effective mass in the lower band (which is presumably responsible for the high heat capacity observed below 13°K) does not appear to warrant drawing any detailed conclusions concerning the nature of these energy levels. We can conclude, however, that they are associated with a rather complex sort of crystal defect. This would seem to follow from the fact that if we insert in Eq. (2) the value 700 millijoule/deg per gram-atom oxygen loss (the average arrived at in Pt. III) we find that the free-electron concentration corresponds to only one electron for each eighteen oxygen atoms lost by reduction. It is thus possible that more than one set of levels is involved, and that we observe the excess heat capacity due only to electrons in one band with very high effective mass. Its disappearance between 13 and 16°K would be expected if this band were (a) narrower than 13°K (about 10^{-3} electron volt), and (b) separated by a gap of rather greater energy than this from the next higher band of levels. Our data are consistent with both of these requirements, since (a) the degeneracy temperatures in the moderately reduced samples are only about one-tenth of 13°K, and (b) at least in the lightly reduced NBS sample, the gap corresponding to the slope of the straight line in Fig. 4 is about eight times larger than 13°K.

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Dynamical Theory of Diffusion in Crystals

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The theory of self-diffusion in a crystal via the vacancy mechanism is investigated from a detailed dynamical model. It is shown that the parameters which determine the diffusion coefficient can be defined in terms of the normal coordinates of the crystal. The effects of lattice imperfections are considered explicitly in the formulation in the normal mode analysis, but no detailed analysis is given. The effects of the correlation in motion of atoms is considered and some comments on the physical nature of the contributions to the enthalpy and entropy of activation are presented.

I. INTRODUCTION

THE theory of diffusion in a crystalline phase is usually developed by an application of absolute rate theory. If it is assumed that the diffusing atom moves by a series of "jumps" of length ΔX in the X direction, and if the frequency with which these jumps occur is denoted by Γ, then the diffusion coefficient may be written in the form[1]

$$\mathfrak{D}=\tfrac{1}{2}\Gamma(\Delta X)^2, \tag{1}$$

the factor $\frac{1}{2}$ arising from the possibility of jumps $-\Delta X$. To compute the frequency of jumps it is supposed that the diffusing particle must surmount a free-energy barrier. A simple application of the formalism of absolute rate theory then leads to the relation[2]

$$\mathfrak{D}=(kT/h)(\Delta X)^2\exp(-\Delta G^\dagger/kT), \tag{2}$$

with $\Delta G^\dagger$ the Gibbs free energy of activation per molecule, and the universal constants k and h have their usual significance. Other formulations, substantially equivalent to the application of absolute rate theory, have also been presented. Thus Zener obtains for the diffusion coefficient the relation[3]

$$\mathfrak{D}=\gamma a^2\nu\exp(-\Delta G^\dagger/kT), \tag{3}$$

with a the lattice parameter, γ a numerical constant, and ν a rather ill-defined vibrational frequency.

Note that both expressions (2) and (3) involve a free energy of activation rather than an energy of activation. It is necessary that the barrier be a free energy rather than an energy in order to account for the inevitable complimentary changes which occur in a dense medium when a single particle is moved. That is to say, the mean force acting on the diffusing atom is the gradient of the local free energy, i.e., the potential of mean force, and not of the potential energy of interaction. Equations (2) and (3) have been used principally for the description of the temperature dependence of the diffusion coefficient and to distinguish between alternative diffusive mechanisms by means of the calculation of $\Delta G^\dagger$. Despite the ambiguity in the definition of various fundamental quantities (such as the frequency ν) this

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[1] S. Chandrasekhar, Revs. Modern. Phys. **15**, 1 (1943).

[2] See, for example, C. Zener, in *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), p. 289.

[3] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955).

program has met with a considerable measure of success.[2]

There are, however, several objections to the formalism embodied in Eqs. (2) and (3). To cite two, we mention first that the basic assumption underlying the application of absolute rate theory to diffusive processes is that there exists a transition state whose existence is sufficiently well defined and whose lifetime is sufficiently long that it makes sense to define the thermodynamic properties of the activated atom. It is usually further assumed that the properties of the transition state are substantially identical with the properties of unactivated states except along certain reaction coordinates. This last assumption is troublesome in that $\Delta G^\dagger$ then refers to a ratio of partition functions with different numbers of degrees of freedom and therefore does not represent the work done in any simple process. The postulation of a thermodynamically definable activated state would seem to require either some experimental demonstration of its existence, or at least a plausibility argument indicating that its mean lifetime is sufficiently long to achieve the equilibrium proposed. It is generally believed, however, the diffusing particle spends most of its time on one or the other side of the barrier and actually crosses very rapidly (in a period covering at most a few vibrations). Under these circumstances the use of an activated state is probably a marked oversimplification.

