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Rate Processes in Solids

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The jump rate k for atomic diffusion via the vacancy mechanism in crystals is evaluated by treating a jump as the result of a particular type of thermal fluctuation in a crystal. The occurrence rate of this fluctuation is found (a) using a dynamical method similar in content to that of Rice and Manley, and (b) using statistical mechanics directly as was done by Vineyard. If the jumps are effected only when the surrounding atoms take up one single distorted configuration (the first approach being limited to describing one configuration only) then both methods are exactly equivalent and give the same k (Sec. II).

The total k is then obtained by summing the contributions to k from the most significant configurations using a saddle point integration (Sec. III). This is done without introducing new (incalculable) "saddle-point" frequencies which in the Vineyard theory, leaves the pre-exponential factor inprecisely defined. In k, all parameters are well defined in terms of the force constants and its mass dependence is always exactly $m^{-1/2}$ [Eq. (27)].

In the discussion, contact is made with earlier forms of the frequency factor, and, by way of example, the expression for k is used to evaluate the self-diffusion coefficient in solid argon giving a value in agreement with experiment (Sec. IV).

I. INTRODUCTION

UNTIL the late 1950's, all derivations[1-5] of the jump rate k for diffusion in crystals were based on the absolute rate theory[6] borrowed from chemical reaction kinetics. In these treatments, k is expressed in the form $k=\bar{\nu}\exp(-\Delta F/kT)$, where ΔF is the height of the free-energy barrier the atom must surmount to pass to the adjacent site and $\bar{\nu}$ is an effective vibration frequency of the atom in the initial site. Although considerable progress along semi-empirical lines has been made using this expression, the whole approach and final expression has a number of limitations from a fundamental viewpoint. Two of these are, (a) that the atom must unrealistically move infinitely slowly up the barrier so that each intermediate state is defined in a thermodynamic sense, and (b) the parameters $\bar{\nu}$ and ΔF are inprecisely defined so that the theory provides little insight for a fundamental calculation of k.

Recently, however, Vineyard[7] has presented a more rigorous, many-body approach using equilibrium statistics which largely eliminates these shortcomings. Thermodynamic arguments are not used so there is no need to specify that the jump proceed slowly. The top of the free-energy barrier, as it was called above, is now a clearly defined special configuration of the crystal atoms; that specific configuration for which the jump is effected with the least increase in the atomic potential energy above the static potential; the activation energy being just this potential increase. Vineyard does, however, introduce a new set of lattice frequencies for the crystal when the atoms are in this special (minimum energy) configuration. This has two drawbacks.

(a) These frequencies, although mathematically definable, do not exist in real crystals as the special configuration is instantaneous (the frequencies could be meaningful only if the lattice stayed near the configuration $O(\nu_m^{-1})$ or greater, where ν_m is the maximum lattice frequency).

(b) As the frequencies do not exist, there is no way of evaluating them so that the frequency factor and its mass dependence remains inprecisely defined.

As well, Rice[8] (and co-workers)[9] and Manley[10] have presented a "dynamical" theory of diffusion which emphasizes the microscopic character of the jump process. Here k is developed by going over to normal coordinates and using the fact that these independent coordinates obey random variable theorems. By transformation, the statistics of the atomic coordinates can then be obtained to evaluate the probability per unit time that the migrating and surrounding atoms attain special amplitude displacements from their rest positions which "allow" the migrating atom to jump. This approach avoids the direct use of equilibrium statistics (employing instead, random variable arguments for the independent normal coordinates) and places no time restrictions during the jump. The resulting expression is, however, difficult to simplify and so provides little help for fundamental calculation of k.

The above treatments assume that equilibrium statistics properly describe the statistics of real atoms in a crystal in which diffusion is taking place. However, let us focus attention on the n atoms in the crystal which have vacancies adjacent to them at time t. After

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[1] R. M. Barrer, *Diffusion in and Through Solids* (Cambridge University Press, London, 1941), p. 291.

[2] C. A. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[3] C. A. Wert, Phys. Rev. **79**, 601 (1950).

[4] C. Zener, in *Imperfections in Nearly Perfect Crystals*, W. Shockley, J. H. Holloman, and F. Seitz, Eds. (John Wiley & Sons, Inc., New York, 1952), p. 265.

[5] A. Seeger, in *Encyclopedia of Physics*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1955), Vol. VII, I.

[6] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co., Inc., New York, 1941).

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

[8] S. A. Rice, Phys. Rev. **112**, 804 (1958).

[9] S. A. Rice and H. L. Frisch, J. Chem. Phys. **32**, 1046 (1960), and references cited therein.

[10] O. P. Manley, J. Phys. Chem. Solids **13**, 244 (1960).

a short time δt, those atoms of this ensemble which have had large amplitude displacements from their rest position (large energies) and velocities in the direction of the vacancy simultaneously will have jumped into the adjacent vacant site. At $t+\delta t$, the remaining atoms (plus average energy additions) are now more likely to have velocities in the reverse direction and smaller energies than would be predicted by the original equilibrium distribution. Use of equilibrium methods to evaluate k for the ensemble at $t+\delta t$ would lead to error. Energy exchange effects between atoms, going on continuously in the crystal, attempt to restore equilibrium and if the rate of jumping, which distorts the distribution, is small compared to the exchange rates, the distribution always remains close to the canonical one. The diffusion discussions of Rockmore and Turner[11] and Prigogine and Bak[12] are particularly concerned with avoiding equilibrium methods and evaluating the effect of the disturbed distribution on k. For the jump rates realized in real crystals, their results show that the equilibrium k is altered only numerically and by $\sim 10\%$, indicating that the equilibrium assumption, which we use here, introduces little error.

All of the above calculations[7–12] are still transition-state treatments in the sense that each introduces an intermediate state from which it is assumed that the jump goes to completion. The rate calculation then reduces to evaluating the rate at which the intermediate state is reached, with no discussion of the process thereafter. This should be a legitimate procedure provided some guarantee is included that the atom does actually jump rather than return part of the time to the original site so that k is not over-counted (the only real concern of a jump rate calculation). We may then refer to other papers[13] for a description of the remainder of the process; the irreversible return of the atomic coordinates towards their mean values which is of the same character whichever site the atom settles in.

In this discussion, we further develop the idea that a jump arises as a result of a fluctuation of a lattice in equilibrium; that fluctuation in which one atom has a large amplitude displacement and the surrounding atoms open up a hole so that this atom can pass to the adjacent vacant site without a tremendous potential energy increase in the lattice. The jump rate is derived from both a dynamical approach, identical in content to those of Rice and Manley (Sec. IIA), and from a straightforward application of equilibrium statistics similarly to that of Vineyard (Sec. IIB). The two approaches give identical results and differ only in the treatment of the minimum potential (and other) configurations of the lattice atoms during the jump. This demonstrates the essential equivalence of the two methods and so, while not providing a proof of validity, gives us more confidence in the simpler equilibrium statistical approach. The minimum potential "hole" configuration is then considered without introducing a new set of lattice frequencies (Sec. III) which (a) avoids requiring that the jumps proceed slowly, and (b) provides an explicit expression of $\tilde{\nu}$ for calculation and determining its mass dependence. Calculation of $\tilde{\nu}$ and the activation energy are discussed in Sec. IV. The treatment is restricted to vacancy diffusion in a lattice in equilibrium (i.e., to self-and impurity self-diffusion) with quantum effects neglected.

