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CORRELATED WALK MODEL OF DIFFUSION IN BINARY SOLID SOLUTIONS

Estela Blaisten - Barojas and Lorenzo Martínez

Instituto de Física, Universidad Nacional Autónoma de México,
Apartado Postal 20 - 364, 01000 México, D. F.
México

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ABSTRACT: The correlated walk model (CWM) of impurity diffusion in metals is used to obtain the diffusion coefficient D of binary metal mixtures. A close analytical expression of D as a function of impurity concentration and temperature is given by providing a parametrization of the step probabilities inherent to the CWM. An application to diffusion of Al, Be, Cd, Si, Sn in alpha-solid copper is given to show the possibilities of the method.

INTRODUCTION

The diffusional processes in solid state materials are determinant of the rate at which phase transitions and other structural changes occur. The substitutional atoms in binary alloys introduce changes in the diffusional properties of both solute and host matrix atoms (1). The usual effect of substitutional impurities is to increase the rate of diffusion (2, 3, 4). There are, however, some cases where the contrary effect is present (5). The influence of impurity concentration on the self diffusion of host matrix atoms is correspondent to the solidus line in phase diagrams (5).

The amount of experimental work dealing with the effect of concentration of alloying elements on the diffusivities is substantial. In smaller scale, there have been several attempts to provide theoretical explanations especially for the increase of the rate of diffusion with impurity concentration (1, 6). The purpose of this work is to report on the use of the correlated walk model (CWM) of atomic diffusion (7, 8) that leads to analytical expressions of the diffusion coefficient D as function of the relative concentration of binary metal mixtures. Further comparison to alpha-solid solutions of copper (9, 10) is based on a proposition of the probabilities pertaining to the theory. The CWM, as it stands today, was developed using a nonsophisticated memory that yielded final expressions valid in the low concentration limit. This limit might be far in a phase diagram from any structural phase transition and yet it is important since it governs the onset of a process.

THE CORRELATED WALK MODEL

The connection between a "walk" and a diffusion process is rather obvious if the later is pictured by atoms migrating on a lattice of a given point symmetry and where the atom jump rate is the same everywhere on the lattice (7). In order to jump, the migrating atom overcomes an energy barrier before moving to a new site. Since the atom carries linear momentum, the jump probabilities are **correlated** when each jump keeps memory of how the previous jump was done. Once the atom moves, it may jump over several sites in succession, adquiring a momentum that now correlates those sites. The CWM describes such correlated motion in terms of step probabilities: 1) the moving probabilities α , β , γ ; 2) the temporary come-to-stop probability σ and; 3) the non-preferent direction start-to-move probability μ, or equivalently, the remain at the site probability σ'. By using the relation between the atomic mean-square displacement and the diffusion coefficient D for a pure metal (11), it was obtained (7)

$$D = \frac{S(\Delta)}{1 + \sigma(1-\sigma')^{-1}} \qquad (1)$$

where $S(\Delta) = 1 + \Delta(1-\Delta)^{-1}$ and $\Delta \equiv \Delta(\alpha, \beta, \gamma)$ is a function depending mostly on the lattice point symmetry. The denominator in Eq. (1) points out the difference between random walks (12) and the CWM in what concerns the actual atomic diffusion. For random walks the denominator equals one.

Suppose that a second component is introduced in such a way that the new atoms do not disturb the host lattice symmetry and are distributed uniformly over the solid with concentration c. Consider now that one atom of the second component starts to move. If the impurities generate significant change in the come-to-stop (σ) and stay-stationary (σ') probabilities only, the denominator in Eq. (1) may be replaced by

$$1 + c\frac{\sigma_i}{1-\sigma'_i} + (1-c)\frac{\sigma_o}{1-\sigma'_o} - c\frac{\sigma_i}{1-\sigma'_i}(1-c)\frac{\sigma_o}{1-\sigma'_o} \qquad (2)$$

The four terms here correspond to the following processes: i) the impurity arrives and leaves with no intermediate stop at any site of the lattice, ii) it arrives (and eventually leaves) at an impurity site which occurs with probability c and is represented by σ_i, σ'_i, iii) it arrives (and eventually leaves) at a regular site of the host lattice wich occurs with probability (1 - c) and is represented by σ_o σ'_o, and iv) it arrives (and eventually leaves) either at an impurity site or a host site. Note that the come-to-stop (σ_o) and stay-stationary (σ'_o) probabilities of the host lattice are not those of the pure metal, but rather those obtained when $c \rightarrow 0$. Introducing Eq. (2) in Eq. (1) and rearranging terms the following expression is obtained for the diffusion of impurities in an impure metal