A second criticism may be directed against the usual calculations of the entropic part of the free energy of activation. These analyses ordinarily proceed by using macroscopic parameters such as elastic constants and with almost total neglect of the details of the local dynamics. It is known that the inclusion of defects in a crystalline lattice modifies the frequency spectrum of the lattice, especially in the vicinity of an impurity.[3] Since it is just the local environment of the lattice defect which is expected to dominate its motion, the description of local dynamical behavior in terms of macroscopic parameters can lead to errors. An extreme example of this local behavior is the existence of a pulsating mode in the vibrational spectrum of a one-dimensional crystal with a vacancy.[3] This mode refers to the out-of-phase motions of the neighbors of the hole and is localized in the vicinity of the vacancy. In the course of time the out-of-phase motions occasionally become in phase and the vacancy thereby diffuses. Clearly, the neglect of this localized mode will markedly alter the computed diffusion coefficient.

From a mechanistic point of view, it would be desirable to formulate the theory of diffusion in terms of a dynamical model, rather than using a thermodynamic description. The use of thermodynamic functions at the very outset to describe molecular behavior results in an averaging procedure which masks much of the physical situation. It is probably advantageous to proceed from the opposite point of view, even if this requires the introduction of approximate procedures. The purpose of this brief communication is to outline the formal theory of diffusion in solids by a method which proceeds directly from a consideration of the lattice dynamics. The formalism is based upon analogies with the theory of unimolecular reaction rates and makes extensive use of some calculations due to Slater.[4] The chief advantages accruing from this procedure are that all average molecular parameters become well-defined and the origins of the energetic and entropic changes involved can be identified. Subsequent notes will deal with the application of the formalism to special models.

Before proceeding, we wish to mention an investigation by Vineyard[5] which treats the process of diffusion in the complete phase space of the system. Vineyard computes the velocity with which the phase point passes over the barrier by a technique essentially identical with that used by Pelzer[4] to discuss the theory of unimolecular reactions. The advantage of performing all the calculations in the complete phase space is that the many-body character of the problem is emphasized. A major point of departure between Vineyard's treatment and that presented herein is that Vineyard's treatment is in the sense of transition state theory and still makes use of the assumption that the state at the top of the col is sufficiently long-lived to permit the definition of thermodynamic functions. The author cannot prove or disprove this assumption, but his personal prejudice is that it is not accurate for the case of diffusion. We do not use this assumption in the development of this paper. The treatment contained herein may be considered to be complimentary to that of Vineyard and represents a different point of view.

II. SOME GENERAL CONSIDERATIONS

It is well known that if the restoring forces acting on an atom in a crystal are linear in the displacement of the particle from its equilibrium position, then it is possible to make a normal mode analysis of the motion of the N-body system.[6] In this harmonic approximation, each of the normal modes is independent of all the others, but the normal modes do not, in general, correspond to the motion of atoms along arbitrarily selected paths in the lattice. Any such motion along a particular trajectory is composed of contributions from many different modes of vibration. If there are no external interactions, any given normal mode remains constant in time, unchanged in energy or phase. However, the particular trajectory mentioned above is composed of a sum of oscillating functions with the result that its energy does change in time, provided only that the individual contributions to the sum are not everywhere in phase.

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[4] A. F. Trotman-Dickenson, *Gas Kinetics* (Academic Press, Inc., New York, 1955). N. B. Slater, Proc. Roy. Soc. (London) **A194**, 112 (1948); Proc. Roy. Soc. (London) **A164**, 161 (1955).

[5] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[6] An extensive analysis of this problem is to be found in M. Born and K. Huang, *The Dynamical Theory of Crystals* (Oxford University Press, Oxford, 1955).

Consider, for definiteness, the motion of an atom in the first shell of neighbors of a vacancy and consider the vacancy mechanism of diffusion. In order that the atom or vacancy change its lattice position it is necessary that the amplitude of vibration of the atom along the line between the lattice points of atom and vacancy be sufficiently large that the force tending to pull the atom into the adjacent vacancy lattice position exceeds the restoring force tending to return it to its own lattice position. In addition to this requirement there are at least two other obvious physical conditions which must be satisfied. If attention is focused on one atom as the migrating species, then the direction in which the vibration occurs is important. For, if we temporarily regard the shell of neighbors as static, only if the direction of the vibration falls into that solid angle corresponding to the location of the vacancy can an exchange of sites occur. Second, examination of hard sphere models of close packed lattices reveal that if the positions of the atoms in the shell immediately surrounding a vacancy remain unaltered, then the migrating central atom cannot reach the vacancy site due to the small cross-sectional area presented by the hole in the shell. In order for diffusion to occur there must be an out of phase motion of the atoms surrounding the vacancy or, in macroscopic language, local expansion of the lattice. Finally, if attention be focused on an atom in the crystal chosen at random, diffusion is possible only if there is a vacancy adjacent to the atom. The diffusion coefficient therefore also depends upon the vacancy concentration.