II. EVALUATION OF THE JUMP RATE

We consider diffusion in a Bravais lattice of N atoms having vacant sites with the lattice points given in terms of the primitive translation sectors by $\mathbf{a}_n = n_1\mathbf{a}_i + n_2\mathbf{a}_j + n_3\mathbf{a}_k$. We use these vectors to define a coordinate system $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ in the lattice and denote the positions and velocities of the N atoms by $\mathbf{r}_1 \cdots \mathbf{r}_N$ and $\dot{\mathbf{r}}_1 \cdots \dot{\mathbf{r}}_N$. In this lattice we wish to obtain the probability of observing a fluctuation which results in, say, atom labeled 1 jumping (along the $\mathbf{i}$ direction) into the adjacent cell 2 which, for the moment, we simply take to be vacant. We denote this probability by $P(r_1{}^i = a_0/2;\ \dot{r}_1{}^i \geq 0;\ r_1{}^j, r_1{}^k, \mathbf{r}_3 \cdots, \mathbf{r}_m)$ which is the probability of observing a fluctuation such that (1) atom 1 has a large amplitude displacement from its rest position which carries it to the cell boundary between cell 1 and 2 ($r_1{}^i = a_0/2$, (2) atom 1 have some positive velocity in the direction of cell 2($\dot{r}_1{}^i \gtrsim 0$), and (3) that the surrounding $(m-1)$ atoms which are sensibly correlated to atom 1 (and the atom 1 along the coordinates j and k) take up positions $r_1{}^j$, $r_1{}^k$, $\mathbf{r}_3 \cdots \mathbf{r}_m$ so that the potential energy $V(\mathbf{r}_1 \cdots \mathbf{r}_m)$ associated with this displacement is not vastly greater than the static potential energy $V(\mathbf{r}_1 = \mathbf{a}_1,\ \mathbf{r}_3 = \mathbf{a}_3 \cdots \mathbf{r}_m = \mathbf{a}_m) = V_0$.

The velocity requirement (2) is introduced to ensure that, with atom 1 on the cell boundary where the choice of return to either cell 1 or cell 2 is equal, the atom continues into cell 2. The lattice will then always return from this fluctuation with the atom in cell 2 provided a second fluctuation does not occur which sends the atom back to cell 1, the likelihood of which is $O(P)$. We must either treat such second fluctuations as a second or new jump, which seems the most consistent procedure, or concede that our jump rate k above is in error by the fraction of times $O(10^{-5})$ this happens. Even detailed considerations of the return from the fluctuation will not eliminate this difficulty entirely and here we consider the second fluctuation as a new jump.

From $P(r_1{}^j = a_0/2,\ \dot{r}_1{}^i \geq 0,\ r_1{}^j, r_1{}^k, \mathbf{r}_3 \cdots \mathbf{r}_m)$, the jump rate k, given by the rate of atomic flow into the adjacent cell is[7]

$$k = \int_0^\infty P(\quad)\, \dot{r}_1{}^i \, d\dot{r}_1{}^i \qquad (1)$$

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[11] D. M. Rockmore and R. E. Turner, Physica **29**, 567 (1963).

[12] I. Prigogine and T. A. Bak, J. Chem. Phys. **31**, 1368 (1959).

[13] G. W. Ford, M. Kac, and P. Mazur, J. Math. Phys. **6**, 504 (1965), and references cited therein.

where we must integrate over all positive velocities $\dot{r}_1^i$ as P will give the probability for a single velocity and we want the probability for any positive velocity. We now proceed to evaluate P and k from (a) dynamical and statistical and (b) purely statistical considerations of the lattice. The reader interested only in the result should omit part (a).

A. Dynamical Approach

If we write the atomic coordinates (and velocities) in terms of the lattice point positions $\mathbf{a}_n$ plus some displacement from them $(\mathbf{r}_n=\mathbf{a}_n+\mathbf{u}_n)$, then the Hamiltonian for the crystal is

$$H=\tfrac{1}{2}\sum_n m_n\dot{\mathbf{u}}_n^2+V_0+\tfrac{1}{2}\sum_{nn'}A_{nn'}\mathbf{u}_n\mathbf{u}_{n'}, \tag{2}$$

where m is the atom mass and the potential $V(\mathbf{r}_1\cdots\mathbf{r}_N)$ has been expanded about the static potential $V(\mathbf{r}_1=\mathbf{a}_1\cdots\mathbf{r}_N=\mathbf{a}_N)$ and terms up to the harmonic retained

$$A_{nn'}\equiv(\partial^2V/\partial\mathbf{r}_n\partial\mathbf{r}_{n'})_{\mathbf{a}_n,\mathbf{a}_{n'}}.$$

Transforming to normal coordinates $q(f,s)$ using the transformation

$$\mathbf{u}_n=\frac{1}{(Nm)^{\frac{1}{2}}}\sum_{f,s}^{3N}\exp\,(i\mathbf{f}\mathbf{a}_n)\,\boldsymbol{\varepsilon}_s(f)\,q(f,s)\equiv\sum_{k=1}^{3N}a_{nk}q_k, \tag{3}$$

where f is the wave vector and $\boldsymbol{\epsilon}_s(f)$ the polarization vectors for the three branches s for each f, the Hamiltonian becomes (taking $V_0=0$)

$$H=\tfrac{1}{2}\sum_{k=1}^{3N}(p_k^2+\omega_k^2q_k^2). \tag{4}$$

Here $p_k=\partial/\partial q_k=q_k$ is the momentum conjugate to q_k and ω_k^2 is the transform of A

$$\omega_k^2=\mathbf{a}^+\mathbf{A}\mathbf{a} \tag{5}$$

with Eq. (3) defining the matrix elements of $\mathbf{a}$. The effect of the vacant sites on the ω_k^2 spectrum is assumed to be included.

On substituting (4) into Hamilton's equations, we obtain the solutions for p_k and q_k from which we may obtain the time dependence of $\mathbf{u}_n$ (and $\dot{\mathbf{u}}_n$ by differentiation). The general solution for q_k gives

$$\mathbf{u}_n=\sum_k a_{nk}(q_k^0\cos\omega_kt+p_k^0/\omega_k\sin\omega_kt) \tag{6}$$

which displays dynamically how large amplitude displacements can arise.

As the normal coordinates and momentum are independent they are, like any independent variable, distributed Gaussianly about zero; the mean square deviation here being obtained by taking the expectation value of (4) $\langle H\rangle=3\ NkT$ using the equipartition theorem. The probability $W(p_k,q_k)$ of observing the coordinates p_k between p_k and p_k+p_k and q_k between q_k and q_k+dq_k is then

$$W(p_k,q_k)=\prod_{k=1}^{3N}\frac{\exp(-p_k^2/2\sigma_{p_k}^2)\cdot\exp(-q_k^2/2\sigma_{q_k}^2)}{(2\pi)\,\sigma_{p_k}\sigma_{q_k}}, \tag{7}$$

where $\sigma_{p_k}^2=kT$ and $\sigma_{q_k}^2=kT/\omega_k^2$.

