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Effect of Static Strains on Diffusion

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A theory is developed that gives the diffusion coefficient in strained systems as an exponential function of the strain. This theory starts with the statistical theory of the atomic jump frequency as developed by Vineyard. The parameter determining the effect of strain on diffusion is related to the changes in the interatomic forces with strain. Comparison of the theory with published experimental results for the effect of pressure on diffusion shows that the experiments agree with the form of the theoretical equation in all cases within experimental error.

I. INTRODUCTION

SINCE the diffusion rate in a crystal depends on the atomic interaction energy, and since this energy depends on the interatomic distances, it is to be expected that the diffusion coefficient of a migrating species will be altered by a strain superimposed on the crystal. Experimental evidence shows that the change in the diffusion coefficients resulting from strains can be considerable. Uniaxial elastic strain can increase the self-diffusion coefficient by as much as a factor of two[1] and large hydrostatic pressures may decrease the self-diffusion coefficient by as much as an order of magnitude.[2–5]

The theory of the effect of pressure on diffusion has been examined on the basis of the dynamic theory of diffusion.[6,7] In this theory, the pressure effect is represented by a parameter that is a function of the normal mode vibrations of the atoms in the crystal, and the diffusion coefficient is an exponential function of the pressure.

The dynamic theory of diffusion was developed as an alternative to the absolute rate theory of diffusion, since it was believed that the absolute rate theory depended on the postulate that the jumping atom spends a long time at the top of the potential barrier. However, it can be shown that the theory of the jump frequency can be developed without reference to such a postulate[8] by considering the motion of a representative point in phase space. The jump frequency then depends on the rate at which phase points move over the potential maximum in configuration space, and not on the length of time the phase points spend at the maximum. In view of this situation, it is of interest to investigate the effect of strain on diffusion in terms of the statistical rate theory.

The statistical rate theory of diffusion in strained crystals as developed in this paper shows that the diffusion coefficient is an exponential function of strain, and that the strain effect can be represented by a parameter that is a function of the interatomic forces. The rate theory, therefore, has an advantage over the dynamic theory in two respects: First, the effect of strain on diffusion in different materials can be correlated with the interatomic potential energy, and second, the interatomic forces provide a basis on which to calculate the magnitude of the strain effect for different diffusion mechanisms. Accordingly, the possibility pre-

[1] T. Liu and H. G. Drickamer, J. Chem. Phys. 22, 312 (1954).
[2] Norman H. Nachtrieb, Wright Air Development Center Technical Report No. 55–68 (unpublished).
[3] J. Petit and N. H. Nachtrieb, J. Chem. Phys. 24, 1027 (1956).
[4] W. Jost and G. Nehlep, Z. physik. Chem. 34, 348 (1936).
[5] Norman H. Nachtrieb, Henry A. Resing, and Stuart A. Rice, J. Chem. Phys. 31, 135 (1959).
[6] Stuart A. Rice, Phys. Rev. 112, 804 (1958).
[7] Stuart A. Rice and Norman H. Nachtrieb, J. Chem. Phys. 31, 139 (1959).
[8] George H. Vineyard, J. Phys. Chem. Solids 3, 121 (1957).

sents itself of deciding among alternative diffusion mechanisms from a comparison of the results of experiments on the effect of diffusion in strained systems with theoretical calculations. Such a program would be considerably more difficult in the framework of the dynamic theory.

The general equation for the diffusion coefficient for the flow of a single species in an isotropic solid may be written

$$D=\alpha\lambda^2 n\Gamma, \tag{1}$$

where D is the diffusion coefficient, λ is the lattice parameter, n is the concentration of carrier defects, Γ is the jump frequency, and α is a constant that is determined by the crystal structure. In the following sections expressions are derived for the effect of homogeneous static strains on the jump frequency and vacancy concentration. The resulting equations are put into a form in which comparisons can be made with existing experimental data.