The preceding paragraph has been couched in terms of a normal mode analysis and of harmonic forces. This is certain to be incorrect for the discussion of vibrations with amplitudes large enough to cause an exchange of lattice sites. However, the simplification introduced by considering the thermal motion to be harmonic is so extensive that we shall use it despite its obvious shortcomings. In justification, it will be recalled that in the Debye model of a crystal the thermal expansion of the lattice is explained as follows. If the forces acting on the atoms were completely harmonic, there would be no thermal expansion and therefore the particles must move in nonlinear fields of force. At any fixed temperature, however, it is a reasonable approximation to regard the thermal motion as harmonic with an origin and frequency which differs from that at another temperature. That is, the thermal expansion is regarded as due to the shift in the mean position of an atom due to the asymmetry of the field, but the vibrations about the shifted mean position are always taken as harmonic. The procedure may be regarded as a perturbation treatment in which the perturbation is sufficiently small not to alter the character of the forces though it may slightly shift their origin. The physical picture presented in this paper does not require that the crystal be harmonic. The long-term average frequency with which the central atom achieves a critical amplitude may be defined for anharmonic forces, but in these cases, the relation between the motions of the central atom and its neighbors is much more difficult to analyze.

A second major approximation which will be made in this note is the treatment of the crystal dynamics only in the classical limit. This restricts the treatment to the temperature range $T > \frac{3}{5}\Theta_D$, where Θ_D is the Debye characteristic temperature. In this temperature region the deviation of the specific heat computed by the Debye model from the classical value $3R$ is a maximum of 15% at $T = \frac{3}{5}\Theta_D$ and smaller at larger T. The deviation of the energy from its classical value is much smaller.

In the following, only the vacancy mechanism for self-diffusion is discussed. The formalism presented can easily be extended to other mechanisms and to more complicated diffusion problems, but for the present these extra complications are omitted to prevent obfuscation of the general principles. Some extensions will be considered along with the detailed effects of lattice imperfections in a subsequent note.

The frequency with which an atom makes a jump of length ΔX in a specified direction may be written in the transparent form

$$\Gamma = \sum_{\text{n.n.}} \rho_{ij}^{(2)} \mathcal{P}(\{\delta\}), \tag{4}$$

where $\rho_{ij}^{(2)}$ is the pair distribution function in coordinate space, i.e., the probability of finding an atom at lattice site i and a vacancy at lattice site j, and $\mathcal{P}(\{\delta\})$ is the frequency of occurrence of a configuration in which the central atom has large amplitude of vibration properly oriented and there is an out-of-phase motion of the surrounding atoms, the symbol $\{\delta\}$ referring to said configuration. The summation is to be taken over all the nearest neighbors of the atom since the vacant site can be located at any one of the positions of the first shell.

The pair distribution function (referring only to lattice sites) is a function of the concentrations of atoms and vacancies. Since the vacancy concentration is very low, it is permissible to neglect the correlation between vacancies and atoms and express $\rho_{ij}^{(2)}$ as

$$\rho_{ij}^{(2)} = \frac{N}{L}\left(\frac{L-N}{L}\right), \tag{5}$$

where the crystal contains L lattice sites and N atoms. Equation (5) is an expression of the approximation that the holes and atoms are randomly mixed. This approximation is likely to be quite adequate at the temperatures ordinarily employed for self diffusion measurements. It should be borne in mind, however, that the attractive force acting between two holes in a lattice will cause them to coalesce and separate as a distinct phase at absolute zero.[3] The incipient clustering preliminary to phase separation may occur in a measurable temperature range, provided that the thermodynamics of hole formation permits a sufficient concentration. To proceed, since $L \simeq N \gg L-N$, Eq. (5) may be written in the abbreviated form

$$\rho_{ij}^{(2)}=(L-N)/L=\phi, \tag{6}$$

where ϕ is the site fraction of vacancies. In the usual manner, the site fraction of vacancies could be related to their free energy of formation. We shall postpone the introduction of this thermodynamic relationship for the present.

To calculate the frequency with which a special configuration occurs requires a consideration of the lattice dynamics. In the next section it is shown that the factor $\mathcal{P}(\{\delta\})$ is of the form

$$\mathcal{P}(\{\delta\})=\nu e^{-U_0/kT}\prod_j e^{-U_j/kT}\prod_{k>l} g_{kl}^{(2)}, \tag{7}$$

where ν is a weighted mean frequency, U_0 is the energy required for the central atom to reach the critical vibrational amplitude along the line connecting the atom and vacancy lattice sites, the U_j are the energies required to shift the shell atoms from their equilibrium positions, and the $g_{kl}^{(2)}$ are the pair correlation functions relating to the positions of atoms k and l. The product is to be taken over all shell atoms required to move before the diffusive displacement can occur, and the $g_{kl}^{(2)}$ include the correlations between all pairs of atoms, especially the migrating atom and all the displaced shell atoms. The weighting factors for the mean frequency will be seen to be just the squares of the contributions from the various normal coordinates. The substitution of Eq. (6) into Eq. (4) leads to the relation

$$\mathcal{D}=\tfrac{1}{2}Z\nu(\Delta X)^2\phi e^{-U_0/kT}\prod_j e^{-U_j/kT}\prod_{k>l} g_{kl}^{(2)}, \tag{8}$$

with Z the number of nearest neighbors to an atom. Note that the energy U_0 is not the energy of activation.