We now employ a theorem on Guassian distributions[14] which states that; if the independent p_k and q_k are distributed according to (7), then coordinates such as $\mathbf{u}_n$, $\dot{\mathbf{u}}_n$, $\mathbf{u}_{n'}$, $\cdots$ (say s in number) which are related to the p_k and q_k by transformations of the form

$$\mathbf{u}_n=\sum_k^{3N}a_{nk}q_k\quad\text{or}\quad\dot{u}_n=\sum_k^{3N}a_{nk}p_k,$$

are distributed according to

$$\begin{aligned}P(\mathbf{u}_1(1),\dot{\mathbf{u}}_1(2),\mathbf{u}_3(3),\dot{\mathbf{u}}_3(4),\cdots\mathbf{u}_n(s-1)\dot{\mathbf{u}}_n(s))\\ =(2\pi)^{-3/2s}\,|\,B\,|^{-\frac{1}{2}}\exp\,(-\tfrac{1}{2}\mathbf{u}^+B^{-1}\mathbf{u})\\ =(2\pi)^{-3/2s}\,|\,B\,|^{-\frac{1}{2}}\exp\,[-\tfrac{1}{2}\sum_{nn'}^{s}b_{nn'}^{-1}\mathbf{u}_n\mathbf{u}_{n'}].\end{aligned} \tag{8}$$

Here $\mathbf{B}$ is a matrix made up of elements

$$\begin{aligned}b_{nn'}&=\sum_k a_{nk}a_{n'k}\langle q_k^2\rangle=\langle\mathbf{u}_n\mathbf{u}_{n'}\rangle,\\ b_{\dot{n}\dot{n}'}&=\sum_k a_{nk}a_{n'k}\langle p_k^2\rangle=\langle\dot{\mathbf{u}}_n\dot{\mathbf{u}}_{n'}\rangle,\\ b_{n\dot{n}'}&=\sum_k a_{nk}a_{n'k}\langle q_kp_k\rangle=\langle\mathbf{u}_n\dot{\mathbf{u}}_{n'}\rangle=0,\end{aligned} \tag{9}$$

(where we have used the symbol $\dot{n}$ to identify elements referring to velocities) and $\mathbf{B}^{-1}$ and $|\,B\,|$ are the inverse and determinant of this matrix $\mathbf{B}$, respectively. The last type of elements in (9) are zero as the equal time correlation function $\langle\mathbf{u}_n(t),\dot{\mathbf{u}}_n(t)\rangle=0$, as can be shown using (6). With (8) we may now obtain the probability of observing any fluctuation in the lattice coordinates, and thus the probability of observing the special fluctuation $p(u_1^i=a_0/2;\ \dot{u}_1^i\geq0;\ u_1^j,\ u_1^k,\ \mathbf{u}_3\cdots\mathbf{u}_n)$ involving $(3m+1)$ coordinates which leads to an atomic jump where now the $\mathbf{u}_n=\mathbf{r}_n-\mathbf{a}_n$ are the variables. This is

$$\begin{aligned}P(\quad)=(2\pi)^{-\frac{1}{2}(3m+1)}\,|\,B\,|^{-\frac{1}{2}}{}_{(3m+1)}\\ \times\exp\,[-\tfrac{1}{2}\sum_{nn'}^{m}b_{nn'}^{-1}\mathbf{u}_n\mathbf{u}_{n'}+\sum_{n}^{m}b_{n\dot{1}}^{-1}\mathbf{u}_n\dot{u}_1^i],\end{aligned} \tag{10}$$

where we have grouped the factors involving $\dot{u}_1^i$ into a separate summation. Using the co-factor definition of the elements $b_{n\dot{1}}^{-1}$ and (9), we find all $b_{n\dot{1}}^{-1}=0$

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[14] Ming Chen Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945); see application in R. E. Turner, Physica **26**, 274 (1960).

except b_{ii}^{-1} (which is $b_{ii}^{-1}=\langle \dot{u}_1^{i2}\rangle^{-1}$) so that the joint velocity and position distribution (10) splits giving

$$P(\quad)=(2\pi)^{-\frac{1}{2}(3m)}\,|B|^{-\frac{1}{2}}{}_{(3m)}\exp\Big[-\tfrac{1}{2}\sum_{nn'}^{m} b_{nn'}{}^{-1}\mathbf{u}_n\mathbf{u}_{n'}\Big]$$

$$\cdot(2\pi\langle \dot{u}_1^{i2}\rangle)^{-\frac{1}{2}}\exp\left[\frac{-\dot{u}_1^{i2}}{2\langle \dot{u}_1^{i2}\rangle}\right]. \tag{11}$$

Substituting (11) into (1) and integrating over the velocity $\dot{u}_1^i$ gives

$$k=\frac{\langle \dot{u}_1^{i2}\rangle^{\frac{1}{2}}}{(2\pi)^{\frac{1}{2}(3m+1)}}\,|B|^{-\frac{1}{2}}{}_{(3m)}\exp\Big[-\tfrac{1}{2}\sum_{nn'}^{m} b_{nn'}{}^{-1}\mathbf{u}_n\mathbf{u}_{n'}\Big]$$

$$=\frac{(kT/m_1)^{\frac{1}{2}}}{(2\pi)^{\frac{1}{2}(3m+1)}}\,|B|^{-\frac{1}{2}}{}_{(3m)}\exp\Big[-\tfrac{1}{2}\sum_{nn'}^{m} b_{nn'}{}^{-1}\mathbf{u}_n\mathbf{u}_{n'}\Big], \tag{12}$$

where the last equality is obtained using

$$\langle \dot{u}_1^{i2}\rangle=(Nm_1)^{-1}\sum_{fs}\epsilon_s{}^i(f)\,\epsilon_s{}^i(f)\,\langle p(fs)\rangle^2=kT/m_1 \tag{13}$$

and where in (12) it should be remembered that u_1^i is fixed at $u_1^i=a_0/2$.

If we now specify that the vectors $\mathbf{u}_1\cdots\mathbf{u}_m$ (other than u_1^i which is fixed at $u_1^i=a_0/2$) are adjusted so that the potential $V(\mathbf{u}_1\cdots\mathbf{u}_m)$ and thus the total energy $E=T+V$ associated with this displacement is a minimum (so that this configuration occurs most often), then (12) is the result obtained by Manley[10] [Eq. (22)] and identical in content with the result obtained by Rice[8] [Eq. (7)] for the jump rate.

To obtain more meaningful expressions for the matrix elements of $\mathbf{B}^{-1}$, we take the expectation value of the Hamiltonian (2) (taking $V_0=0$) which, using the Virial and equipartition of energy theorems, gives

$$\langle H\rangle=2\langle T\rangle=2\langle V\rangle=\sum_{nn',ij}A_{nn'}{}^{ij}\langle u_n^i u_{n'}^j\rangle=3NkT. \tag{14}$$

Dividing by kT we have

$$(kT)^{-1}\sum_{nn',ij}A_{nn'}{}^{ij}u_n^i u_{n'}^j=3N. \tag{15}$$

Now by definition of the inverse of a matrix $\mathbf{B}^{-1}\mathbf{B}=\mathbf{I}$, where $\mathbf{I}$ is a unit matrix of the same dimensionality as $\mathbf{B}$($3N$ in this case). This requires that

$$\sum_{n'j} b_{n''k,n'j}{}^{-1}b_{n'j,ni}=\delta_{n''k,ni} \tag{16}$$

and summing over (16) (taking the trace) gives

$$\sum_{nin'j} b_{ni'n'j}{}^{-1}\langle u_{n'}{}^j u_n{}^i\rangle=3N, \tag{17}$$

where in (17) we have used the δ function condition (16) to write, $b_{n''k,n'j}{}^{-1}=b_{ni,n'j}{}^{-1}$ and the definition of $b_{n'j,ni}$. Subtracting (17) from (15) we have

$$\sum_{nn'ij}\big[(A_{nn'}{}^{ij}/kT)-b_{ni,n'j}{}^{-1}\big]\langle u_{n'}{}^j u_n{}^i\rangle=0 \tag{18}$$

which must hold for arbitrary values of the $\langle u_{n'}{}^j u_n{}^i\rangle$ so that term for term

$$b_{ni,n'j}{}^{-1}=A_{nn'}{}^{ij}/kT. \tag{19}$$

In matrix notation (19) is $\mathbf{B}^{-1}=(kT)^{-1}\mathbf{A}$. Also as $\mathbf{B}^{-1}\mathbf{B}=\mathbf{I}$, we have $|B^{-1}|\,|B|=1$ or $|B^{-1}|=|B|^{-1}$ so that $|B|^{-\frac{1}{2}}=|B^{-1}|^{\frac{1}{2}}$. Thus, the $|B|^{-\frac{1}{2}}$ of dimensionality $3m$ is, using (19)

$$|B|^{-\frac{1}{2}}{}_{(3m)}=(kT)^{-\frac{1}{2}(3m)}\,|A|^{\frac{1}{2}}{}_{(3m)}. \tag{20}$$

On substituting (19) and (20) in (12) we have

$$k=|A|^{\frac{1}{2}}{}_{(3m)}\big[(2\pi)^{3m+1}(kT)^{3m-1}m_1\big]^{-\frac{1}{2}}$$

$$\times\exp\Big[-\tfrac{1}{2}\sum_{nn'\neq 2}A_{nn'}\mathbf{u}_n\mathbf{u}_{n'}\Big]. \tag{21}$$

We now pass on to re-derive (21) from equilibrium statistics.