II. DEPENDENCE OF JUMP FREQUENCY ON STRAIN

According to the statistical theory of rate processes, the jump frequency is determined by the ratio of two configurational integrals, one referring to the activated state and the other referring to the normal state. In analyzing the effect of strain on the jump frequency, the formulation of the rate process theory in solids given by Vineyard[8] is used, in which the jump frequency is given in terms of these integrals by

$$\Gamma=\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}\int_\sigma e^{-\varphi/kT}d\sigma \Big/ \int_A e^{-\varphi/kT}dA, \tag{2}$$

where k is Boltzmann's constant, T is the temperature, and φ is the potential energy of the system as a function of all the coordinates of all the atoms in the crystal. The integral in the numerator of Eq. (2) is evaluated over a hypersurface σ in the configuration space such that the surface passes through the point corresponding to the diffusing atom at its activated position with all other atoms at their equilibrium positions. The hypersurface is also required to be perpendicular to contours of constant potential energy in the configuration space. The hypersurface defined in this manner divides the configuration space into two symmetric parts. The integral in the denominator is evaluated over the configuration volume A of one of these symmetric parts.

Equation (2) was derived for the case of an unstrained crystal. However, it is applicable to strained crystals if the potential energy φ is taken to be a function of the six strain components $\epsilon_{\alpha\beta}$ as well as the atomic coordinates q_i. A similar procedure has been used by Born[9] in an analysis of the statistical mechanics of crystal lattices. The potential energy in Eq. (2) is given by

$$\varphi=\varphi(q_i,\epsilon_{\alpha\beta}), \tag{3}$$

where q_i represents the set of all atomic coordinates and $\epsilon_{\alpha\beta}$ represents the set of six independent strain components.

The potential φ can be expanded as a Taylor series in the strains about the point of zero strain with the result that

$$\varphi(q_i,\epsilon_{\alpha\beta})=\varphi(q_i,0)+\sum_{\alpha,\beta}C_{\alpha\beta}\epsilon_{\alpha\beta}+\sum_{\alpha,\beta,\rho,\sigma}C_{\alpha\beta\rho\sigma}\epsilon_{\alpha\beta}\epsilon_{\rho\sigma}+\cdots, \tag{4}$$

where the coefficients $C_{\alpha\beta}$ and $C_{\alpha\beta\rho\sigma}$ are defined by

$$C_{\alpha\beta}=\left(\frac{\partial\varphi}{\partial\epsilon_{\alpha\beta}}\right)_{q_j,0}, \tag{5}$$

$$C_{\alpha\beta\rho\sigma}=\frac{1}{2}\left(\frac{\partial^2\varphi}{\partial\epsilon_{\rho\sigma}\partial\epsilon_{\alpha\beta}}\right)_{q_j,0}. \tag{6}$$

The subscripts indicate that the derivatives are evaluated when the strains are zero and the coordinates have the value q_j.

Substituting Eq. (4) into Eq. (2) gives the jump frequency in terms of the strain:

$$\Gamma(\epsilon_{\alpha\beta})=\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}\int_\sigma e^{-\varphi(q_j,0)/kT}\exp\left(-\frac{1}{kT}\sum_{\alpha,\beta}C_{\alpha\beta}\epsilon_{\alpha\beta}\right)d\sigma \Big/ \int_A e^{-\varphi(q_j,0)/kT}\exp\left(-\frac{1}{kT}\sum_{\alpha,\beta}C_{\alpha\beta}\epsilon_{\alpha\beta}\right)dA, \tag{7}$$

where terms of order higher than the first have been ignored. It will be shown later that the first-order contribution of the strain to the jump frequency depends on the difference of the average value of $C_{\alpha\beta}$ evaluated near the normal configuration and near the activated configuration, and on similar differences in the averages of $C_{\alpha\beta\rho\sigma}$, etc. It is extremely difficult to give an *a priori* estimate of the relative magnitudes of these differences. At any rate, for small enough strains the first-order terms predominate and the higher order terms can be neglected. It will be seen later that the form of experimental results is adequately described by considering only the first-order terms in the strains. For zero strain, Eq. (7) gives the jump frequency as

$$\Gamma_0=\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}\int_\sigma e^{-\varphi(q_j,0)/kT}d\sigma \Big/ \int_A e^{-\varphi(q_j,0)/kT}dA. \tag{8}$$

[9] Max Born, Proc. Cambridge Phil. Soc. 36, 160 (1940).

