AD 730 087

ARPA Order No. 1479

Program Code 1E20

Name of Contractor:
The Regents of the University of California
Contract and Grant Officer
[illegible] Building 301, Matthews Campus
University of California, San Diego
La Jolla, California 92037

Effective Date of Contract:
From: 1 August 1968

Amount of Contract: $180,000

Contract No. N00014-69-A-0200-6018

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Short Title of Work:
A Random Walk MOdel of Interstitial Thermal Diffusion in Crystals

To: 31 July 1972

Sponsored by
Advanced Research Projects Agency
ARPA Order 1479

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Department of Chemistry University of California, San Diego La Jolla, California 92037	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

A Random Walk Model of Interstitial Thermal Diffusion in Crystals

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*

John D. Weeks and Kurt E. Shuler

6. REPORT DATE September 1971	7a. TOTAL NO. OF PAGES 25	7b. NO. OF REFS 14

8a. CONTRACT OR GRANT NO. N00014-69-A-0200-6018	9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. 9
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* ARPA Order No. 1479
d.	

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Office of Naval Research Physics Branch Washington, D. C. 20360

13. ABSTRACT

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UNCLASSIFIED
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Diffusion						
Thermal Diffusion						
Interstitial Diffusion						
Random Walk Model						
Cell Model						

DD FORM 1 NOV 65 1473 (BACK)
(PAGE 2)

Security Classification

A RANDOM WALK MODEL OF INTERSTITIAL THERMAL DIFFUSION IN CRYSTALS[*]

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[*] Supported in part by the Advanced Research Projects Agency of the Department of Defense as monitored by the U. S. Office of Naval Research under Contract N00014-69-A-0200-6018.

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ABSTRACT

We have developed a random walk model of interstitial diffusion of light impurity atoms in a host lattice of heavy atoms in the presence of a thermal gradient. To take account of the effect of the thermal gradient on the flux of impurity atoms we introduce a bias in the jump direction of the interstitial impurity. We assume that this bias is due to the temperature dependence of the excluded volume effects which arise during the jump of the impurity atom between interstitial sites. The resulting random walk equation for thermal diffusion is consistent with both positive and negative heats of transport in agreement with experimental data. Using a cell model approach and the assumption of local equilibrium, we then develop equations which permit the calculation of the bias in jump direction. The theory of interstitial diffusion developed here clarifies and supports the classic Wirtz model for interstitial thermal diffusion.

I. INTRODUCTION

The dynamics of diffusion in a crystalline solid maintained at constant temperature is fairly well understood at the present time. Both the simple random walk models$^{(1-3)}$ and the recently developed "dynamical" theories$^{(4-6)}$ give much insight into the process of diffusion and produce at least qualitative agreement with experiment. For the more complicated problem of diffusion in solid subjected to a temperature gradient, the theoretical description is less satisfactory.$^{(7)}$

Allnatt and Rice$^{(3)}$ have derived general random walk equations which describe the flux of matter in a crystalline solid with both concentration and temperature gradients present. To apply this general theory to any specific problem, certain parameters which predict both the magnitude and the direction of the matter flux must be determined outside this theory. An example of such a parameter is the heat of transport. Using the random walk model together with certain specific physical assumptions, Allnatt and Rice concluded that the heat of transport is always positive and equal to the activation energy of isothermal diffusion. Experiments, however, have shown that the heat of transport can be positive or negative, depending upon the specific system under study. The random walk model itself is consistent with, and can predict, both negative and positive heats of transport. Further work on the determination of the parameters entering into the random walk theory is thus desirable.

In order to be able to examine in some detail the physical basis of the parameters in a random walk model for thermal diffusion we decided to study a particularly simple system. The system we chose is that of interstitial diffusion under the influence of a thermal gradient of a dilute solution of light impurity atoms in a stationary host lattice of heavy atoms.

In order to develop the relevant random walk equations we consider first interstitial diffusion in an isothermal system and then extend our equations to interstitial diffusion in a thermal gradient (Sections II and III). By introducing a bias in the jump direction of the random walker due to the thermal gradient we are able to obtain both positive and negative heats of transport. To evaluate this bias we introduce a simple physical model according to which the bias is due solely to the temperature dependence of excluded volume effects which arise from the repulsive forces between host lattice and impurity atoms during the jump of the impurity atom between interstitial sites (Section IV). This simple model does not take into account other possible mechanisms which might also produce a bias in jump direction under the influence of a thermal gradient such as, for instance, chemical host-impurity interactions. From our model we then calculate the jump bias to a first approximation and use it to estimate heats of transports for the diffusion of H and C in α-(bcc)Fe. These estimated heats of transport are in order of magnitude agreement with experimentally determined ones and have the correct sign.

We find that there is a close relationship between the random walk approach, Rice's "dynamical" theory(4) and the Wirtz model(8) for thermal diffusion. These relationships are discussed in some detail in the last section of this paper.