B. Equilibrium Statistics Development

Here we divide the lattice of N atoms up into identical sublattices (systems) containing m atoms ($m\ll N$) so that we may treat the lattice as a canonical ensemble of identical sublattices. A physically reasonable choice for the independent sublattice size is such that the range of atomic force is $\sim m\,a_0$ so that correlations of significance do not exist between the m and $N-m$ atoms. The statistics for each sublattice is then given by the canonical distribution function so that the probability of observing the fluctuation $P(\quad)$ is

$$P(r_1^i=a_0/2;\,\dot{r}_1^i\geq 0;\,r_1^j r_1^k\mathbf{r}_3\cdots\mathbf{r}_m)$$

$$=\left(\int\cdots\int\exp\big[-\beta H_{3m}(\dot{\mathbf{r}}_n\mathbf{r}_n)\big]\,d\dot{r}_1^j\,d\dot{r}_1^k\,d\dot{\mathbf{r}}_3\cdots d\dot{\mathbf{r}}_m\Big/\int\cdots\int\exp\big[-\beta H_{3m}(\dot{\mathbf{r}}_n\mathbf{r}_n)\big]\,d\dot{\mathbf{r}}_1\cdots d\dot{\mathbf{r}}_m,\,d\mathbf{r}_1\cdots d\mathbf{r}_m\right), \tag{22}$$

where $\beta=(kT)^{-1}$ and $H_{3m}(\dot{\mathbf{r}}_n\mathbf{r}_n)$ is

$$H_{3m}(\dot{\mathbf{r}}_n\mathbf{r}_n)=\tfrac{1}{2}\sum_{n=1}^{m}m_n\dot{\mathbf{r}}_n^2+V(\mathbf{r}_1\cdots\mathbf{r}_m). \tag{23}$$

With the Hamiltonian (23) the integrations over the velocities in (22) may be performed directly; the integration over each component (ni say) giving a factor $(2\pi/m_n\beta)^{\frac{1}{2}}$. To integrate over the coordinates in the denominator we notice that $-V(\mathbf{r}_1\cdots\mathbf{r}_m)$ appears in an exponential. Thus, nearly all the contribution to the integral will come from near the minimum of V, which is the static potential V_0 when all $\mathbf{r}_n=\mathbf{a}_n$. Expanding in a Taylor's series above V_0 and keeping up to harmonic terms gives [see Eq. (2)]

$$P(\quad)=\frac{\exp\left[-\beta V_{3m}(r_1{}^i=a_0/2;\, r_1{}^j r_1{}^k \mathbf{r}_3\cdots\mathbf{r}_m)\right]\cdot\exp\left(-\tfrac{1}{2}\beta m_1 \dot{r}_1{}^{i2}\right)}{\left(\dfrac{2\pi}{m_1\beta}\right)^{\frac{1}{2}}\exp\left(-\beta V_0\right)\displaystyle\int\cdots\int\exp\left[-\tfrac{1}{2}\beta\sum_{nn'}^{m}A_{nn'}\delta\mathbf{r}_n\delta\mathbf{r}_{n'}\right]d\delta\mathbf{r}_1\cdots d\delta\mathbf{r}_m}. \tag{24}$$

The value of the integral in the denominator, a standard matrix integral,[15] is $(2\pi)^{3m/2}(kT)^{3m/2}\,|\,A\,|^{-\frac{1}{2}}{}_{(3m)}$ so that on substituting (24) into (1) and integrating over $\dot{r}_1{}^i$, we have

$$k=|\,A\,|^{\frac{1}{2}}{}_{(3m)}\left[(2\pi)^{3m+1}(kT)^{3m-1}m_1\right]^{-\frac{1}{2}}\exp\left\{\left[-V\left(r_1{}^i=\frac{a_0}{2};\, r_1{}^j r_1{}^k\mathbf{r}_3\cdots\mathbf{r}_m\right)-V_0\right](kT)^{-1}\right\}. \tag{25}$$

If we now expand $V(r_1{}^i=a_0/2;\, r_1{}^j r_1{}^k\mathbf{r}_3\cdots\mathbf{r}_m)$ about the static potential V_0 we reproduce exactly expression (21). This demonstrates the equivalence at this stage of the dynamical and equilibrium statistical approaches. They differ really only in the choice of independent units on which to base statistical arguments; the normal coordinates and momentum in the dynamical approach and the independent systems (sublattices), as is usual, in the equilibrium statistical approach. Both rest on the same two assumptions which are (1) that the lattice is in equilibrium and (2) that the independence of the chosen units is maintained up to the peak of fluctuation $(r_j{}^i=a_0/2)$ during the jump so that the statistics remain applicable. Assumption (2) makes the dynamical approach based on mode independence much more restrictive. The two approaches differ only in proceeding from this point (where the real difficulties begin) in the treatment of the minimum energy jump configuration which we consider in the following section.

The only difference between the derivations of Rice and Manley, and the present dynamical one is the use of different random variable theorems to obtain $P(\quad)$ from the normal coordinates.

III. THE COMPLETE JUMP RATE

As k stands in (21) and (25) it is incomplete. It gives the jump rate when the surrounding atoms take up a single particular configuration only whereas the real jump rate is the probability per unit time of a jump for any configuration of the surrounding atoms. To complete k we must include in it the contributions from all possible configurations; each configuration being characterized by a potential $V(\mathbf{r}_1\cdots\mathbf{r}_m)$ to appear in (25).

Instead of summing over all configurations, Rice postulates the existence of a minimum potential configuration. As the potential appears exponentially in k, this configuration will contribute much more to k than any other and so he considers all others negligible. However, there will be configurations (and thus energies) infinitely close to this minimum energy configuration and these will definitely make some contribution to k. Also the pre-exponential factor in (25) depends on the temperatures as $(kT)^{-\frac{1}{2}(3m-1)}$ which from an experimental point of view seems incorrect. This difficulty also arises in the treatments of Rockmore and Turner[11] and Prigogine and Bak[12] where a single "activation" energy only is included, with temperature dependences in the pre-exponential factor of $(kT)^{-\frac{1}{2}}$ and $(kT)^{-\frac{3}{2}}$ appearing in their one- and three-dimensional treatments, respectively.

There is, however, no other way to proceed from (21) which represents a drawback to the dynamical approach. Strictly, once having expanded $V(\mathbf{r}_1\cdots\mathbf{r}_m)$ about the rest positions $\mathbf{r}_n=\mathbf{a}_n$, the minimum of $V(\mathbf{r}_1\cdots\mathbf{r}_m)$ will always occur with the $(m-1)$ atoms at their rest positions irrespective of the position of atom 1. There is thus no true second minimum about which to make a saddle-point integration of some sort.