Now take the ratio of Eqs. (7) and (8). The result is

$$\frac{\Gamma(\epsilon_{\alpha\beta})}{\Gamma_0}=\left\langle \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta} C_{\alpha\beta}\epsilon_{\alpha\beta}\right)\right\rangle_\sigma \Big/ \left\langle \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta} C_{\alpha\beta}\epsilon_{\alpha\beta}\right)\right\rangle_A. \quad (9)$$

The angular brackets indicate that a statistical average has been taken of the quantity within the brackets, and the subscripts σ and A indicate that the averages are taken over the regions of configuration space σ and A, respectively. The explicit expressions for these averages are

$$\left\langle \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta} C_{\alpha\beta}\epsilon_{\alpha\beta}\right)\right\rangle_\sigma = \int_\sigma e^{-\varphi(q_j,0)/kT} \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta} C_{\alpha\beta}\epsilon_{\alpha\beta}\right) d\sigma \Big/ \int_\sigma e^{-\varphi(q_j,0)/kT} d\sigma, \quad (10)$$

$$\left\langle \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta} C_{\alpha\beta}\epsilon_{\alpha\beta}\right)\right\rangle_A = \int e^{-\varphi(q_j,0)/kT} \exp\left(-\frac{1}{kT}\sum_{\alpha,\beta} C_{\alpha\beta}\epsilon_{\alpha\beta}\right) dA \Big/ \int_A e^{-\varphi(q_j,0)/kT} dA. \quad (11a)$$

For small strains and high temperatures, the conditions under which the experimental effects of strain on diffusion are usually determined, the exponents in Eq. (9) can be expanded into a series, and only the first two terms need be retained. Thus, Eq. (9) can be written as

$$\frac{\Gamma(\epsilon_{\alpha\beta})}{\Gamma_0}=\left(1-\frac{1}{kT}\sum_{\alpha,\beta}\langle C_{\alpha\beta}\rangle_\sigma \epsilon_{\alpha\beta}\right) \Big/ \left(1-\frac{1}{kT}\sum_{\alpha,\beta}\langle C_{\alpha\beta}\rangle_A \epsilon_{\alpha\beta}\right), \quad (11b)$$

where $\langle C_{\alpha\beta}\rangle_\sigma$ and $\langle C_{\alpha\beta}\rangle_A$ are given by

$$\langle C_{\alpha\beta}\rangle_\sigma = \int_\sigma \left(\frac{\partial\varphi}{\partial\epsilon_{\alpha\beta}}\right)_{q_j,0} e^{-\varphi(q_j,0)/kT} d\sigma \Big/ \int_\sigma e^{-\varphi(q_j,0)/kT} d\sigma, \quad (12)$$

$$\langle C_{\alpha\beta}\rangle_A = \int_A \left(\frac{\partial\varphi}{\partial\epsilon_{\alpha\beta}}\right)_{q_j,0} e^{-\varphi(q_j,0)/kT} dA \Big/ \int_A e^{-\varphi(q_j,0)/kT} dA. \quad (13)$$

Taking logarithms of Eq. (11) and utilizing the fact that $\ln(1-x)\approx -x$ for small x, gives

$$\ln\frac{\Gamma(\epsilon_{\alpha\beta})}{\Gamma_0}=\frac{1}{kT}\{\sum_{\alpha,\beta}[\langle C_{\alpha\beta}\rangle_A-\langle C_{\alpha\beta}\rangle_\sigma]\epsilon_{\alpha\beta}\}, \quad (14)$$

or, defining a parameter $m_{\alpha\beta}$ by

$$m_{\alpha\beta}=\langle C_{\alpha\beta}\rangle_A-\langle C_{\alpha\beta}\rangle_\sigma. \quad (15)$$

Equation (14) can be written as

$$\Gamma(\epsilon_{\alpha\beta})=\Gamma_0 \exp\left(\frac{1}{kT}\sum_{\alpha,\beta} m_{\alpha\beta}\epsilon_{\alpha\beta}\right). \quad (16)$$

Since Γ_0 can always be written as[8]

$$\Gamma=\nu^* e^{-\Delta E^*/kT}, \quad (17)$$

where ΔE^* is the energy of activation for the atomic jump and ν^* is an effective frequency, it is evident from Eq. (16) that the strain affects the jump frequency by an effective change in the energy of activation.

Equation (16) shows that the jump frequency has a simple exponential dependence on the strains and that this dependence is controlled by the derivatives of the potential energy with respect to the strains evaluated at the saddle point of the activated state.

Equation (16) gives the general relation between the jump frequency and the strain that will be used in this paper.