II. INTERSTITIAL DIFFUSION OF IMPURITIES

A. Isothermal Diffusion

In order to describe the isothermal diffusion of impurity atoms via an interstitial mechanism we make the following assumptions: (a) the light impurity atoms diffuse in a stationary host lattice of heavy atoms, (b) the impurity atom concentration is sufficiently low that interstitial lattice sites on either side of a given interstitial impurity atoms can be taken as unoccupied and that we can work with concentration rather than activities, i.e. the system is ideal, (c) the diffusion is one dimensional (in cubic crystals diffusion in the three normal directions can be treated independently).

Consider now two interstitial planes 1 and 3 which are a distance a apart. (See Figure 1.) Let the number of impurity atoms per unit area on plane 1 be n(1) and on plane 3 be n(3). The total jump rate Γ, which is assumed to be a function of temperature only, is defined so that $n(1)\Gamma(1)$ gives the total number of atoms per second per unit area jumping from plane 1 to planes on both sides of 1. We wish to consider the net flux J of impurity atoms across the host lattice plane 2 between interstitial planes 1 and 3. This is clearly given by

$$J(2) = P_R(1)\Gamma(1)n(1) - P_L(3)\Gamma(3)n(3) \qquad (2.1)$$

where $P_R(1)$ represents the probability on a given jump that an atom on plane 1 will jump to the right and where $P_L(3)$ is the probability of an atom on plane 3 jumping to the left. Right and left refer respectively to jumps toward positive or negative x in Figure 1. In the isothermal case jumps to the right and left are equally probable so $P_R(1) = P_L(3) = \frac{1}{2}$ and the jump rate $\Gamma(T)$ is the same in planes 1 and 3. Equation (2.1) then becomes

$$J(2) = \frac{1}{2}\left[n(1) - n(3)\right]\Gamma(T) \qquad (2.2).$$

Since $n(1) = ac(1)$, where $c(1)$ is the number of atoms per unit volume around plane 1 we can write

$$J(2) = \frac{1}{2} a \left[c(1) - c(3) \right] \Gamma(T) \tag{2.3}$$

We assume that the concentration is a slowly varying function of x over the range of the jump distance a and write

$$c(1) - c(3) = -a \frac{\partial c}{\partial x} \tag{2.4}$$

Equation (2.3) now takes the form of Fick's first law of diffusion:

$$J = -\frac{1}{2} a^2 \Gamma(T) \frac{\partial c}{\partial x} \tag{2.5}$$

We can then identify the empirical diffusion constant $D(T)$ in Fick's first law

$$J = -D(T) \frac{\partial c}{\partial x} \tag{2.6}$$

with

$$D(T) = \frac{1}{2} a^2 \Gamma(T) \tag{2.7}$$

Thus, as is well known, the isothermal jump rate $\Gamma(T)$ can be determined from measurements of the diffusion constant $D(T)$ over a range of temperatures.

B. Diffusion in a Temperature Gradient

We consider now the effect of imposing a temperature gradient across the crystal. The host lattice diffusion is assumed to be negligible and a well-defined temperature distribution $T(x)$ is therefore established which can be defined in terms of the mean square oscillations of the host lattice atoms around their equilibrium positions. In a given experimental situation, this temperature gradient could either be measured by appropriate probes or calculated by Fourier's law. A local temperature $T_1 \equiv T(x_1)$ and local temperature gradient $\Delta T(x_1)$ at plane 1 can be defined by

$$\Delta T(x_1) \equiv \Delta T_1 \equiv a \left.\frac{\partial T(x)}{\partial x}\right|_{x=x_1} \simeq T(x_3) - T(x_1) \qquad (2.8).$$

We assume that the total jump rate Γ for the impurity atoms on plane 1 in the presence of a temperature gradient ΔT is a function of T_1 and ΔT_1 such that when $\Delta T_1=0$ the jump rate is that of an isothermal system at temperature T_1. We expand Γ in a Taylor series in ΔT

$$\Gamma(T,\Delta T) = \Gamma(T) + A(T)\Delta T + B(T)(\Delta T)^2 + \ldots \qquad (2.9)$$

where $\Gamma(T)$ is the total jump rate in an isothermal system and $A(T)$ and $B(T)$ are functions describing the effect of the temperature gradient on the jump rate Γ. However, the term proportional to ΔT must vanish, i.e. $A(T)=0$, because the total jump rate $\Gamma(T,\Delta T)$ must not change if the direction of the temperature gradient is reversed. Thus to first order in ΔT, the total jump rate $\Gamma(T)$ at a local temperature T_i and a local temperature gradient ΔT_i is the same as that in an isothermal system at the temperature T_i. The temperature gradient, to first order, thus does not cause a change in the total jump rate but rather a bias in the jump direction -- i.e. a redistribution of the fraction of molecules going to the right or the left. For the isothermal case, $P_R(T,\Delta T=0) = P_L(T,\Delta T=0) = \frac{1}{2}$; in a temperature gradient we write an expansion in ΔT

$$P_R(T,\Delta T) = \frac{1}{2} + W(T)\Delta T + \ldots \qquad (2.10)$$

where $W(T)\Delta T$ gives the bias in the jump direction to first order in ΔT due to the effects of the temperature gradient on the host lattice. Analogously

$$P_L(T,\Delta T) = \frac{1}{2} - W(T)\Delta T + \ldots \qquad (2.11),$$

where we assume the temperature increases in the positive x direction. From

Eqs. (2.1), (2.10) and (2.11) we now find for the flux across plane 2

$$J(2) = \left[\frac{1}{2} + W(T_1)\Delta T_1\right] \Gamma(T_1)n(1) - \left[\frac{1}{2} - W(T_3)\Delta T_3\right] \Gamma(T_3)n(3) \quad (2.12).$$