Vineyard, with the earlier rate calculations, also postulates the existence of a minimum $V(\mathbf{r}_1\cdots\mathbf{r}_m)$. He then expands $V(\mathbf{r}_1\cdots\mathbf{r}_m)$ about this minimum and includes energies near the minimum using a saddle-point integration. He, however, introduces a new set of lattice frequencies for vibration about this minimum, (to do the integration) the drawbacks of which were discussed in the introduction.

Here we also postulate the existence of (one) minimum $V(\mathbf{r}_1\cdots\mathbf{r}_m)$ (when $r_1{}^j=r_1{}^{j+}\cdots\mathbf{r}_m=\mathbf{r}_m{}^+$) and expand $V(\mathbf{r}_1\cdots\mathbf{r}_m)$ about this configuration retaining up to 2nd derivative terms

$$\begin{aligned}V(\mathbf{r}_1\cdots\mathbf{r}_m)&=V(\mathbf{r}_1{}^+\cdots\mathbf{r}_m{}^+)+\sum_{n}^{3m-1}\left(\frac{\partial V}{\partial\mathbf{r}_n}\right)_{\mathbf{r}_n{}^+}\delta\mathbf{r}_n\\&\quad+\tfrac{1}{2}\sum_{n'n\neq 1i}^{3m-1}\left(\frac{\partial^2 V}{\partial\mathbf{r}_n\partial\mathbf{r}_{n'}}\right)_{\mathbf{r}_n{}^+,\mathbf{r}_{n'}{}^+}\delta\mathbf{r}_n\delta\mathbf{r}_{n'}\\&=V_{\min}+0+\tfrac{1}{2}\sum_{nn'\neq 1i}^{3m-1}A_{nn'}{}^+\delta r_n\delta r_{n'}.\end{aligned} \tag{26}$$

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[15] A. C. Aitken, *Determinants and Matrices* (Interscience Publishers, Inc., New York, 1954), example 25, p. 138.

Substituting (26) in (25) and integrating over $r_1{}^j$, $r_1{}^k$, $\mathbf{r}_3\cdots\mathbf{r}_m$ [following the integration procedure used for the denominator of (24)] gives

$$k=(|A|^{\frac{1}{2}}{}_{3m}/|A^{+}|^{\frac{1}{2}}{}_{(3m-1)})(2\pi m_1{}^{\frac{1}{2}})^{-1}$$
$$\times\exp[-(V_{\mathrm{min}}-V_0)/kT]$$
$$=\tilde{\nu}\exp(-\Delta V^{+}/kT) \qquad (27)$$

as the complete jump rate k.

It is to be emphasized that the $A^{+}{}_{nn'}$ appearing in (27) have meaning only as their definitions as second derivatives. They are derivatives evaluated at a special local configuration which survives only for an instant so that there is no possibility of determining $\mathbf{A}^{+}$ from a macroscopic time averaged experiment on the equilibrium lattice. The appearance of $|A|$ and $|A^{+}|$ in $\tilde{\nu}$ should be viewed as arising from including regions around the static and minimum potentials, respectively, in the integrations over the coordinates. These regions will be included as accurately as the harmonic approximation is accurate up to the point where V is $\gg$ than either minimum.

IV. DISCUSSION

A. Pre-Exponential Factor

The pre-exponential factor in (27) is defined solely in terms of the force constants $\mathbf{A}$ and clearly predicts a mass dependence for k of exactly $m^{-\frac{1}{2}}$ for a diffusing species of mass m however much the surrounding atoms are displaced during the jump. (Any departure from this dependence for the vacancy mechanism should then represent a failure of the equilibrium statistical approach.) For those crystals in which the force constants are known then both $\tilde{\nu}$ and the activation energy may be evaluated directly and it is for these cases that (27) is primarily intended. There are, however, many systems (notably metals) for which the force constants are not known and for these systems (27) has little advantage over earlier expressions. To discuss these cases a simpler, approximate expression for $\tilde{\nu}$ which makes contact with earlier forms is useful.

If we assume that the harmonic approximation adequately describes the displacements of all the m atoms, then all the 2nd derivatives $\mathbf{A}^{+}=\mathbf{A}$. Transforming from the matrix $\mathbf{A}$ to the matrix $\mathbf{B}$, $\mathbf{A}=(kT)^{-N}\mathbf{B}$ [Eq. (20)], the elements of which are the expectation values $\langle\mathbf{u}_n\mathbf{u}_{n'}\rangle$, $\tilde{\nu}$ becomes

$$\tilde{\nu}=(kT)^{\frac{1}{2}}(|B|^{-\frac{1}{2}}{}_{(3m)}/|B|^{-\frac{1}{2}}{}_{(3m-1)})(2\pi m_1{}^{\frac{1}{2}})^{-1}. \qquad (28)$$

The diagonal and off-diagonal elements of $\mathbf{B}$ are, using the classical expectation values $\langle q^2(fs)\rangle=kT/\omega^2(fs)$,

$$\langle\mathbf{u}_n\mathbf{u}_n\rangle=(kT/Nm_n)\sum_{fs}[\omega^2(fs)]^{-1}$$

and

$$\langle\mathbf{u}_n\mathbf{u}_{n'}\rangle=(kT/N)$$
$$\times\sum_{fs}\exp\{[\mathrm{if}(\mathbf{a}_n-\mathbf{a}_{n'})]/(m_nm_{n'})^{\frac{1}{2}}\}[\omega^2(fs)]^{-1}. \qquad (29)$$

For any reasonable frequency spectrum for which none of the $\omega^2(fs)=0$, the off-diagonal elements must be $O(1/N)$ of the diagonal elements as the exponential factor $\exp[-if(\mathbf{a}_n-\mathbf{a}_{n'})]$ sums incoherently. Thus, we need retain only the diagonal term in $\mathbf{B}$ as all others contain at least two factors $O(1/N)$. If we now define the axes $\mathbf{j}$ and $\mathbf{k}$ $\perp$ to $\mathbf{i}$ so that $\langle u_1{}^iu_1{}^{j,k}\rangle=0$, then the diagonal elements of $|B|_{3m}$ and $|B|_{3m-1}$ cancel leaving only the extra element $\langle u_1{}^iu_1{}^i\rangle$ in $|B|_{3m}$ so that

$$\tilde{\nu}=(kT)^{\frac{1}{2}}\langle u_1{}^iu_1{}^i\rangle^{-\frac{1}{2}}(2\pi m_1{}^{\frac{1}{2}})^{-1}$$
$$=(2\pi)^{-1}\{N^{-1}\sum_{fs}\epsilon_s{}^i(f)\epsilon_s{}^i(f)[\omega^2(fs)]^{-1}\}^{-\frac{1}{2}}. \qquad (30)$$

This expresses $\tilde{\nu}$ clearly in terms of the lattice frequencies and their contribution to the displacements of atom 1 in the jump direction $\mathbf{i}$. For very light (heavy) impurities a single local (resonance) mode[16] makes the dominant contribution to the impurity displacements so that, provided the effect of the adjacent vacancy was included, (30) could be a useful expression for $\tilde{\nu}$.

Finally, if we invoke the Einstein model, which with $\langle\mathbf{u}_n\mathbf{u}_{n'}\rangle\approx(1/N)\langle\mathbf{u}_n\mathbf{u}_n\rangle$ at high temperatures suggests itself, then all $\omega^2(fs)=\omega_E{}^2$ and

$$\tilde{\nu}=\omega_E/2\pi=\nu_E. \qquad (31)$$

$\tilde{\nu}=\nu_E$ is the approximate expression most frequently used to estimate $\tilde{\nu}$ in metals.