To illustrate the application of Eq. (16), three special cases will be considered:

(1) Uniform compression or expansion, in which

$$\epsilon_{xx}=\epsilon_{yy}=\epsilon_{zz}=\epsilon, \quad (18)$$

(all other strains=0)

(2) Simple shear, in which

$$\epsilon_{xy}=\epsilon_{yx}=\epsilon_s, \quad (19)$$

(all other strains=0)

(3) Simple elastic tension or compression in the x direction, in which

$$\epsilon_{xx}=\epsilon_L, \qquad \epsilon_{yy}=\epsilon_{zz}=-\mu\epsilon_L, \quad (20)$$

where μ is Poisson's ratio. For these three cases, Eq. (16) gives the following results: For uniform compression or expansion,

$$\Gamma(\epsilon)=\Gamma_0 e^{(3m/kT)\epsilon}, \quad (21)$$

where

$$m=\langle C\rangle_A-\langle C\rangle_\sigma, \quad (22)$$

and

$$\langle C\rangle_\sigma = \int_\sigma \left(\frac{\partial\varphi}{\partial\epsilon}\right)_{q_j,0} e^{-\varphi(q_j,0)/kT} d\sigma \Big/ \int_\sigma e^{-\varphi(q_j,0)/kT} d\sigma, \quad (23)$$

$$\langle C\rangle_A = \int \left(\frac{\partial\varphi}{\partial\epsilon}\right)_{q_j,0} e^{-\varphi(q_j,0)/kT} dA \Big/ \int e^{-\varphi(q_j,0)/kT} dA. \quad (24)$$

For simple shear,

$$\Gamma(\epsilon_s)=\Gamma_0 e^{(2m_s/kT)\epsilon_s}, \tag{25}$$

where

$$m_s=\langle C_s\rangle_A-\langle C_s\rangle_\sigma, \tag{26}$$

$\langle C_s\rangle_A$ and $\langle C_s\rangle_\sigma$ are given by statistical averages similar to Eqs. (23) and (24), i.e.,

$$\langle C_s\rangle_\sigma=\left\langle\left(\frac{\partial\varphi}{\partial\epsilon_s}\right)_{q_j,0}\right\rangle_\sigma, \tag{27}$$

$$\langle C_s\rangle_A=\left\langle\left(\frac{\partial\varphi}{\partial\epsilon_s}\right)_{q_j,0}\right\rangle_A. \tag{28}$$

For simple elastic tension or compression in the x direction,

$$\Gamma(\epsilon_L)=\Gamma_0 e^{(m_l/kT)(1-2\mu)},$$

where

$$m_l=\langle C_l\rangle_A-\langle C_l\rangle_\sigma, \tag{29}$$

or

$$m_l=\left\langle\left(\frac{\partial\varphi}{\partial\epsilon_L}\right)_{q_j,0}\right\rangle_A-\left\langle\left(\frac{\partial\varphi}{\partial\epsilon_L}\right)_{q_j,0}\right\rangle_\sigma. \tag{30}$$

III. DEPENDENCE OF VACANCY CONCENTRATION ON STRAIN

The n appearing in Eq. (1) has a different significance for different mechanisms of diffusion. Broadly speaking, n is the probability that a diffusing particle has a site available to jump into. For dilute interstitial diffusion this probability is nearly unity whether or not the system is strained. For diffusion by a vacancy mechanism, however, n is the atomic fraction of vacancies in the crystal, given by

$$n=n_v/N_T, \tag{31}$$

where n_v is the vacancy concentration, and N_T is the total number of lattice sites per cubic centimeter. It is therefore necessary to investigate the variation of n_v with strain.

The atomic fraction of vacancies in a crystal at equilibrium is given by (see Appendix)

$$n_v=\int\cdots\int e^{-\psi_v(p_j,q_j)/kT}\prod_j dp_j dq_j \Big/ \int\cdots\int e^{-\psi_0(p_j,q_j)/kT}\prod_j dp_j dq_j, \tag{32}$$

where ψ_v is the energy of the crystal containing a vacancy and ψ_0 is the energy of the perfect crystal. Performing the integrations over the momenta p_j converts Eq. (32) into

$$n_v=\int\cdots\int e^{-\varphi_v(q_j)/kT}\prod_j dq_j\prod_k(\nu_0)_k \Big/ \int\cdots\int e^{-\varphi_0(q_j)/kT}\prod_j dq_j\prod_k(\nu_v)_k, \tag{33}$$

where $\varphi_v(q)$ and $\varphi_0(q)$ are the potential energies in a crystal containing a vacancy and in a perfect crystal, respectively, each taken as a function of all the coordinates; $(\nu_v)_k$ is the frequency of the kth vibrational mode in the crystal containing a vacancy; and $(\nu_0)_k$ is the frequency of the kth normal mode in a perfect crystal. In a strained crystal, the φ and the ν must be written as functions of strain, so that (33) becomes

$$n_v(\epsilon_{\alpha\beta})=\int\cdots\int\exp[-\varphi_v(q_j,\epsilon_{\alpha\beta})/kT]\prod_j dq_j\prod_k(\nu_0{}^\epsilon)_k \Big/ \int\cdots\int\exp[-\varphi_0(q_j,\epsilon_{\alpha\beta})/kT]\prod_j dq_j\prod_k(\nu_v{}^\epsilon)_k. \tag{34}$$