Note that the $\Gamma(T)$ refer to the jump rates in an isothermal system (at temperatures T_1 and T_3 respectively) and that, to first order, the effect of the temperature gradient shows up only in the W's. We take $\Delta T_1 = \Delta T_3$ since the temperature gradient cannot change significantly over distances of the order of a lattice spacing. Also since $W(T)\Delta T$ is already first order in ΔT we can set $W(T_3)\Delta T = W(T_1)\Delta T$ in Eq. (2.12) to obtain

$$J(2) = \left[\frac{1}{2} + W(T_1)\Delta T_1\right] \Gamma(T_1)n(1) - \left[\frac{1}{2} - W(T_1)\Delta T_1\right] \Gamma(T_3)n(3) \quad (2.13).$$

Setting

$$n(3) = n(1) + \frac{\partial n}{\partial x} a \quad (2.14)$$

$$\Gamma(T_3) = \Gamma(T_1) + \frac{\partial \Gamma(T)}{\partial T} \Delta T \quad (2.15),$$

substituting the relations (2.14) and (2.15) into Eq. (2.13) and keeping only terms proportional to the first power of ΔT or $\frac{\partial n}{\partial x}$, we obtain

$$J(2) = -\frac{1}{2} a\Gamma(T_1) \frac{\partial n(1)}{\partial x} - \frac{1}{2} \frac{\partial \Gamma(T_1)}{\partial T} \Delta T n(1) + 2W(T_1)\Delta T \Gamma(T_1) n(1) \quad (2.16).$$

The use of the relation $n_1 = ac_1$ and Eq. (2.8) finally yields the thermal diffusion equation

$$J(2) = -\frac{1}{2} a^2\Gamma(T) \frac{\partial c}{\partial x} - \frac{1}{2} a^2 c\Gamma(T) \frac{\partial T}{\partial x} \left[\frac{\partial \ell n \Gamma(T)}{\partial T} - 4W(T)\right] \quad (2.17)$$

where $\Gamma(T)$, $\frac{\partial c}{\partial x}$, c, $\frac{\partial T}{\partial x}$ and W are all to be evaluated on plane 1. Using Eq. (2.7), which relates $\Gamma(T)$ to the isothermal diffusion constant D(T), we can also write Eq. (2.17) in the form

$$J(2) = -D(T)\left\{ \frac{\partial c}{\partial x} - c \frac{\partial T}{\partial x} \left[\frac{\partial \ell n D(T)}{\partial T} - 4W(T)\right] \right\} \quad (2.18)$$

The first term in Eq. (2.18) is the familiar isothermal result. The second term which is, proportional both to the temperature gradient and the local concentration, reflects the effect of the temperature gradient. Our subsequent discussion is concerned with the analysis and interpretation of the thermal diffusion Eqs. (2.17) and (2.18).

We can relate our jump bias parameter W to an experimental parameter Q_m, usually referred to as the "measured heat of transport." It is defined by the equation(7b)

$$-kT \frac{\partial \ell n c}{\partial x} = Q_m \frac{\partial \ell n T}{\partial x} \tag{2.19}$$

from which Q_m is to be evaluated when the measured concentration gradient of the diffusing species has become independent of time. In our approach the concentration gradient becomes independent of time when there is no net flux. Thus we set J(2) = 0 in Eq. (2.18) and rewrite the resulting equation as

$$-kT \frac{\partial \ell n c}{\partial x} = kT^2 \left(\frac{\partial \ell n D}{\partial T} - 4W \right) \frac{\partial \ell n T}{\partial x} \tag{2.20}$$

Comparing Eqs. (2.19) and (2.20) we see that our random walk theory relates W to Q_m by

$$Q_m = kT^2 \left(\frac{\partial \ell n D}{\partial T} - 4W \right) \tag{2.21}$$

It will be noted that the heat of transport, Q_m, is given by the difference between two quantities. The first of these, $\frac{\partial \ell n D}{\partial T}$ can be evaluated from measurements on isothermal systems. The second, the jump bias W(T), can be estimated, in principle, on the basis of an appropriate physical model. We present such a model in Section IV. It is clear from Eq. (2.21) that Q_m can be positive or negative depending upon the relative magnitudes of $\frac{\partial \ell n D}{\partial T}$ and W.

III. PHYSICAL INTERPRETATION OF THE THERMAL DIFFUSION EQUATION (2.18)

Equations (2.17) and (2.18) give the flux across a lattice plane as a function of the diffusion constant, the concentration gradient and the temperature gradient. The only term in (2.18) which cannot be evaluated from isothermal measurements is W, the bias in jump direction due to the effect of the temperature gradient on the host lattice. An a priori evaluation of W is very difficult. It could be taken as a disposable parameter to be evaluated from experimental data. This approach would be similar to that taken by Girifalco(9) and our theory can easily be related to his.