III. ROLE OF LATTICE DYNAMICS

Consider some one atom adjacent to a vacancy. The conditions which must be fulfilled for a diffusive motion to occur have been discussed in Sec. II. It is fairly evident, from physical considerations, that the motions which must be made by the shell atoms in order to permit a central atom to migrate are vibrations of much smaller amplitude than the particular very large amplitude vibration which affects the translation of the central atom from one site to the next. It is also physically clear that the frequency with which any atom explores a given configuration decreases with decreasing probability of occurrence of the configuration. We may therefore safely conclude that the frequency with which shell motions of the proper amplitude occur is probably much greater than the frequency with which the central atom reaches the critical vibrational amplitude. These considerations permit us to make the following physical approximation. It will be assumed that the frequency factor $\mathcal{P}(\{\delta\})$ is equal to the frequency with which the central atom achieves the necessary critical amplitude multiplied by the multiparticle distribution function describing the configuration of all the atoms involved when in the critical spatial configuration. This specific assumption about the rate-determining step greatly simplifies the mathematical treatment. It is not necessary to make this approximation but the mathematical complications then completely obscure the mechanical situation. Note that this approximation involves the assumption that the amplitude of the shell atom vibrations is sufficiently small that the product of a number of exponential factors, with negative exponents $-U_j/kT$, is still much larger than the one term involving in the Boltzmann factor the large energy U_0. This assumption appears accurate on the harmonic oscillator model for which the energy is proportional to the square of the amplitude. We first focus attention on the motion of the migrating atom.

In the following paragraphs we shall make extensive use of Slater's[4] results. We repeat many of them here since they are unfamiliar to most investigators interested in solid-state physics.

We assume that a normal mode analysis of the crystal has been made including the effects of lattice defects[3] and that therefore the normal coordinates Q_i and frequencies ν_i are known. Consider some very large crystal with a low density of vacancies. About each vacancy site excise a volume element sufficiently large that the motion of an atom in the shell surrounding the vacancy in an arbitrary direction is essentially uncorrelated with the motions of atoms outside the volume. Under these circumstances the rest of the crystal serves as a heat bath for the subvolume under consideration.

Let the displacement in the direction of the line between the occupied and vacant sites be denoted by q_1. Then q_1 may be represented as the superposition of normal coordinates with various weights, α_{1i},

$$q_1=\sum\nolimits_i \alpha_{1i}Q_i, \tag{9}$$

and

$$Q_i=\epsilon_i^{\frac{1}{2}}\cos[2\pi(\nu_i t+\delta_i)], \tag{10}$$

with ν_i, ϵ_i, and δ_i the frequency, energy and phase of the ith normal coordinate. The $\{\epsilon_i\}$ and $\{\delta_i\}$ change only through the interaction of the volume element with the surrounding heat bath. However, although the energy and phase of a single normal coordinate does not change except due to external interactions, the amplitude of a particular atomic motion does change due to the time dependence of the superposition of the normal coordinates.

The atom is assumed to jump from one lattice point to another if and when the particular coordinate q_1 reaches a critical value q_0. For this to happen, the contributions to q_1 of the normal coordinates must satisfy the relation

$$\sum\nolimits_i |\alpha_{1i}|\epsilon_i^{\frac{1}{2}} > q_0. \tag{11}$$

If there are n modes of vibration which contribute to the coordinate q_1, then the total energy is easily seen to be

$$U=\sum_{i=1}^{n} \epsilon_i, \tag{12}$$

since there are no interactions between the normal coordinates. The number of contributing modes, n, may be very much smaller than the total number of modes of vibration. Symmetry effects prevent certain modes from contributing to q_1 and the establishment of a precision to within which q_1 is to be specified provides a cutoff for many others. From Eq. (11) it is readily found that the minimum energy satisfying the condition expressed in Eq. (11) is of the form

$$U_0=q_0^2/\sum_1^n \alpha_{1i}^2, \tag{13}$$

where it must be emphasized that U_0 is the minimum energy required for the atom to achieve the critical amplitude and is not the activation energy. We shall discuss the choice of q_0 in Sec. IV.