An estimate of the effect of strain on the frequency ratios can be made from Grüneisen's relation[10]

$$d\ln\nu/d\ln V=-\gamma, \tag{35}$$

where V is the volume and γ is a positive constant. Integrating Eq. (35) for each vibrational mode as the crystal goes from the strained to the unstrained state

$$\frac{(\nu_0{}^\epsilon)_k}{(\nu_0)_k}=\left(1+\frac{\delta V}{V}\right)^{-\gamma}, \tag{36}$$

$$\frac{(\nu_v{}^\epsilon)_k}{(\nu_v)_k}=\left(1+\frac{\delta V}{V}\right)^{-\gamma}, \tag{37}$$

where δV is the volume change arising from the strain. Grüneisen's relation, therefore, leads to an equality of frequency ratios in the strained and unstrained systems:

$$\prod_k(\nu_0{}^\epsilon)_k/\prod_k(\nu_v{}^\epsilon)_k=\prod_k(\nu_0)_k/\prod_k(\nu_v)_k. \tag{38}$$

Therefore, the ratio of Eqs. (34) and (33) is

$$\frac{n_v(\epsilon_{\alpha\beta})}{n_v}=\int\cdots\int\exp[-\varphi_v(q_j,\epsilon_{\alpha\beta})/kT]\prod_j dq_j \Big/ \int\cdots\int e^{-\varphi_v(q_j)/kT}\prod_j dq_j \times\int\cdots\int e^{-\varphi_0(q_j)/kT}\prod_j dq_j \Big/ \int\cdots\int\exp[-\varphi_0(q_j,\epsilon_{\alpha\beta})/kT]\prod_j dq_j. \tag{39}$$

[10] John Clarke Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), p. 238.

The potential-energy functions $\varphi_v(q_j,\epsilon_{\alpha\beta})$ and $\varphi_0(q,\epsilon_{\alpha\beta})$ can be expanded as Taylor series in the strain just as in the development beginning with Eq. (4) and leading to Eq. (16). The result is

$$\frac{n_v(\epsilon_{\alpha\beta})}{n_v}=\exp\left(\frac{1}{kT}\sum_{\alpha,\beta}w_{\alpha\beta}\epsilon_{\alpha\beta}\right), \tag{40}$$

where

$$w_{\alpha\beta}=\left\langle\left(\frac{\partial\varphi_0}{\partial\epsilon_{\alpha\beta}}\right)_{q_j,0}\right\rangle-\left\langle\left(\frac{\partial\varphi_v}{\partial\epsilon_{\alpha\beta}}\right)_{q_j,0}\right\rangle. \tag{41}$$

For the special case of uniform compression or expansion, Eqs. (40) and (41) become

$$\frac{n_v(\epsilon)}{n_v^0}=e^{(3w/kT)\epsilon}, \tag{42}$$

$$w=\left\langle\left(\frac{\partial\varphi_0}{\partial\epsilon}\right)_{q_j,0}\right\rangle-\left\langle\left(\frac{\partial\varphi_v}{\partial\epsilon}\right)_{q_j,0}\right\rangle, \tag{43}$$

where ϵ is the volume strain.