We shall now indicate how our model of interstitial thermal diffusion and the flux Eqs. (2.17) and (2.18) resulting from it can be used to interpret the available experimental data. It is clear that $\frac{\partial \ln D}{\partial T}$ or $\left(\frac{\partial \ln \Gamma}{\partial T}\right)$ is a positive quantity – the total jump rate Γ certainly increases as the temperature is increased, and experimental measurements confirm that the diffusion constant is an increasing function of the temperature. We would also expect, in general, that W is positive since a temperature gradient biases the jump direction towards the region of higher temperature (which for simplicity we shall call the hot side). This is due to the fact that the host lattice atoms have, on the average, larger vibration amplitudes on the hot side and thus the interstitial atom can jump more easily in this direction. Equation (2.20) shows that it is the interplay between W and $\frac{\partial \ln D}{\partial T}$ that determines the steady state concentration gradient established by a temperature gradient. If the lattice bias effect is sufficiently large so that $4W > \frac{\partial \ln D}{\partial T}$ then $\frac{\partial c}{\partial x} > 0$ in the steady state, i.e. there is a net motion of the impurity atoms towards the hot side starting from an initial homogenous distribution. When the lattice bias W is small and $4W < \frac{\partial \ln D}{\partial T}$ then $\frac{\partial c}{\partial x} < 0$. In this case there is a net motion of impurity atoms towards the cold side. This would tend to be the case for small interstitial impurities. In the limit of no lattice bias on the jump direction, i.e. for $W=0$, one has $\frac{\partial c}{\partial x} < 0$ and the impurity atoms always move toward the cold side simply because the total jump rate, $\Gamma(T)$ is higher in the high temperature region than in the low temperature one.

Allnatt and Rice$^{(3)}$ implicitly assumed $W=0$ in their random walk treatment of interstitial diffusion and thus concluded that Q_m is always positive and, from Eq. (2.21), equal to the activation energy for isothermal diffusion, $kT^2 \frac{\partial \ell n D}{\partial T}$. In the general case where there is a lattice bias effect one must, however, consider both terms in Eq. (2.21) to predict the sign and magnitude of the heat of transport.

IV. ESTIMATION OF THE LATTICE BIAS EFFECT

A. Isothermal Cell Model

We assume that the lattice bias effect W is primarily determined by the relative size of the impurity atom as compared to the interstitial cavity in the host lattice. The impurity atom causes a lattice strain and a jump from one interstitial site to another can occur only when (a) the amplitude of vibration of the impurity atom is large and directed towards the adjacent interstitial site, and (b) the atoms immediately surrounding the impurity atom move apart to permit the impurity to fit between them, and there is at the same time a local expansion of the lattice at the adjacent interstitial site which permits the impurity to fit comfortably into its new site. This dynamical description of diffusion has been discussed extensively by Rice.(4) In a temperature gradient it seems reasonable that condition (b) occurs more frequently on the hot side, where the lattice atoms will more often have sufficient energy to reach the "critical configuration." This then establishes a bias in the jump direction.

We present below a method for the calculation of W which makes use of the ideas in Rice's dynamical theory of diffusion. This treatment also leads to a more precise description of the ideas behind the Wirtz model(8) and suggests that it has some validity in the description of interstitial diffusion.

Following Rice,(4) we assume that a particle moves irreversibly to a neighboring interstitial site whenever (a) fluctuations cause it to achieve a critical displacement along the line joining the old to the new site and (b) all host lattice particles which might interfere with the jump have moved out of the way. The jump rate Γ is given by the frequency with which conditions (a) and (b) occur simultaneously. Rice then makes the physically reasonable approximation that condition (a), which involves a very large amplitude fluctuation, occurs less frequently than (b). The jump rate in a particular direction $\underset{\sim}{X}$ can then be written symbolically as

$$\Gamma_{\underset{\sim}{X}} \equiv P_{\underset{\sim}{X}}\Gamma = \nu(a)\rho(b) \tag{4.1}$$

where $\nu(a)$ is the frequency with which condition (a) occurs and $\rho(b)$ is the probability that the neighboring host lattice atoms have the appropriate configuration for the passage of the interstitial impurity independent of the position of the jumping interstitial atom. In our one dimensional model the total jump rate Γ is given by $\Gamma_R + \Gamma_L$.

The computation of $\nu(a)$ is very difficult since the motion of the interstitial impurity during a jump involves large fluctuations which certainly cannot be well described by the harmonic approximation customarily used. Furthermore the critical amplitude of this fluctuation leading to diffusion and the appropriate "reaction coordinate" cannot be obtained from the dynamical theory itself. Fortunately, under certain approximations to be detailed below, the lattice bias effect in a thermal gradient depends only upon $\rho(b)$ so that one does not have to calculate $\nu(a)$.