B. Application to Self-Diffusion in Solid Argon

1. The Migration Energy $E_m=\Delta V^{+}$

To evaluate ΔV^{+} following the procedure laid out in Sec. III, we consider a region of fcc argon crystal containing one vacancy. In the region each atom interacts with its 12 first, 6 second and 24 third neighbors through a Mie–Lennard-Jones potential

$$V(r)=\epsilon\left(\frac{6m}{m-6}\right)\left\{\frac{1}{m}\left(\frac{r_0}{r}\right)^m-\frac{1}{6}\left(\frac{r_0}{r}\right)^6\right\} \qquad (32)$$

with parameters[17]

(a) $m=14$, $\epsilon=171.9\times10^{-16}$ ergs, $r_0=3.792$ Å

(b) $m=12$, $\epsilon=164.3\times10^{-16}$ ergs, $r_0=3.818$ Å.

With all atoms at their rest positions and site 2 vacant,

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[16] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **A273**, 222 (1963).

[17] G. K. Horton and J. W. Leech, Proc. Phys. Soc. (London) **82**, 816 (1963).

TABLE I. The migration energy E_m, the vacancy creation energy E_v, and activation energy Q for self-diffusion in solid argon.

T°K	$E_m=\Delta V^+$ (cal/mole)		$E_v=h_v$ (cal/mole)		E_m/E_v		$Q=\Delta V^+ + h_v$ (cal/mole)	
	(6,14)	(6,12)	(6,14)	(6,12)	(6,14)	(6,12)	(6,14)	(6,12)
60	1330	1215	1958	1950	0.68	0.63	3290	3165
70	1225	1130	1937	1933	0.63	0.59	3160	3065
80	1115	1050	1910	1910	0.59	0.56	3025	2960

the crystal potential obtained using $V(r)$ is taken as the reference potential V_0 from which ΔV^+ is measured.

To locate the saddle configuration, we move the migrating atom 1 a distance $a_0/2$ towards the vacancy, so that it sits half way between two vacancies, and adjust the positions of the surrounding atoms so that the crystal potential increase ΔV above V_0 is reduced to a minimum. This minimum ΔV^+ was found using an I.C.T. Atlas Computer to compute the potential of all reasonable configurations and select the lowest potential one. The position of up to 34 surrounding atoms were adjusted, but adjustment of only the inner 20 significantly affected ΔV^+. In looking for the minimum it was found that there was indeed only one minimum and that potentials close to ΔV^+ corresponded to atomic configurations close to that giving ΔV^+. This shows that, in this case at least, the assumption of one minimum and the expansion of $V(\mathbf{r}_1\cdots\mathbf{r}_m)$ about it in Eq. (26) is valid.

The three-neighbor-shell binding approximation should be a good one as the distortion is local. Thus the binding of each atom due to distant neighbors is nearly the same in both the saddle and rest configurations.

The values of ΔV^+ obtained using (a) the (6,14) and (b) the (6,12) potential are listed in Table I. We see that the (6,12) gives generally lower values for ΔV^+. This arises physically as ΔV^+ depends critically on the positioning of the four nearest neighbors to the migrating atom in the saddle configuration. The (6,12) provides a much wider well (almost certainly too wide) for these atoms to move in so that they may get well out of the way of the migrating atom to reduce ΔV^+ before running into the hard cores of other atoms. The analysis of Horton and Leech[17] indicates that the (6,14) is the better potential for solid argon.

Finally, we note that ΔV^+ (and thus $Q=\Delta V^+ + h_v$) is significantly temperature-dependent; the crystal temperature being fixed in each case by using the appropriate value of $a_0(T)$,[18] the interatom spacing, in the calculation. As the expansivity of argon is so large ($\sim 10^2$ that in Cu) $a_0(T)$ changes significantly over 20°K. The space available for the atoms to manoeuver themselves into a low potential saddle configuration then changes significantly giving a higher ΔV^+ when there is less space to the lower temperatures.

2. *The Frequency Factor* $\tilde{\nu}$

To evaluate the ratio of the determinants in $\tilde{\nu}$ we restrict ourselves to nearest-neighbor forces which in solid argon account for more than 95% of the restoring force. The determinant $|A|$ is then of the order $3(11)\times 3(11)$. In $|A|$, with each atom in its rest position, there are still many zero elements and each nonzero element is just $\alpha = V''(a_0)$, the force constant between nearest neighbors. In $|A^+|$, with the atoms in the saddle position, the force between atom 1 and its four nearest neighbors is $\sim 10^2$ that between 1 and any other atom; the separation of 1 and these four neighbors 3–6 being only 0.858 a_0. Thus, in $|A^+|$, terms containing an element $a_{1n}{}^+$. $n\neq 3$–6 may be neglected. With these approximations, the determinants may be evaluated directly by expansion giving an effectively temperature-independent result of

$$\tilde{\nu} = (2\pi m_1{}^{\frac{1}{2}})^{-1}(|A|/|A^+|) = 0.6\times 10^{12}\ \mathrm{sec}^{-1}\ (6,14)$$
$$= 0.9\times 10^{12}\ \mathrm{sec}^{-1}\ (6,12). \tag{33}$$

$\tilde{\nu}$ may be compared with the maximum and Einstein frequencies in argon[19] of $\nu_m = 2.0\times 10^{12}$ sec^{-1} and $\nu_E = 1.3\times 10^{12}$ sec^{-1}. From inspection of (33) it is clear that $\tilde{\nu}$ must correspond to a "frequency" which is less than the average or Einstein frequency as the force constants in $|A^+|$ refer to a "strained" configuration and must be generally greater than those in $|A|$.

3. *Diffusion Coefficient and Comparison with Experiment*

In a general analysis, Chandrasekhar[20] has shown that for sperically symmetric, random jumps of equal length l, the jump rate k is related to the diffusion coefficient by $D=\frac{1}{6}kl^2$. This expression may be applied directly to homogeneous solids having cubic symmetry.

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[18] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phil. Mag. **12,** 1193 (1965).

[19] E. R. Dobbs and G. O. Jones, Rept. Progr. Phys. **20,** 516 (1957).

[20] S. Chandrasekhar, Rev. Mod. Phys. **15,** 1 (1943).

(It is this sort of relation between the microscopic k to the macroscopic D which contains an explanation of the irreversible nature of diffusion, and not the discussions on jump rate statistics in the introduction.)

For vacancy diffusion, we must introduce a correlation factor f to characterize the extent to which the jumps are not completely random due to the asymmetry left by the vacant site. For self-diffusion this is a constant being $f=0.78146$ in fcc crystals.[21] Also we must include a factor $p_v=\exp(s_v/RT)\ \exp\ (-h_v/RT)$ giving the probability that the adjacent site is vacant which up to now was simply assumed to be vacant. Here s_v and h_v are the entropy and enthalpy change of the perfect crystal when it contains a vacancy next to the diffusing species. Collecting then, with $l^2=a_0^2$, we have

$$D=\tfrac{1}{6}ka_0^2fp_v=\tfrac{1}{6}a_0^2\tilde{\nu}f\ \exp(s_v/R)\cdot\exp(-Q/RT), \quad (34)$$

where Q and $\tilde{\nu}$ are listed in Table I and Eq. (33), respectively, $a_0\approx3.85\times10^{-8}$ cm, and $s_v/R=4.0$.[22]