Due to the exchange of energy by the region of the crystal under examination with its surrounding heat bath, the subvolume fluctuates in energy. Let ω be the frequency with which these fluctuations in energy occur. If the rate at which an atom jumps into a vacant lattice site is small relative to the frequency with which the energy of the subvolume (more particularly the n normal coordinates contributing to the coordinate q_1) fluctuates, then the subvolume under consideration will be essentially in thermal equilibrium with the surrounding thermostat. Now, the combination of the condition expressed in Eq. (11) with the expansion of Eq. (9) leads to the following definition of the critical configuration which must be realized for diffusion to occur:

$$q_1-q_0=\sum_{i=1}^{n} \alpha_{1i}\epsilon_i^{\frac{1}{2}} \cos[2\pi(\nu_i t+\delta_i)]-q_0=0. \tag{14}$$

Consider an ensemble of subvolumes of the type described. The assumption that the frequency of fluctuations, ω, is very much larger than the frequency with which q_1-q_0 passes through zero from the region $q_1-q_0<0$ permits us to replace an ensemble average by the long term time average behavior of the sum (14). Let $M(\{\epsilon_i\})$ be the long term average frequency of zeros of Eq. (14) defined as

$$M(\{\epsilon_i\})=\text{frequency of zeros of } \tfrac{1}{2}\lim_{\tau\to\infty} \times\left[\frac{1}{\tau}\sum_{i=1}^{n} \alpha_{1i}\epsilon_i^{\frac{1}{2}} \cos[2\pi(\nu_i t+\delta_i)]-q_0\right], \tag{15}$$

where the factor one-half arises from the fact that we are interested only in the frequency of approach to zero from the region $q_1-q_0<0$. As indicated, the frequency of zeros is a function of the energies ϵ_i, the definition (15) implying constant total energy in the n normal coordinates. The total rate at which an atom reaches the critical amplitude is then equal to the probability of finding the system with total energy given by Eq. (12) multiplied by the long term average frequency of zeros corresponding to that total energy, integrated over all values of the energy larger than a lower limit, U_0,

$$\Gamma_1=\int_{U>U_0} M \exp\left(-\frac{1}{kT}\sum_{i=1}^{n} \epsilon_i\right)\frac{d\epsilon_1}{kT}\cdots\frac{d\epsilon_n}{kT}. \tag{16}$$

The frequency of zeros of the trigonometric sum has been found by Kac to be[4,7]

$$M=\frac{1}{4\pi^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\cos(q_0 x)}{y^2}\prod_{i=1}^{n}\{J_0(\alpha_{1i}\epsilon_i^{\frac{1}{2}}x) -J_0(\alpha_{1i}[\epsilon_i(x^2+4\pi y^2\nu_i^2)]^{\frac{1}{2}})\}dxdy, \tag{17}$$

with $J_0(x)$ the Bessel function of zero order. Equation (17) automatically satisfies the condition that $M(\{\epsilon\})=0$ when $U<U_0$, so that the range of integration in Eq. (16) can be over all values of the energy. Insertion of Eq. (17) into Eq. (16), followed by the indicated integrations, leads to the exact result

$$\Gamma_1=\nu e^{-U_0/kT}, \tag{18}$$

with the mean frequency ν defined by the relation

$$\nu^2=\sum_{i=1}^{n} \alpha_{1i}^2\nu_i^2/\sum_{i=1}^{n} \alpha_{1i}^2, \tag{19}$$

and where U_0 is given in Eq. (12). Note that the frequency lies between the greatest and smallest frequencies contributing to q_1. The role of imperfections in determining the rate of diffusion is contained in the normal-mode analysis, presumed known. With this knowledge a calculation of ν can be made from physical approximations to the normal-coordinate contributions to q_1.

To complete the specification of the frequency of atomic jumps now requires consideration of the multiparticle distribution function in configuration space. In general, the probability density for finding molecule one in the volume element $d\tau_1$ about $q_1\cdots$ and molecule h in volume element $d\tau_h$ about q_h is given by[8]

$$\mathcal{P}^{(h)}(q_1,\cdots q_h)=\int\cdots\int e^{-U/kT}d\tau_{h+1}\cdots d\tau_N \Big/ \int\cdots\int e^{-U/kT}d\tau_1\cdots d\tau_N. \tag{20}$$

In a crystal, the many-body probability density may be expressed as the product of probability densities in pair

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[7] M. Kac, Am. J. Math. 65, 609 (1943).

[8] See, for example, T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956).

space. In contrast to the case of liquids, this superposition principle is correct in the harmonic crystal. To illustrate, consider that only two shell atoms must move to provide a large enough hole for diffusion. The probability density in triplet space may be decomposed as follows[8]:

$$\mathcal{P}^{(3)}(q_1,q_2,q_3)=\frac{\mathcal{P}^{(2)}(q_1,q_2)\mathcal{P}^{(2)}(q_1,q_3)\mathcal{P}^{(2)}(q_2,q_3)}{\mathcal{P}^{(1)}(q_1)\mathcal{P}^{(1)}(q_2)\mathcal{P}^{(1)}(q_3)}. \qquad (21)$$