IV. PROOF THAT THE STATISTICAL AVERAGES $\langle(\partial\varphi/\partial\epsilon)_{q_j,0}\rangle$ DO NOT VANISH

The preceding theory depends on the statistical averages of the derivatives of the potential energy of the crystal with respect to strain. It has been assumed that these averages are not zero, and that a first-order expansion in the strains is therefore adequate for small strains. This assumption can be justified by expanding the crystal energy in normal coordinates. The statistical averages of interest all have the form

$$\left\langle\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0\right\rangle=\int\cdots\int\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0 e^{-\varphi/kT}\prod_j dq_j\Big/\int\cdots\int e^{-\varphi/kT}\prod_j dq_j, \tag{44}$$

where φ is the total potential energy of the crystal as a function of all the coordinates q_j, and the subscript zero means that the derivative is evaluated at zero strain. If the q_j are taken to be the normal coordinates, φ can be written to the second order as

$$\varphi=\varphi(0)+\tfrac{1}{2}\textstyle\sum_j\omega_j^2q_j^2, \tag{45}$$

where $\varphi(0)$ is the potential energy when all the atoms are at their mean positions, and the ω_j are the normal mode frequencies. Differentiating Eq. (45) with respect to strain gives

$$\frac{\partial\varphi}{\partial\epsilon}=\frac{\partial\varphi(0)}{\partial\epsilon}+\sum_i\omega_j\frac{d\omega_j}{d\epsilon}q_j^2, \tag{46}$$

and, since at zero strain the first term on the right is zero,

$$\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0=\sum_i\omega_j\frac{d\omega_j}{d\epsilon}q_j^2. \tag{47}$$

For the purposes of this discussion, ϵ will be taken to be the strain corresponding to uniform compression or expansion, so that for small strains the volume is given by

$$V=V_0(1+3\epsilon), \tag{48}$$

V_0 being the volume at zero strain. Introducing the Grüneisen parameter γ_j by the relation

$$d\ln\omega_j/d\ln V=-\gamma_j, \tag{49}$$

where the γ_j are a set of positive constants, and using Eq. (48), Eq. (47) becomes

$$\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0=-3\sum_i\gamma_j\omega_j^2q_j^2. \tag{50}$$

Substituting Eqs. (45) and (50) into Eq. (44) gives

$$\left\langle\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0\right\rangle=-3\int\cdots\int\left(\sum_i\gamma_j\omega_j^2q_j^2\exp\left(-\frac{1}{2kT}\sum_i\omega_j^2q_j^2\right)\right)\prod dq_j\Big/\int\cdots\int\exp\left(-\frac{1}{2kT}\sum_i\omega_j^2q_j^2\right)\prod dq_j. \tag{51}$$

Now perform a coordinate transformation according to the following definition:

$$u_j\equiv\omega_jq_j. \tag{52}$$

Then, after a few simple algebraic manipulations, Eq. (51) becomes

$$\left\langle\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0\right\rangle=-3\sum_i\gamma_j\int_{-\infty}^{\infty}u_j^2\exp\left(-\frac{u_j^2}{2kT}\right)du_j\Big/\int_{-\infty}^{\infty}\exp(-u_j^2/2kT)du_j \tag{53}$$

and performing the integrations gives

$$\left\langle\left(\frac{\partial\varphi}{\partial\epsilon}\right)_0\right\rangle=-3kT\sum_i\gamma_j. \tag{54}$$

Equation (54) shows that the averages of the first derivatives are never zero and that these averages are proportional to the temperature.

It is extremely difficult to make any *a priori* decisions concerning the signs of $m_{\alpha\beta}$ and $w_{\alpha\beta}$ defined by Eqs. (15) and (41). Such a decision requires a detailed in-

vestigation of the variation of localized normal mode vibrations with strain in the vicinity of a defect. However, on the basis of general physical considerations, it is to be expected that both $m_{\alpha\beta}$ and $w_{\alpha\beta}$ are positive.

V. EFFECT OF PRESSURE ON DIFFUSION CONSTANT

Using Eqs. (1), (21), and (42), and the fact that the lattice parameter in the strained system is $(1+\epsilon)$ times the lattice parameter in the unstrained system, the relation between the diffusion coefficients in the strained and unstrained systems for uniform compression or expansion is

$$D(\epsilon)=D_u(1+\epsilon)^2\exp\left(\frac{M}{kT}3\epsilon\right), \tag{55}$$

where D_u is the diffusion coefficient in the unstrained system, and M is given by

$$M=m+w \quad \text{(vacancy mechanism)}, \tag{56}$$

$$M=m \quad \text{(interstitial, ring or exchange mechanism)}. \tag{57}$$

In terms of the volume strain, $\epsilon=\frac{1}{3}(\Delta V/V_0)$ for small strains, where ΔV is the initial volume, so that Eq. (55) takes the form

$$D\left(\frac{\Delta V}{V_0}\right)=D_u\left(1+\frac{\Delta V}{V_0}\right)^{\frac{1}{3}}\exp\left[\frac{M}{kT}\left(\frac{\Delta V}{V_0}\right)\right]. \tag{58}$$

Therefore, it is evident that a plot of $\ln[D(\Delta V/V_0)\times(1+\Delta V/V_0)^{-\frac{1}{3}}]$ against $\Delta V/V_0$ should be linear with a slope a given by

$$a=M/kT, \tag{59}$$

and an intercept given by $\ln D_u$.