Since Q is temperature-dependent, some care must be taken in comparing (34) with experiment. Expanding Q as a power series in T to represent this dependence analytically, we have

$$\begin{aligned} Q&=Q^{\circ}+Q'T+Q''T^2+\cdots\\ &=4080-13.2T(6,14)\,\text{cal/mole}\\ &=3790-10.4T(6,12)\,\text{cal/mole}, \quad (35)\end{aligned}$$

where we have neglected terms above $Q'T$ and used Fig. 1 to obtain Q° and Q' for each potential. Experimentally we write D in the form

$$D=D_0\exp\ (-H/RT), \quad (36)$$

where D_0 and H, by definition, are taken to be the best temperature-independent constants which fit the experimental data in the temperature ranged considered. To compare (34) with the experimental form we must substitute (35) in (34) giving

$$\begin{aligned} D&=\tfrac{1}{6}a_0^2\tilde{\nu}f\ \exp\ (s_v/R)\ \exp\ (Q'/R)\cdot\ \exp\ (-Q^{\circ}/RT)\\ &=4.7\ \exp\ (-4080/RT)\ (6,14)\,\text{cm}^2\text{sec}\\ &=1.6\ \exp\ (-3790/RT)\ (6,12)\,\text{cm}^2/\text{sec} \quad (37)\end{aligned}$$

so that the parameters in the exponential and pre-exponential positions are also temperature-independent as in the experimental expression (36). This can then be compared directly with two experimental values.

$$D=(0.3^{+2.7}{}_{-0.27})\ \exp\ [-(3930\pm400/RT]\text{cm}^2/\text{sec}$$

and

$$D=(8.1\pm3.0)\ \exp\ [-(3830\pm100)/RT]\ \text{cm}^2/\text{sec} \quad (38)$$

the first being obtained from self-diffusion measurements directly in solid argon[23] and the second from measurements in solid xenon[24] using a corresponding states law. (The errors in the second value are estimated by the author to include possible errors in the corresponding states law.) The theoretical result using the better (6,14) potential agrees well with experiment justifying in a quantitative manner the use of equilibrium methods to derive k. The theoretical evaluation of Q°, due to errors in potential used and location of ΔV^{+}, could be in error by 100 cal/mole. It could be in error by a further 100 cal/mole due to the uncertainty in p_v.

In previous comparisons[23,25] of theoretical prediction[26] with experiment, agreement was not found. This is largely because H was compared directly to Q and D_0 to $\frac{1}{6}a_0^2\cdot\tilde{\nu}f\ \exp\ (s_v/R)$, as one would expect to be able to do if Q were constant. The previous theoretical results[26] differ from the present ones only in the $\tilde{\nu}\ \exp\ (s_v/R)$ term; being 10^{-2} that found here.

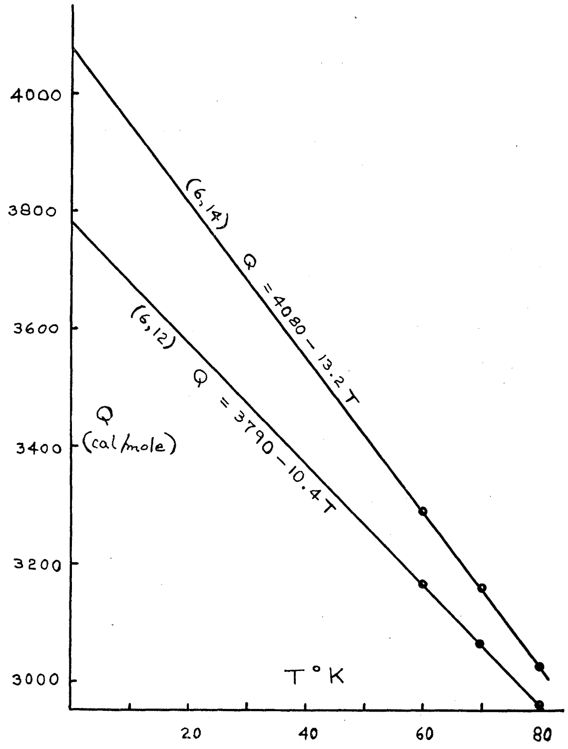

FIG. 1. The activation energy Q for self-diffusion in solid argon as calculated using the (6,14) and (6,12) interatom potentials.

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[21] A. D. LeClaire and A. B. Lidiard, Phil. Mag. **1**, 518 (1956).

[22] H. R. Glyde, J. Phys. Chem. Solids **27**, 1659 (1966).

[23] A. Berne, G. Boato, and M. De Paz, unpublished work and Nuovo Cimento **24**, 1179 (1962).

[24] W. M. Yen and R. E. Norberg, Phys. Rev. **131**, 269 (1963).

[25] G. Boato, R. Fieschi, and G. F. Nardelli, Nuovo Cimento Suppl. **1**, No. 1 (1963).

[26] R. Fieschi, G. F. Nardelli, and A. Rapani, Phys. Rev. **123**, 141 (1963).

In comparing with experiment, we see it is important to realize that $Q(T)$ can depend on T so that equivalent parameters are compared. With $Q(T)=Q^\circ(T)+TQ'(T)$ in (37) a plot of log D vs $1/T$ would have slope $Q^\circ(T)$ so that $H=>Q^\circ(T)$. In an experiment we might still find that $H=Q^\circ(T)$ varies with temperature. This reflects only that $Q(T)$ is not well represented by a two parameter fit $Q(T)=Q^\circ+Q'T$ unless the parameters themselves, $Q^\circ(T)$ and $Q'(T)$, are allowed to vary with T. The chief dependence of the activation energy $Q(T)$ on T through the $TQ'(T)$ term, however, would not be observed. In solid xenon,[24] for example, log D vs $1/T$ is a good straight line over the range covered indicating that $Q(T)$ is well represented by $Q(T)=Q^\circ+Q'T$ in this case. It is to be emphasized that Q° has no physical significance and that Q is the real activation energy of physical interest.

A similar problem arises in the study of mixtures[27] but in mixtures it is possible to obtain the true temperature-dependent binding energy from a separate experiment. In diffusion it would be possible to reconstruct $Q(T)$ from $Q(T)=Q^\circ+Q'T$ if the other parameters in the pre-exponential factor (28) were well enough known.

We could have introduced thermodynamic functions for comparison with experiment. Fluctuation theory[28] shows that to reach ΔV^+ the fluctuating region must undergo a Gibbs free-energy change so that $\Delta V^+=>\Delta G_m=\Delta H_m-T\Delta S_m$ with ΔH_m and ΔS_m defined by this equation. (This correspondence is not quite exact here as some of the entropy is already in the pre-exponential factors.) Should ΔV^+ depend on T, then only with $\Delta V^+=\Delta G_m$ will the resulting ΔH_m and ΔS_m satisfy the usual thermodynamic relations.[29] Thus with $\Delta V^+=V^\circ-V'T$, $\Delta H_m=V^\circ$ and $\Delta S_m\approx V'$. The introduction of ΔG_m adds nothing new and as we did not have p_v in thermodynamic form we felt it more accurate to obtain Q as above. The dependence of ΔV^+ on T could be significant in metals as well. The theoretical values for Cu[30] disagree with experiment[31] in just the way to be expected if Q were temperature-dependent [H(theory) $<H$(exptl); D_0(theory) $<D_0$(exptl)][32] and ΔS_m is generally larger than expected in most metals.

V. CONCLUSION

1. The dynamical theories of Rice and Manley and the equilibrium statistical theory of Vineyard are completely equivalent both in principle and expression for k.

2. The mass dependence of k for a diffusing atom of mass m predicted by equilibrium methods is always $m^{-\frac{1}{2}}$ for the vacancy mechanism. Any departure from this dependence represents a failure of equilibrium methods.

3. With the expression for k given in (27) it is possible to evaluate k on a fundamental basis from a knowledge of the crystal force constants.

4. Using expression (27) for k, the self-diffusion coefficient for solid argon is evaluated giving a value [when written in the experimental form $D=D_0$ exp $(-H/RT)$] of $D=4.7$ exp $(-4080/RT)$. Both D_0 and H agree with their experimental values demonstrating that quantitatively correct results can be obtained using equilibrium statistical methods.