It is convenient to define the pair correlation function $g_{kl}^{(2)}$ by the relation

$$\mathcal{P}^{(2)}(q_k,q_l)=\mathcal{P}^{(1)}(q_k)\mathcal{P}^{(1)}(q_l)g_{kl}^{(2)}, \qquad (22)$$

thus enabling Eq. (21) to be rewritten as

$$\mathcal{P}^{(3)}(q_1,q_2,q_3)=\mathcal{P}^{(1)}(q_1)\mathcal{P}^{(1)}(q_2)\mathcal{P}^{(1)}(q_3)g_{12}^{(2)}g_{13}^{(2)}g_{23}^{(2)}, \qquad (23)$$

and from Eq. (20) $g_{kl}^{(2)}$ is seen to be

$$g_{12}^{(2)}=v^2\int\cdots\int e^{-U/kT}d\tau_3\cdots d\tau_N \Big/ \int\cdots\int e^{-U/kT}d\tau_1\cdots d\tau_N, \qquad (24)$$

and

$$\begin{aligned} v\mathcal{P}^{(1)}(q_1)&=e^{-U_1/kT},\\ v\mathcal{P}^{(1)}(q_2)&=e^{-U_2/kT}, \end{aligned} \qquad (25)$$

where U_1 and U_2 are the energies required to place particles one and two at distances q_1 and q_2 from their lattice points and v is the volume available to an atom, the volume of a cell. The pair correlation function defined herein is normalized differently than the one used in the theory of fluids.[8] The outstanding feature of a fluid is the constant singlet density, $\mathcal{P}^{(1)}\sim 1/V$, whereas crystals have a periodic structure. The existence of this periodic structure makes it convenient to define coordinates in terms of displacement from lattice points. The probability densities which we are using and the corresponding pair correlation functions all are taken to refer to displacements from lattice points and not to general points in space.

Let the total potential energy of the crystal be written in the form

$$2U=\sum_{i>j}a_{ij}q_iq_j, \qquad (26)$$

where, as before, the q_i are displacements from the lattice positions and the a_{ij} are coefficients. To compute the integral in the denominator of Eq. (24), we make a normal-mode analysis for all N atoms, which leads to the well-known result

$$\prod_{\mu=1}^{3N}\left[\frac{kT}{2\pi m\nu_\mu^2}\right]^{\frac{1}{2}}, \qquad (27)$$

where the spectrum of frequencies is to be determined, including lattice defects, from a more extended analysis and m is the mass of an atom. To reduce the integral in the numerator, we require a different normal-mode analysis in which the coordinates of particles one and two are omitted from the diagonalization of the quadratic form.[9] To do this, transform Eq. (26) to the equivalent form

$$2U=\sum_{i>j=3}^{3N}a_{ij}q_iq_j+\sum_{i\geq 3}^{3N}a_{1i}q_1q_i+\sum_{j\geq 3}^{3N}a_{2j}q_2q_j +a_{11}q_1^2+2a_{12}q_1q_2+a_{22}q_2^2. \qquad (28)$$

Let the determinant of the matrix which diagonalizes the first term of Eq. (28) be denoted by $A^{(N-2)}$. Then the potential energy U is transformed to the form

$$U=\tfrac{1}{2}\sum_{i=3}^{3N}m\omega_i^2Q_i^2+\tfrac{1}{2}\sum_{l}\sum_{i\geq 3}a_{1i}q_1R_{il}Q_l +\tfrac{1}{2}\sum_{l'}\sum_{j\geq 3}a_{2j}q_2R_{jl'}Q_{l'} +\tfrac{1}{2}a_{11}q_1^2+a_{12}q_1q_2+\tfrac{1}{2}a_{22}q_2^2, \qquad (29)$$

where, ω_i is the angular frequency associated with the ith normal coordinate Q_i and R_{il} and R_{jl}, are the normal eigenvectors corresponding to columns i and j of the transformation matrix. The integration indicated in the numerator of Eq. (24) may now be performed by completing the square, the final result being[10]

$$g_{12}^{(2)}=v^2\exp\left[-\frac{1}{2kT}(a_{11}q_1^2+2a_{12}q_1q_2+a_{22}q_2^2)\right] \times\prod_\mu |A^{(N-2)}|^{-(3N-6)/2}\exp\left(-\frac{L_\mu^2}{4m\omega_\mu^2kT}\right) \times\left[\frac{2\pi kT}{m\omega_\mu^2}\right]^{\frac{1}{2}}\Big/\prod_\mu\left[\frac{2\pi kT}{m\omega_\mu^2}\right]^{\frac{1}{2}}, \qquad (30)$$

where

$$L_\mu=(1/\surd 2)\textstyle\sum_i(a_{1i}q_1+a_{2i}q_2)R_{i\mu}. \qquad (31)$$

By decompositions similar to that expressed in Eqs. (21) and (22), higher order distribution functions may also be decomposed. The final form of the diffusion coefficient is thus seen to be, collecting Eqs. (1), (4), (18), (20), (23), and (25),

$$\begin{aligned}\mathfrak{D}&=\tfrac{1}{2}\int\sum_{\text{n.n.}}\phi\Gamma_1\mathcal{P}^{(h)}e^{U_0/kT}(\Delta x)^2\prod_j^h\delta(q_j-q_{j0})dq_j\\ &=\tfrac{1}{2}Z\nu(\Delta x)^2\phi e^{-U_0/kT}\prod_j e^{-U_j/kT}\prod_{k>l}g_{kl}^{(2)}(q_k,q_l),\end{aligned} \qquad (32)$$

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[9] I am indebted to Dr. R. M. Mazo for pointing out the possibility of this transformation.