Rice has pointed out that in the isothermal case the probability $\rho(b)$ could be estimated fairly accurately by a harmonic potential model since the vibrations of the host lattice atoms will be of relatively small amplitude about their equilibrium positions and since the equilibrium positions of the host lattice atoms are fixed in space. To extend the calculation of $\rho(b)$ to a crystal in a thermal gradient we make two basic assumptions. First, we assume a cell model for the crystal and second, we assume that the magnitude of the vibrations of a host lattice atom in its cell is a function of the local cell temperature. In addition to these fundamental approximations we will make several additional non-essential approximations for computational and conceptual simplicity. We will first discuss the calculation of $\rho(b)$ for an isothermal system.

Since most thermal diffusion experiments occur at high temperatures (500°C to 2000°C), it seems reasonable to consider the simple Einstein independent oscillator model to describe the host lattice vibrations.(10) To apply this model to our calculation of $\rho(b)$ we make use of a single occupancy cell model for the crystal (in the presence of the impurity atoms) where each atom moves within its cell in the potential fields of its neighbors which are taken to be fixed at their static equilibrium positions. This is simply the Lennard-Jones and Devonshire theory,(11) which though developed for liquids, is really a theory for the solid state.(12) To simplify the problem, the nearest neighbors are now treated as uniformly "smeared" over a spherical surface. This yields a spherically symmetric potential which can be expanded to second order about the potential minimum and in this form leads to the Einstein independent oscillator model. Let $\underset{\sim}{r}_i$ represent the displacement of molecule i from its equilibrium position at the center of its cell. The subscript 1 will refer to the interstitial atom. For this simple cell model the classical canonical n particle probability density $P^{(n)}(\underset{\sim}{r}_2\underset{\sim}{r}_3\ldots\underset{\sim}{r}_{n+1})$, that is, the probability density for finding host lattice atom 2 in $d\underset{\sim}{r}_2$ at $\underset{\sim}{r}_2$, atom 3 in $d\underset{\sim}{r}_3$ at $\underset{\sim}{r}_3$ etc., is the product of single probability densities

$$P^{(n)}(\underset{\sim}{r}_2\underset{\sim}{r}_3\ldots\underset{\sim}{r}_{n+1}) = P^{(1)}(r_2)P^{(1)}(r_3)\ldots P^{(1)}(r_{n+1}) \qquad (4.2)$$

where

$$P^{(1)}(r_i) = \frac{e^{-\beta V_i(r_i)}}{\int e^{-\beta V(r_i)}\,d\underset{\sim}{r}_i} \qquad (4.3)$$

and $\beta = \frac{1}{kT}$. Here $V_i(r_i)$ is the spherically symmetric (smeared) potential which atom i feels when displaced a distance r_i from its equilibrium position.

Within the harmonic lattice approximation, we expand $V_i(r_i)$ about the minimum $r_i=0$ to obtain

$$V_i(r_i) = V_i(0) + \frac{1}{2}K_i r_i^2 \qquad (4.4).$$

We furthermore assume that the normalization integral in Eq. (4.3), which properly should extend only over the i^{th} cell, can be extended to infinity since $V_i(r_i)$ dies off so rapidly. With these approximations Eq. (4.3) becomes

$$P^{(1)}(r_i) = \left(\frac{\beta K_i}{2\pi}\right)^{3/2} e^{-\frac{\beta K_i}{2} r_i^2} \qquad (4.5).$$

The probability density $P^{(n)}(\mathcal{X}_2\mathcal{X}_3\ldots\mathcal{X}_{n+1})$ in Eq. (4.2) can now be calculated for all those *n* host lattice atoms which can conceivably interfere with the jump of the interstitial atom in a particular direction.

The physical basis of our calculation is that a jump can take place only when the host lattice atoms have moved in such a way that a passage has been opened for the interstitial atom. Note that by considering only those particular configurations of the host lattice atoms which permit a jump we are in effect improving the inaccurate treatment of the repulsive forces between the host lattice and interstitial atoms inherent in the harmonic lattice model.

We assume for simplicity that the repulsive forces between the host and interstitial atoms can be approximated by hard core interactions. The host lattice configurations which permit a jump of the interstitial atoms can then be estimated from the geometry of the system. From the geometry one can determine a critical displacement ξ_i of the i^{th} lattice atoms along a particular direction $\mathcal{X}_i$ which is essential for the passage of the impurity between interstitial sites.(4) For example, the nearest neighbor cell atoms to the impurity must move sufficiently far in a direction perpendicular to the "jump path" of the impurity that the radius of the resulting hole is equal to or larger than the hard sphere radius of the interstitial atoms. Motions of these host lattice atoms in other directions are probably less important and for simplicity, we assume that they do not effect the jump probability. With these assumptions, whose validity can admittedly be verified only *a posterori*, the probability

$\rho(b)$ can be written as the product of the probabilities $\Omega_i(\xi_i)$ for all the n neighboring atoms that the i^{th} host lattice atom has a displacement along $\underset{\sim}{X}_i$ equal to or greater than the necessary critical displacement ξ_i. From Eq. (4.5) we find

$$\Omega_i(\xi_i) = \frac{1}{2}\,\mathrm{erfc}\left[\left(\frac{K_i\xi_i^2}{2kT}\right)^{1/2}\right] \tag{4.6}$$

where the integration over r_i is from ξ_i to infinity in the direction $\underset{\sim}{X}_i$ and from minus infinity to infinity in the other normal directions. The complementary error function used in Eq. (4.6) is defined by

$$\mathrm{erfc}\ z = \frac{2}{\sqrt{\pi}}\int_z^{\infty} e^{-t^2}dt \tag{4.7}.$$

With these approximations, the jump rate Γ_R of our one-dimensional model in the absence of a temperature gradient then becomes [see Eq. (4.1)]

$$\Gamma_R(T_1,\Delta T=0) = \nu(a)\rho(b) = \nu(a,T_1)\prod_{i=2}^{n+1}\Omega_i(\xi_i,T_1) \tag{4.8}$$

where we have explicitly indicated the temperature dependence of the terms.

