

where \mathbf{a}_k is the set of vectors which connects a site with its nearest neighboring sites. This equation gives a more detailed spatial information of the diffusive motion compared with ordinary diffusion Eq. (5). To recover the latter equation we may expand the probability distribution around \mathbf{r} , and use the symmetry. The diffusion Eq. (5) is then obtained with $D_s = (1/6) \cdot (a^2/\tau n)$.

Equation (16) is most easily solved in Fourier space. We obtain

$$I^s(\mathbf{q}, t) \equiv \int d\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} p(\mathbf{r}, t) = e^{-\Gamma(\mathbf{q})t} \quad (17)$$

and

$$S^s(\mathbf{q}, \omega) \equiv \int \frac{dt}{2\pi} e^{-i\omega t} I^s(\mathbf{q}, t) = \frac{1}{\pi} \frac{\Gamma(\mathbf{q})}{\omega^2 + \Gamma^2(\mathbf{q})} \quad (18)$$

with

$$\Gamma(\mathbf{q}) = \frac{1}{n\tau} \sum_k (1 - e^{-i\mathbf{q}\cdot\mathbf{a}_k}) \quad (19)$$

Quasi-elastic neutron scattering can be used to study diffusion [3]. In that case the incoherent scattering cross-section is directly related to $S^s(\mathbf{q}, \omega)$ and by determining the width of the quasi-elastic peak as function of the scattering wave-vector a very detailed description of the diffusive motion may be obtained. In practise only relatively fast diffusing atoms can be studied with neutrons. Interstitial solutions of hydrogen in metals and fast ion conductors are among those which have been extensively studied in this way.

The same quantities can also be obtained using the numerical molecular-dynamics (MD) simulation technique. In Fig. 3 results from a MD simulation for hydrogen diffusion in palladium are compared with quasi-elastic neutron scattering data [9]. The width of the quasi-elastic peak is shown as function of wave-vector. The temperature is 623 K and a classical description of the hydrogen motion should be quite reasonable. The simulation data agree with experiments provided energy dissipation to both the lattice vibrations and the electron excitations are taken into account.

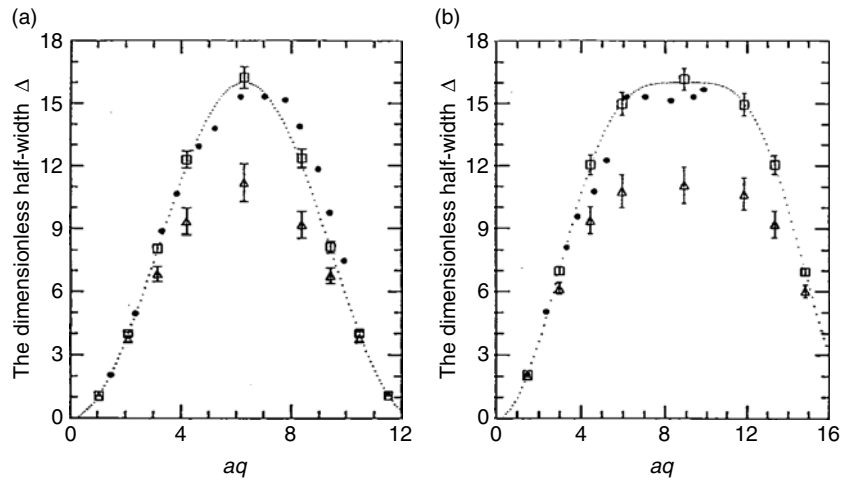


Figure 3. The half-width ($\Delta \equiv \Gamma(\mathbf{q})a^2/D_s$) of the quasi-elastic peak as function of wave-vector, in units of a , along (a) the $\langle 100 \rangle$ direction and along (b) the $\langle 110 \rangle$ direction at $T = 623$ K. \bullet : quasi-elastic neutron scattering data; \triangle : molecular-dynamics simulation data (with coupling to lattice vibrations); \square : molecular-dynamics simulation data (with coupling to lattice vibrations and electronic excitations). The dotted line shows the results from Eq. (19). Reprinted with permission from Ref. [9]. Copyright (1992) by the American Physical Society.