[10] L. Van Hove, Phys. Rev. **95**, 249 (1954).

with the q_{j0}'s the required critical amplitudes of shell atoms, and where the factor $e^{U_0/kT}$ has been inserted in the first form to account for the fact that Γ_1 contains as a factor $\mathcal{P}^{(1)}(q_0)$ which also appears in the probability density $\mathcal{P}^{(h)}$.

IV. DISCUSSION

It is of interest to transform Eq. (32) to a form similar to Eq. (3) and to determine the activation energy. Assuming that the details of the diffusive mechanism are known, i.e., the numbers of atoms involved and their directions of motion, etc., Eq. (32) may be rewritten in the form

$$\mathfrak{D}=\gamma a^2\nu \exp\left(-\frac{1}{kT}\sum_i U_0+U_j\right)\exp\left(-\frac{1}{kT}\sum_{k>l} W_{kl}\right)\times\exp\left[-\frac{1}{kT}(\Delta H_h-T\Delta S_h)\right], \quad (33)$$

where the constant γ is composed of the number of nearest neighbors and the geometric parameters which convert the jump length ΔX to the lattice parameter a, the potential of mean force W_{kl} is defined by

$$g_{kl}^{(2)}=e^{-W_{kl}/kT}, \quad (34)$$

and ΔH_h and ΔS_h are the enthalpy and entropy of formation of a hole. This latter factor is just the thermodynamic relation between the site fraction of holes and the energetics of formation. If the enthalpy of activation is now defined by

$$\frac{\partial \ln\mathfrak{D}}{\partial(1/T)}=-\frac{\Delta H^\dagger}{k}, \quad (35)$$

we readily find that

$$\Delta H^\dagger=U_0+\sum_j U_j+\sum_{k>l}\Delta H_{kl}+\Delta H_h, \quad (36)$$

where ΔH_{kl} is the energetic contribution to the potential of mean force.[11] In a similar manner, an entropy of activation may be *defined* as

$$\Delta S^\dagger=\Delta S_h+\sum_{k>l}\Delta S_{kl}, \quad (37)$$

$$W_{kl}=\Delta H_{kl}-T\Delta S_{kl}, \quad (38)$$

where the new symbols have obvious meanings. The total entropy of activation is composed of the entropy of formation of the lattice vacancies plus the entropic contributions to the potential of mean force. It is not immediately obvious that the entropic contributions ΔS_{kl} will be related to the temperature coefficient of the elastic moduli.[2] For, if this suggestion of Zener's is carried to its logical conclusion, it is implied that the total entropy of activation is due to the temperature dependence of the elastic energy with the complete neglect of the entropic changes due to changes in vibrational amplitudes, etc. In a crude approximation, this amounts to neglecting terms of order of magnitude $\Delta S_{\text{amp}}=R\ln(q_0^2/Z\langle q_1^2\rangle)$ for the migrating atom. The mean square amplitude of vibration may be estimated for a Debye crystal for which

$$\langle q_1^2\rangle=\frac{3h^2T}{4\pi^2mk\Theta_D^2}+\left(\frac{h}{2\pi}\right)^2\frac{1}{12mkT}.$$

When $\Theta_D=200°$, $T=300°$, $m=50$ amu and $q_0=a/2=10^{-8}$ cm, we obtain $\Delta S_{\text{amp}}=7.3$ entropy units/mole. The estimate is probably not too accurate but does indicate that an appreciable error can be made by considering only the elastic contribution to $\Delta S^\dagger$.

It is pertinent to point out that the energy U_0 calculated from Eq. (13) will be a very poor approximation to the energy required to reach q_0 in a real crystal due to the neglect of anharmonic forces. This does not detract from the theoretical utility of Eq. (13) which expresses a relationship between the energetics of the motion and the contributions of the various normal modes. The critical distance q_0 is not given by the theory. It must be assumed from some model of the lattice and the diffusive process or calculated in a manner to be discussed below. If we choose q_0 as half the distance between sites, the simplest procedure to use would then be to calculate the q_{j0} from the geometry and for hard spheres. In view of the steepness of the repulsive potential this is probably an adequate approximation. It is important to note that the q_{j0} are fixed by the geometry and the choice of q_0. We have shown that an "activation energy" can be defined by the temperature derivative of the diffusion coefficient, and this activation energy contains U_0 additively. The remaining terms should be amenable to fairly accurate approximation on the harmonic potential model because they refer to displacements of much smaller magnitude. If then an experimental value of the activation energy (enthalpy) is given, we can in principle calculate U_0 by difference with reasonable accuracy. From U_0 and the normal-mode analysis, q_0 could be calculated. Owing to the inaccuracy of the harmonic potential it is probably preferable to calculate U_0 in the manner indicated rather than from Eq. (13).