$$D = \frac{S(\Delta)}{1 + \sigma_o(1 - \sigma'_o)} \quad \frac{1}{1 - c\,\alpha_1 + c^2\,\alpha_2} \tag{3}$$

where

$$\alpha_1 = \left[1 + \frac{\sigma_o}{1 - \sigma'_o}\right]^{-1} \left[\frac{\sigma_o}{1 - \sigma'_o} - \frac{\sigma_i}{1 - \sigma'_i} + \frac{\sigma_o}{1 - \sigma'_o} \; \frac{\sigma_i}{1 - \sigma'_i}\right]$$

$$\alpha_2 = \left[1 + \frac{\sigma_o}{1 - \sigma'_o}\right]^{-1} \frac{\sigma_o}{1 - \sigma'_o} \; \frac{\sigma_i}{1 - \sigma'_i} \tag{4}$$

PARAMETRIZATION OF THE STEP PROBABILITIES

Next let us propose the following model for the step probabilities in Eq. (3) and (4):

$$\sigma_o = \exp(-E_B / KT) - \exp(-E_o / KT)$$

$$\sigma'_o = 1 - \exp(-E_o / KT) \tag{5}$$

where T is the temperature, K is Boltzmann's constant, E_B is the energy at the bottom of the potential barrier that surrounds a diffusing impurity and E_o is the energy at the barrier top. When the metal becomes impure, E_o may be modified to be E_i. This new energy can be either, larger or smaller than E_o. In the first case, $E_i > E_o$

$$\sigma_i = \exp(-E_B / KT) - \exp(-E_i / KT) - \sigma_o$$

$$= \exp(-E_o / KT) - \exp(-E_i / KT) \tag{6a}$$

in the second case, $E_i < E_o$

$$\begin{aligned} \sigma_i &= \sigma_o - [\exp(-E_B/KT) - \exp(-E_i/KT)] \\ &= \exp(-E_i/KT) - \exp(-E_o/KT) \end{aligned} \qquad (6b)$$

For both cases the following definition is proposed for σ_i'

$$\sigma_i' = 1 - \exp(-E_i/KT) \qquad (6c)$$

This modified stay-stationary probability is larger than σ_o' if $E_i > E_o$ (smaller if $E_i < E_o$). In terms of E_o, E_i and E_B it is possible to define the following energy differences

$$\begin{aligned} Q_o &\equiv E_o - E_B \\ Q_i &\equiv E_i - E_B \end{aligned} \qquad (7)$$

as a measure of the energy necessary to activate diffusion in the metal without impurities (Q_o) and in the mixed solid (Q_i).

After substitution of Eq. (5), (6) and (7) in Eq. (3) and (4) the diffusion coefficient takes the form

$$D = \frac{S(\Delta)\ \exp(-Q_o/KT}{1 - c\alpha_1 + c^2\alpha_2} \qquad (8)$$

where, if $E_i > E_o$ and thus $Q_i > Q_o$

$$\begin{aligned} \alpha_1 &= \exp[(Q_i - Q_o)/KT][1 - 2\exp(-Q_o/KT) + \exp(-Q_i/KT)] \\ \alpha_2 &= \exp[(Q_i - Q_o)/KT] - 1 - \exp[(Q_i - 2Q_o)/KT] + \exp(-Q_o/KT) \end{aligned} \qquad (9)$$

and if $Q_i < Q_o$

$$\alpha_1 = 2 - \exp (Q_i / KT) - 3 \exp (-Q_o / KT) + \exp [(Q_i - 2Q_o) / KT]$$

$$\alpha_2 = 1 - \exp (-Q_o / KT) - \exp [(Q_i - Q_o) / KT] + \exp [(Q_i - 2Q_o) / KT] \qquad (10)$$

If $Q_o >> KT$, Eq. (8) gives an increasing diffusion coefficient with increasing concentration, if $Q_i > Q_o$. When $Q_i < Q_o$ an increase or decrease of D can be obtained as a function of concentration.

To summarize, Eq. (8-10) give the diffusion coefficient of impurities in an impure metal in terms of $S(\Delta)$ and two parameters: Q_o, or energy necessary to iniciate the diffusion process in a solid with $c \rightarrow o$ impurities, and Q_i the excess energy necessary to trigger the process when the concentration c is small but finite.

DIFFUSION IN ALPHA-SOLID SOLUTIONS OF COOPER

Based on the proposition of the previous section, a comparison to some experimental values results possible. For small impurity concentration ($c \sim 0.04$) there are data for several binary solutions as the classical results reported by Rhines et. al. (10) for solid solutions of Al, Be, Cd, Si and Sn in alpha-copper. This type of experiments are usually fitted to an Arrhenius expression $D = D_o \exp (-Q / KT)$ where both D_o and Q are concentration dependent. Alternatively, the previously derived expressions (8) to (10) give an explicit expression of D as a function impurity concentration c and temperature. The quantities Q_o, Q_i and S are concentration and temperature independent in the range T ± 100 °C.