B. Cell Model in a Temperature Gradient

According to the local equilibrium approximation, Eq. (4.8) will still be valid in a thermal gradient where now each cell is characterized by its own temperature T_i. In general to first order in ΔT we can write

$$T_i = T_1 + \alpha_i\Delta T \tag{4.9}$$

where α_i is a dimensionless quantity given by

$$\alpha_i = \frac{\Delta X_i}{a}, \tag{4.10}$$

ΔX_i is the distance from plane 1 at temperature T_1 to cell i at temperature T_i and $\underline{a}$ is the jump length defined earlier. Thus, in a temperature gradient, Eq. (4.8) becomes

$$\Gamma_R(T_1,\Delta T) = \nu(a,T_1) \prod_{i=2}^{n+1} \Omega_i(\xi_i, T_1+\alpha_i\Delta T) \tag{4.11}$$

The frequency $\nu(a)$ in our local equilibrium model is a function only of the local temperature T_1 of the cell around the impurity atom and not of the temperature gradient. It is now easy to relate the quantities of Eq. (4.11) to $W(T)$, the parameter in our random walk model. By definition, to first order in ΔT, we have

$$P_R(T_1,\Delta T) \equiv \frac{1}{2} + W(T_1)\Delta T = \frac{\Gamma_R(T_1,\Delta T)}{\Gamma_R(T_1,\Delta T)+\Gamma_L(T_1,\Delta T)}$$

$$= \frac{1}{2}\,\frac{\Gamma_R(T_1,\Delta T)}{\Gamma_R(T_1,\Delta T=0)} = \frac{1}{2}\left[1 + \frac{\partial \ln \Gamma_R(T_1,\Delta T=0)}{\partial(\Delta T)}\,\Delta T\right] \tag{4.12}$$

where we have used the fact [see Eq. (2.9)] that the total jump rate $\Gamma_R + \Gamma_L$ is the same, to first order in ΔT, as that for the isothermal system with $\Delta T=0$. Substitution of Eq. (4.11) into (4.12) yields for $W(T_1)$

$$W(T_1) = \frac{1}{2}\sum_{i=2}^{n+1} \frac{\partial \ln \Omega_i(\xi_i,T_1)}{\partial T}\,\alpha_i \tag{4.13}$$

Note that $\nu(a,T_1)$, which would be difficult to calculate, drops out of the theory as discussed above. The bias in jump direction is thus due to the different probabilities $\rho(b)$ with which the host lattice can achieve the critical configurations on either side of the impurity in a thermal gradient.

Equation (4.13) allows us to relate the random walk parameter W to the local lattice geometry and the force constants K_i. From Eq. (4.6) we obtain

$$\frac{\partial \ln \Omega_i(\xi_i,T_1)}{\partial T} = \frac{\left(\frac{\gamma_i}{2T_1}\right) e^{-\gamma_i^2}}{\int_{\gamma_i}^{\infty} e^{-t^2}\,dt} \tag{4.14}$$

where

$$\gamma_i = \left(\frac{K_i\xi_i^2}{2kT_1}\right)^{1/2} \tag{4.15}$$

Using the inequalities(13)

$$\frac{1}{z+(z^2+2)^{1/2}} < e^{z^2} \int_z^\infty e^{-t^2} dt \le \frac{1}{z+\left(z^2+\frac{4}{\pi}\right)^{1/2}} \qquad (4.16),$$

Eq. (4.14) becomes

$$\frac{\partial \ln \Omega_i(\xi_i, T_1)}{\partial T} = \frac{\gamma_i^2}{2T_1}\left[1 + (1+\eta/\gamma_i^2)^{1/2}\right] \qquad (4.17)$$

where

$$\frac{4}{\pi} \le \eta < 2 \qquad (4.18).$$

Usually $\gamma^2 \gg \eta$ since $\frac{1}{2} K_i \xi_i^2$, the potential energy of the host lattice oscillator at its critical displacement, is much greater than kT_1, the average energy per degree of freedom of the host lattice oscillator at temperature T_1. To a first approximation we can therefore neglect the η/γ^2 term in Eq. (4.17) and write

$$\frac{\partial \ln \Omega_i(\xi_i, T_1)}{\partial T} = \frac{K_i \xi_i^2}{2kT_1^2} \qquad (4.19).$$

We then finally obtain from Eq. (4.13), for the bias $W(T_1)$ in the jump direction

$$W(T_1) = \frac{1}{2T_1} \sum_{i=2}^{n+1} \left(\frac{K_i \xi_i^2}{2kT_1}\right) \alpha_i \qquad (4.20).$$

The lattice bias around the impurity site 1 is thus simply related to the sum of the reduced potential energies of the n nearest neighbor independent oscillators (atoms) of the host lattice at their critical displacement weighted by the distance parameters α_i.