The necessity of choosing q_0 from considerations external to the formal theory is an expression of the unsatisfactory manner in which irreversibility has been introduced. In this theory, as in all other crystal diffusion theories, irreversibility is introduced by fiat. It is assumed that once the top of the col has been passed, or once a critical amplitude attained, the motion becomes irreversible. That is, the Einstein relation, Eq. (1), is tacitly accepted and all that is computed by the

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[11] ΔH_{kl} is defined by the relation $\partial \ln g_{kl}^{(2)}/\partial(1/T)=-\Delta H_{kl}/k$ with analogous formal definition of ΔS_{kl}.

theory is the frequency factor. To the author's knowledge, no *general* theory of irreversible processes has been constructed for the crystal. The arbitrary nature of the introduction of irreversibility is reflected in the necessity for a col, or for q_0.

To proceed with the analysis presented herein, it is in principle possible to evaluate ΔH_{kl} and ΔS_{kl} by taking suitable derivatives of W_{kl} as defined by Eqs. (30) and (34). This procedure is, unfortunately, algebraically complicated. A crude approximation to the activation energy may be obtained by neglecting the terms ΔH_{kl} relative to the other contributions. In that case, if every displacement coordinate is represented as the sum of contributing normal coordinates, it is easily seen that

$$U_j = q_{j0}^2 / \sum_{i=1}^{n} \alpha_{ji}^2, \tag{39}$$

and is determinable from the normal-mode analysis. No such approximation can be made for the entropy of activation where the dominant terms are likely to be just the ΔS_{kl}. At present the best procedure would seem to be the use of the suitable derivative of Eq. (30).

The dynamical analysis of diffusion presented in this note has been based on several implicit assumptions not mentioned in Sec. I. The first and most obvious of these is the tacit acceptance of the Einstein relation, Eq. (1). The analysis given is not a complete dynamical theory of the diffusion coefficient, but only of the frequency factor Γ. In the process of evaluation of the frequency Γ it was assumed that the incidence of fluctuations in energy of the subvolume considered is random. This leads to the conclusion that the incidence of the critical configuration is also random. So long as the frequency of the fluctuations is large relative to Γ, it does not matter whether or not this is rigorously correct. It may be shown[4] that the frequency with which the central atom reaches the critical configuration is, in general, $M(1-\langle e^{-\omega\tau}\rangle)$ where the averaging is over the intervals between zeros of the sum (14). The mean frequency of zeros will be proportional to τ^{-1}, and if $\omega \gg \tau^{-1}$, then $\omega\tau \gg 1$ and the frequency with which the central atom achieves the proper amplitude and position is just M independently of the actual distribution of fluctuations or zeros. It is extremely likely that the frequency of energy fluctuations fulfills the condition $\omega \gg \Gamma$. The model considered exchanges energy with the heat bath at every lattice point on the surface of the subvolume. The frequency with which the energy of a surface atom coupled to the heat bath exceeds the mean thermal energy is clearly larger than M, and since there are $N^{\frac{2}{3}}$ atoms on the surface, the condition $\omega \gg \Gamma$ is likely to be satisfied.

Turning to a consideration of the thermodynamic functions for vacancy formation, it should be noted that Vineyard[12] and Dienes have proposed that the entropy of formation of a vacancy is just $RZ\ln(\nu'/\nu)$, where ν' and ν are respectively the frequencies (on an Einstein crystal model) of the unperturbed atoms and the atoms neighboring a vacancy. This estimate neglects the very large perturbation which leads to the localized imperfection mode discussed previously. Further, the use of an Einstein model would be valid if the spectrum of frequencies remained unaltered in the vicinity of the imperfection, but this is not the case. The formula proposed by Vineyard and Dienes is a very useful approximation if the reservations mentioned are kept in mind.

The dynamical theory presented herein is seen to provide unique definitions of all the fundamental parameters appearing in Eq. (3), as well as some physical interpretation of the relationship between the motion of a migrating atom and its surroundings. It is in principle now possible to compute every parameter of Eq. (3) from a microscopic model, though the calculations will involve considerable labor and the energy U_0 will be poor due to the harmonic potential. Further investigation of the details of the effects of lattice imperfections along with simplifications of the calculations will be presented later.

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[12] G. H. Vineyard and G. J. Dienes, Phys. Rev. **93**, 265 (1954).