5. The Atomic Jump Frequency

The random walk model relates the atomic jumps to the macroscopic diffusion phenomena. An understanding of parameters entering the expression for the atomic jump frequency and related quantities is therefore of great interest. Direct calculations of those parameters are important, in particular, if accurate calculations can be performed without fitting to experimental data, so called first-principles or *ab initio* calculations.

In vacancy and interstitial diffusion the diffusion coefficient will depend on the concentration of defects and the atomic jump frequency k . In vacancy diffusion the relevant jump frequency is the one of an atom into an adjacent vacancy and in interstitial diffusion it is the jump rate between different interstitial sites. Using equilibrium statistical mechanics the defect concentration can be expressed in terms of formation enthalpies and entropies. The atomic jump frequency k is most often approximated using the absolute rate theory, or transition state theory, according to

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q} \quad (20)$$

where Q and Q^\ddagger are the statistical mechanical partition functions evaluated for the system at a stable site and at the transition site, respectively. The

transition site is defined as the hypersurface separating two stable sites. Assuming harmonic lattice vibrations Vineyard [10] derived the following expression for the transition rate

$$k = \frac{\prod_{j=1}^N \nu_j}{\prod_{j=1}^{N-1} \nu_j^*} e^{-\Delta E/k_B T} \quad (21)$$

where the activation energy ΔE (cf Eq. (8)) is the energy difference between the system located at a stable site and at the transition site or saddle point configuration. ν_j are the N normal mode frequencies of the entire system at the stable site and ν_j^* the $N-1$ normal mode frequencies of the system constrained in the transition site.

The various parameters entering the expressions for the defect concentration and the jump frequencies can be evaluated from first principles. In particular, the density functional theory has been applied extensively. Dynamics and finite temperature effects have also been considered from first principles. In Fig. 4 we show the result from such a calculation [7]. It is found that for aluminum the mono-vacancy diffusion alone dominates over diffusion due to divacancies and interstitials for all temperatures up to the melting point. The calculated diffusion rate agrees with experimental data over 11 orders of magnitude.

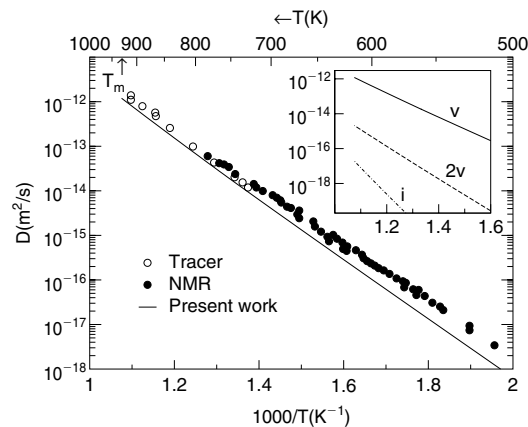


Figure 4. Temperature dependence for the self-diffusion coefficient in aluminum as function of the inverse temperature. Open and filled circles are experimental data and the lines are from molecular-dynamics simulations. The inset shows calculated diffusion coefficients for vacancies (v), divacancies ($2v$), and interstitials (i). The contribution from divacancies and interstitials is less than 1% of that from mono-vacancies at the melting temperature. Reprinted with permission from Ref. [7]. Copyright (2002) by the American Physical Society.

6. Outlook

In the past diffusion studies have been dominated by various experimental techniques and the development of the theoretical description. Software has been developed for accurate simulation of diffusion in solids based on experimental input. More recently *ab initio* computations and computer simulations have gained in importance.

The first-principles or *ab initio* methods can be used to get insight and to obtain data for various elementary properties in relation to diffusion. If the diffusivity is high the MD simulation technique can be used to study diffusion in a very direct way. It provides well-controlled “experiments” and allows a proper check of the validity of the various theoretical descriptions. The method requires a description of the inter-atomic interaction as input and if that is sufficiently reliable the method provides a fairly reliable substitute to actual experiments. The Monte Carlo simulation technique can also be used to study diffusion. In that case a model for the kinetic description has to be established. The method is particularly useful for the study of diffusion in complex systems, like concentrated alloys and disordered materials.

To conclude; it is not unlikely that the present time of diffusion studies will be characterized as the computational period.

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