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Note added in proof. The work of Berné, Boato, and De Paz on self-diffusion in argon has now appeared [Nuovo Cimento **46B**, 182 (1966)]. They now quote $D=4\exp(-3865\pm200/RT)$ cm²/sec.

APPENDIX ON ISOTOPE EFFECTS

In part (i) we reconsider the equilibrium statistics treatment of the atomic velocities during the jump process. This is done to clarify, where the present treatment differs from that due to Vineyard[7] and why it predicts a different mass dependence for k. In part (ii) recent experimental evidence on isotope effects is discussed.

(i). Velocity Considerations

The expression for k used by Vineyard is

$$k=\frac{I}{\rho_1}=\frac{1}{\rho_1}\int_S\int_V \rho(\mathbf{X},\,\mathbf{V})\;\mathbf{V}\,d\mathbf{V}\,d\mathbf{S} \tag{A1}$$

which is a normalized atomic flow through a surface S which cuts the saddle point and separates cell 1 and 2. It differs from expression (1) used here only in that the total system velocity

$$V=\sum_{ni}^{3m} v_n{}^i$$

is considered rather than the single velocity of the migrating atom $\dot{r}_1{}^i=v_1{}^i$. In integrating over the vector

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[27] E. A. Guggenheim, *Mixtures* (Oxford University Press, London, 1952), p. 78.

[28] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1959), p. 350.

[29] G. S. Rushbrooke, *Statistical Mechanics* (Oxford University Press, London, 1949), p. 316.

[30] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).

[31] A. Kuper, H. Letaw, L. Slifkin, and C. Tomizuka, Phys. Rev. **98**, 1870 (1955).

[32] P. G. Shewmon, *Diffusion in Solids* (McGraw-Hill Book Co., Inc., New York, 1963), p. 68.

velocity **V** the condition

$$V\cdot dS\geq 0 \tag{A2}$$

is introduced so that integration of V from 0 to ∞ rather than from $-\infty$ to ∞ is taken. We now suggest that this condition (A2) should reduce to the one used here.

We integrated over $\dot{r}_1{}^i$ from 0 to ∞ in Eq. (1) rather than $-\infty$ to ∞ so that we include in k only those situations in which atom 1 and the crystal reaches the saddle point P with atom 1 traveling toward cell 2. We do not want to include those cases in which the crystal is at P but atom 1 is traveling back to cell 1. We do not need and should not impose an equivalent condition on the other atoms as they may have any velocity at P. A jump can occur with the surrounding atom velocities at any value and to include all possibilities in k we must not limit these velocities as we have done $\dot{r}_1{}^i$. Thus the condition $(\sum\dot{r}_n{}^i)\cdot dS\geq 0$ should be just

$$\dot{r}_1{}^i\cdot dS\geq 0+\sum_{n\neq 1}\dot{r}_n{}^i.$$

Although we set no condition on $\dot{r}_n$, $n\neq 1$, the requirement that the system be at P and $\dot{r}_1{}^i\geq 0$ may naturally introduce one; i.e., introduce a statistical correlation so that $<\dot{r}_n>\cdot dS\neq 0$. However, with a Hamiltonian of the form (23), the correlation functions of $\dot{r}_n$ with position or another $\dot{r}_{n'}$ in equilibrium statistics (equal time functions) are zero

$$\begin{aligned}&\langle\dot{r}_n, r_n{}'\rangle=0 \qquad n'=1\cdots m\\&\langle\dot{r}_n, \dot{r}_n{}'\rangle=0 \qquad n'\neq n, n'=1\cdots(m-1).\end{aligned} \tag{A3}$$

Thus each velocity fluctuates independently. At P we would observe the usual statistical values for each $\dot{r}_{n\neq 1}$; $\langle\dot{r}_n{}^i\rangle=0$, $\langle\dot{r}_n{}^{i2}\rangle=kT/m_n$.

Using the condition

$$\dot{r}_1{}^i\cdot dS\geq 0+\sum_{n\neq 1}\dot{r}_n$$

in (A1) and integrating over all velocities except $\dot{r}_1{}^i$ gives

$$k=\int_s\left(\int_0^\infty P(\quad)\dot{r}_1{}^i d\dot{r}_1{}^i\right)dS, \tag{A4}$$

which is (1) with the integration over S[33] being done in (27). It is this point, that we should not introduce a condition on the velocity of atoms other than the migrating atom and that in equilibrium statistics each $\dot{r}_n$ fluctuates independently, which leads to k exactly $\propto m^{-\frac{1}{2}}$. It is here that the present treatment differs from Vineyards. Should the above argument be incorrect then so is our prediction that an equilibrium statistics treatment must give $k\propto m^{-\frac{1}{2}}$.

We may obtain a reduction of k from $k\propto m^{-\frac{1}{2}}$ as follows. A chemist discussing the above would introduce a reaction path of length δl along which the system passes as atom 1 goes to cell 2.[34] We may treat the fluctuation leading to P as a thermodynamic one, i.e., one in which the time to reach P is much less than the relaxation time of the system back to its mean value. Starting $\delta l(t=0)$ at P then, the system decays from the fluctuation along δl. The decay rate of each coordinate along δl is some function of its value at P; to first order[35] $\dot{r}_n=-\lambda r_n{}^+$. Taking a time average of the quantities appearing in k along δl (over a time $\tau\sim\delta l/\langle\dot{r}_1\rangle$) we have

$$k=\int_s\int_0^\tau\int_{\dot{r}}\rho(x, v)\,(\sum_n\dot{r}(t))\,d\dot{r}_1\cdots d\dot{r}_n\cdot dS\,dt/\tau. \tag{A5}$$

The expectation values of the $\dot{r}_n$ now appearing in k will not be zero but proportional to the displacement $r_n{}^+$[i.e., $\langle\dot{r}_n\rangle\sim(kT/m_n)\lambda r^+$] giving

$$k\propto r_1{}^+\left(\frac{\lambda(\tau)}{m_1}\right)+\sum_{n\neq 1}^{m}\left(\frac{\lambda(\tau)r_n{}^+}{m_n r_1{}^+}\right). \tag{A6}$$

This development is by no means exact but its general form leads to a reduction of k from $k\propto m_1{}^{-\frac{1}{2}}$ depending on how much each atom is displaced at P. This reduction should less for light migrating atoms for as $\tau->0$, $\langle\dot{r}_n\rangle\ ->0$ and $k->\propto m_1{}^{-\frac{1}{2}}$. A proper treatment would involve double-time-correlation functions which are outside the realm of equilibrium statistics.

(ii). The Experimental Situation

There is now accurate evidence demonstrating that k is not proportional to $m_1{}^{-\frac{1}{2}}$. In a recent contribution[36] where all evidence is reviewed, it is suggested that the reduction of k from exactly $\propto m_1{}^{-\frac{1}{2}}$ is related to how far the surrounding atoms must move to reach the saddle point. An intuitive expression for this reduction has been developed by LeCalire[37] and its relation to experiment and correlation factors is discussed. This evidence points to the need for treating carefully the kinetics of the migrating atom through the saddle point.

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[33] In the text we required $r_1{}^i=\frac{1}{2}a_0$ always so that the surface S will be parallel to the line joining lattice points 1 and 2. It is possible to remove this restriction so that S can have any shape and show that the mass dependence of k is unaltered (development available on request).

[34] Reference 6, p. 186.

[35] Reference 28, p. 377.

[36] J. N. Mundy, L. W. Barr, and F. A. Smith, Phil. Mag. **14**, 785 (1966).

[37] A. D. LeClaire, Phil. Mag. **14**, 1271 (1966).