If we assume that the isothermal diffusion constant can be written as

$$D(T) = D_o e^{-\frac{\Delta E}{kT}} \qquad (4.21)$$

where ΔE is the activation energy for diffusion, then the heat of transport, defined in Eq. (2.21), becomes, using Eqs. (4.20) and (4.21),

$$Q_m = \Delta E - \sum_{i=2}^{n+1} (K_i \xi_i^2)\alpha_i \qquad (4.22).$$

The heat of transport for interstitial thermal diffusion can thus, in principle, be calculated from Eq. (4.22) if the isothermal activation energy for diffusion is known.

There are, however, some ambiguities in calculating the parameters K_i, ξ_i and α_i for any given host lattice-impurity system. These ambiguities are compounded by the paucity of experimental data for Q_m for the type of interstitial diffusion we consider here — reliable data seems to be available only for a few systems.(7) This lack of data and the ambiguities inherent in the calculation of K_i, ξ_i and α_i makes it impossible to check at this time, by comparing calculated and measured heats of transport, whether heats of transport calculated from Eq. (4.22) are in reasonable agreement with experimental values. We have obtained order of magnitude agreement, as well as the correct sign, for Q_m for the thermal diffusion of C and H in α-(bcc)Fe(7a) by calculating K_i from compressibility data using the simple Einstein theory(14) and estimating ξ_i, α_i and n from the atomic radii of C, H and Fe and the known crystal structure of the body centered cubic Fe lattice. This agreement is encouraging and suggests that this theory should get a more careful test when additional data becomes available. Hopefully, this attempt at a theory will stimulate some relevant experimental work.

V. RELATION TO THE WIRTZ MODEL

The spirit of this treatment and the resulting Eq. (4.22) are very reminiscent of the classic Wirtz model.(8) The Wirtz model for interstitial diffusion can be interpreted to state that the jump rate to the right, Γ_R, is given by

$$\Gamma_R = \nu \exp \frac{1}{k}\left(E_1/T_1 + E_2/T_2 + E_3/T_3\right) \qquad (5.1)$$

where ν is a vibration frequency. The quantity E_1 is interpreted as that part of the total activation energy needed to move the impurity atom away from its initial site on plane 1, (see Fig. I), E_2 that part needed to move apart the adjacent lattice atoms on lattice plane 2 and thus permitting the impurity atom to pass through, and E_3 the part necessary to enlarge the adjacent interstitial site on plane 3 to accomodate the impurity. Thus a very specific distribution of the overall activation energy is considered and it is assumed that each component is supplied at the local temperature of the particular plane involved. Using Eq. (4.12) we find that the Wirtz model predicts a lattice bias W given by

$$W(T_1) = \frac{1}{2kT_1^2}\left|\alpha_2 E_2+\alpha_3 E_3\right| \quad . \qquad (5.2)$$

where $\alpha_2 = \frac{1}{2}$ and $\alpha_3 = 1$. As expected, E_1 does not contribute to W. From Eqs. (2.21) and (4.21) the predicted heat of transport is then

$$Q_m = \Delta E - \left(2\alpha_2 E_2 + 2\alpha_3 E_3\right) \qquad (5.3).$$

Wirtz takes the activation energy ΔE to be $\Delta E=E_1+E_2+E_3$ which yields

$$Q_m = E_1-E_3 \qquad (5.4)$$

for the heat of transport. Equation (5.4) predicts that the heat of transport is always less than the activation energy ΔE and indeed obeys the stronger inequality

$$|Q_m| \leq \Delta E \qquad (5.5).$$

This latter result has been criticized since negative heats of transport, larger in magnitude than ΔE, have been observed experimentally.(7)

Our random walk treatment, together with the Einstein model of independent oscillators, has lead to an equation for Q_m [Eq. (4.22)] which is very similar to Eq. (5.3) of the Wirtz model. The random walk model predicts that the heat of transport will be less than the activation energy ΔE, though (depending on the values of α_i, K_i and ξ_i)negative heats of transport larger in magnitude than ΔE may occur. This conclusion is in agreement with the experimental data of Allnatt and Chadwick(7a) and of Oriani.(7b) The parameters E_2 and E_3 in the Wirtz model are related to the probabilities of achieving critical configurations in the host lattice. The cell model suggests that E_3, the part of the activation energy related to enlarging the adjacent interstitial site on plane 3, should involve an α_3 of $\frac{3}{2}$ rather than 1 since host lattice atoms must move on the two planes adjacent to the new interstitial site. In this case Eq. (5.4) now reads

$$Q_m = E_1 - 2E_3 \tag{5.6}$$

and the Wirtz model can predict a negative Q_m with $|Q_m| > \Delta E$. The Wirtz model also predicts that the heat of transport is independent of temperature (to the degree that E_1 and E_3 are), though a temperature dependence is sometimes observed experimentally. Both the general random walk model, Eq. (2.21), and the cell model, Eq. (4.13), clearly permit a temperature dependent Q_m. When the Einstein model approximations are valid and Eq. (4.22) holds, this predicted temperature dependence will be small.