In Table I are reported the values obtained by fitting the experiments to Eq. (8). For all impurities it comes out that $Q_i > Q_o$, so expressions (9) where used in addition to Eq. (8). The fit was carried out as follows. First, at the experimental value of $T = 800°C$, $S(\Delta)$ and Q_o were taken equal to those reported for copper with $c \rightarrow 0$ impurities (2). Secondly, Q_i was obtained by fitting the $c = 0.04$, $T = 800°C$ value of D.

In Fig. 1 it is shown the variation of D with concentration for $c < 0.04$ and in Fig. 2 the temperature variation of D is reported at a fixed concentration of the solid solutions. As expected, Fig. 1 shows an increase of the diffusion coefficient. In Fig. 2 it is clear that the log D plot versus T is not linear in the range of temperatures shown in the figure.

	$S(\Delta)$ (cm^2 / seg)	Q_o (Kcal / mole)	Q_i (Kcal / mole)	α_1	α_2
Al	1.71×10^{-2}	37.7	40.18	3.21	2.2
Be	2.32×10^{-4}	28	31.07	4.22	3.2
Cd	1.97×10^{-9}	8	18.67	148.9	147.9
Si	3.7×10^{-2}	40	45.68	14.34	13.3
Sn	1.13	45	50.82	15.33	14.3

TABLE I

Values of the parameters $S(\Delta)$, Q_o, Q_i obtained from the fit to experimental values of Rhines et. al. (10) at 800°C.

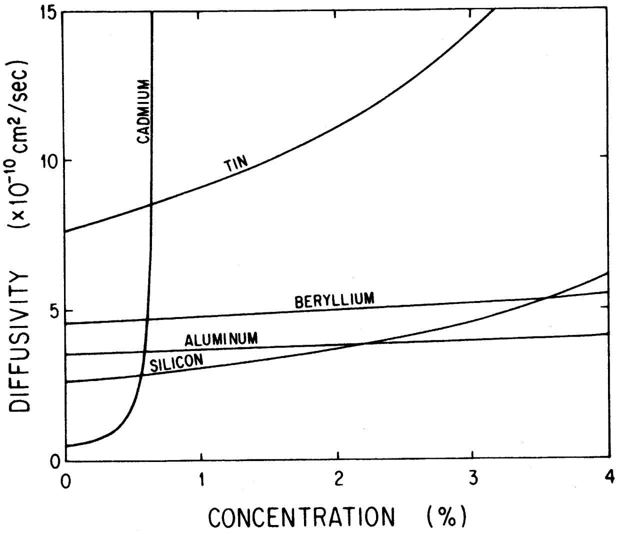

Figure 1. Increase in the diffusivity of impurities in copper as a function of concentration.

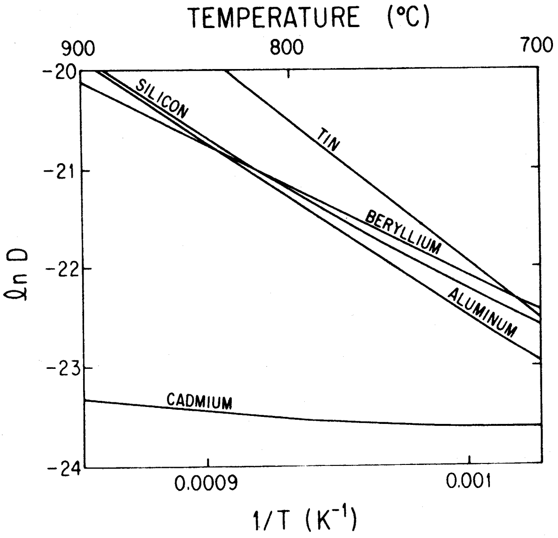

Figure 2. Curves L_n D versus T^{-1} for the different alloying elements, all of them at $c = 0.04$

The CWM expression for the diffusion coefficient examined in this paper seems to be quantitatively successful in representing the process of diffusion in alpha-copper solid solutions. The experiments chosen for this comparison are old but classical in the field of metallurgy. The model has the advantage of giving explicitely a dependence of D with impurity concentration and temperature. The analytical expression contains three parameters whose interpretation is clear, i. e., $S(\Delta)$, associated to the point symmetry of the solid, Q_0 or the energy necessary to start the diffusing process in a solid with $c \rightarrow 0$ impurities, Q_i the excess (or defect) energy when the metal has impurities.

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