One can thus interpret the Wirtz model of thermal diffusion as a local equilibrium generalization of Rice's isothermal diffusion model. The specific equations of the model, e.g. Eq. (5.1) for the jump rate and Eq. (5.4) for Q_m, are over-simplified versions of a more complicated cell model approach, but under certain circumstances the cell model theory gives expressions closely resembling the Wirtz model. The physical picture behind the Wirtz model appears to be a plausible and suggestive description of thermal diffusion by an interstitial mechanism for those systems where the bias in jump direction is primarily due to an "excluded volume" effects.

VI. ACKNOWLEDGEMENTS

The authors had the benefit of a number of stimulating conversations with Dr. John Howe and several members of his group of the Research and Development Division of Gulf General Atomics. We also acknowledge with thanks many helpful discussions with our colleagues, Professors John Weare and John Wheeler.

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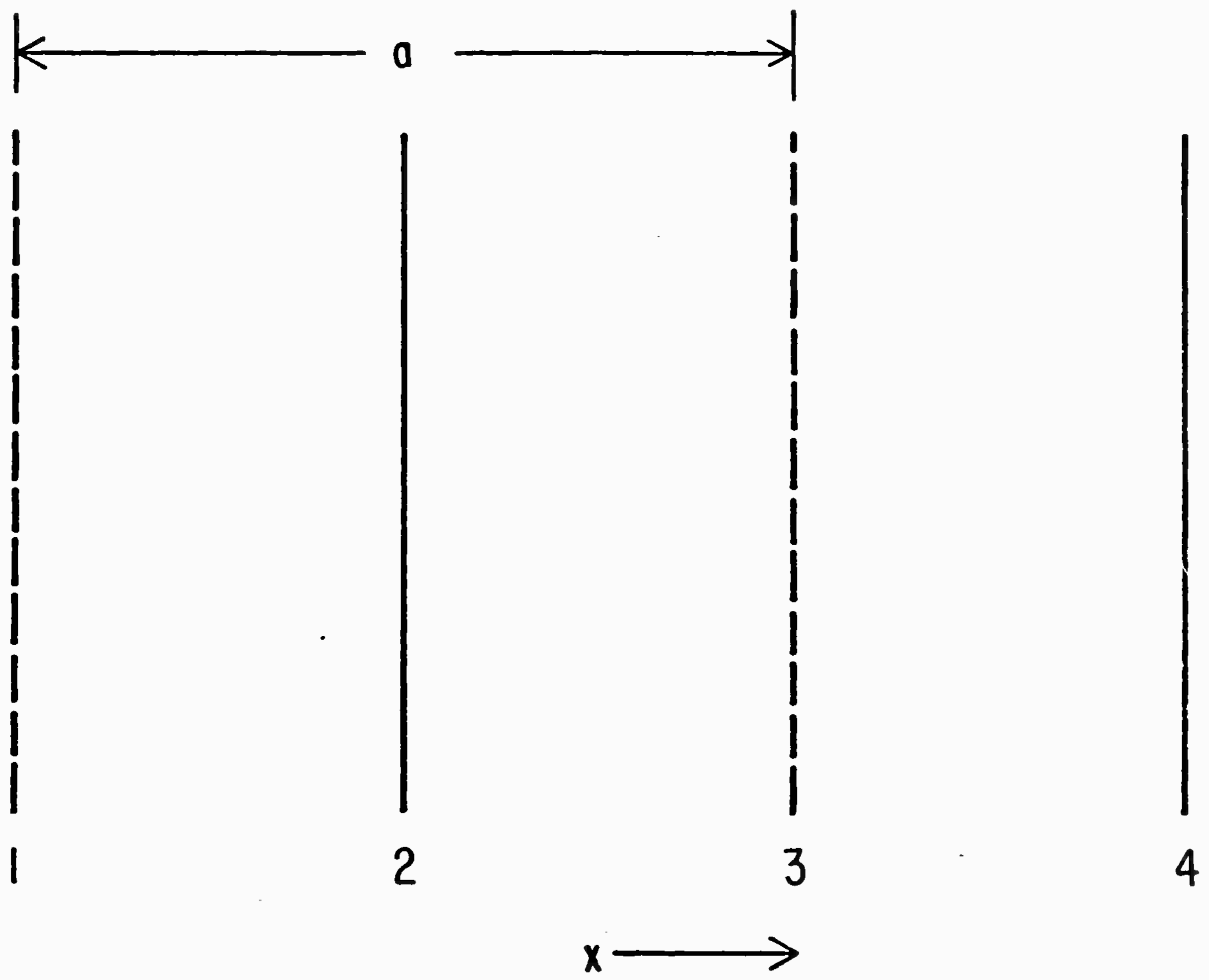
FIGURE CAPTION

Figure 1: Schematic representation of interstitial planes 1 and 3 separated by lattice plane 2 in the one dimensional model.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