Several investigators have obtained data on the variation of the diffusion coefficients with pressure that is suitable for testing Eq. (58). Reference 2 presents data for the self-diffusion coefficient as a function of pressure for sodium, phosphorous, and mercury up to pressures of 12 000, 4000, and 8000 atmospheres, respectively. The self-diffusion coefficient of liquid gallium up to pressures of 10 000 atmospheres is given in reference 3. The self-diffusion coefficient for single-crystal zinc up to pressures of 10 000 atmospheres for diffusion in the directions parallel to and perpendicular to the c axis is given in reference 1. The self-diffusion coefficient of lead up to pressures of 8000 atmospheres at two temperatures is given in reference 5.

The electrical conductivities of silver chloride and silver bromide have been measured as a function of pressure up to 300 atmospheres.[4] Since in these silver halides it has been shown that the conductivity depends almost entirely on the mobility of the silver ion, the conductivity is proportional to the diffusion coefficient of the silver ion by the Nernst-Einstein relation, and the data of reference 4 are suitable for testing Eq. (58).

Plots of the variation of the quantity of $\log[D(\Delta V/V_0)\times(1+\Delta V/V_0)^{-\frac{1}{3}}]$ against $\Delta V/V_0$ for the self-diffusion of sodium, phosphorous, mercury, gallium, and lead are shown in Fig. 1. The quantities $\log[D(\Delta V/V_0)\times(1+\Delta V/V_0)^{-\frac{1}{3}}]$ for single-crystal zinc were plotted against the fractional change in lattice parameter $\Delta\lambda/\lambda$, since this is a more natural unit for discussing diffusion in anisotropic crystals and the linear compressions perpendicular and parallel to the c-axis are available. The zinc data are plotted in Fig. 2.

Figure 3 gives $\log(1/R)$ plotted against $\Delta V/V_0$ for silver chloride and silver bromide, where R is the resistivity. The volume change $\Delta V/V_0$ is small enough for the pressure range considered so that $(1+\Delta V/V_0)^{-\frac{1}{3}}$ does not appreciably affect the results and can be ignored.

Compressibility data[11–16] were used to obtain the appropriate value of $\Delta V/V_0$ for zinc, sodium, mercury, lead, silver chloride, and silver bromide. For gallium, $\Delta V/V_0$ was computed from the data of Richards and Boyer[17] assuming that the form of $\Delta V/V_0$ as a function of pressure is the same as that for mercury. The values of $\Delta V/V_0$ for white phosphorus were computed from data in reference 16 assuming that the variation of the fractional volume change with pressure has the same form as that observed[18] for black and red phosphorus.

In all cases, the available compressibility data were extrapolated to the diffusion temperature.

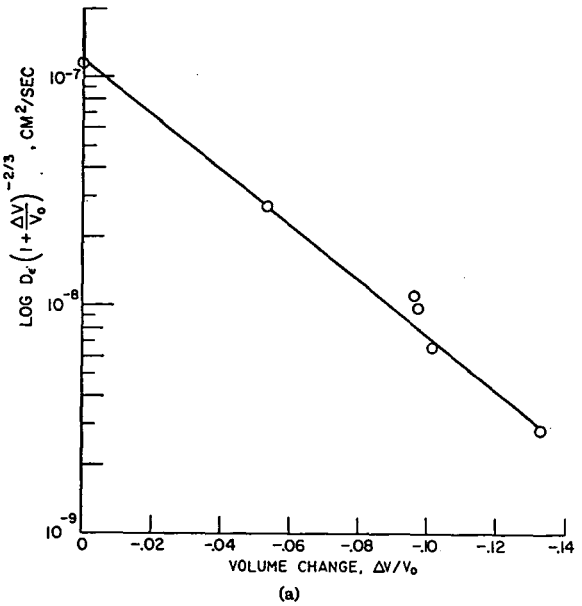
The linearity of the plots presented in Figs. 1 to 3 shows that the form of Eq. (58) is valid for those systems investigated within the probable inaccuracies of the experiments and the calculations.

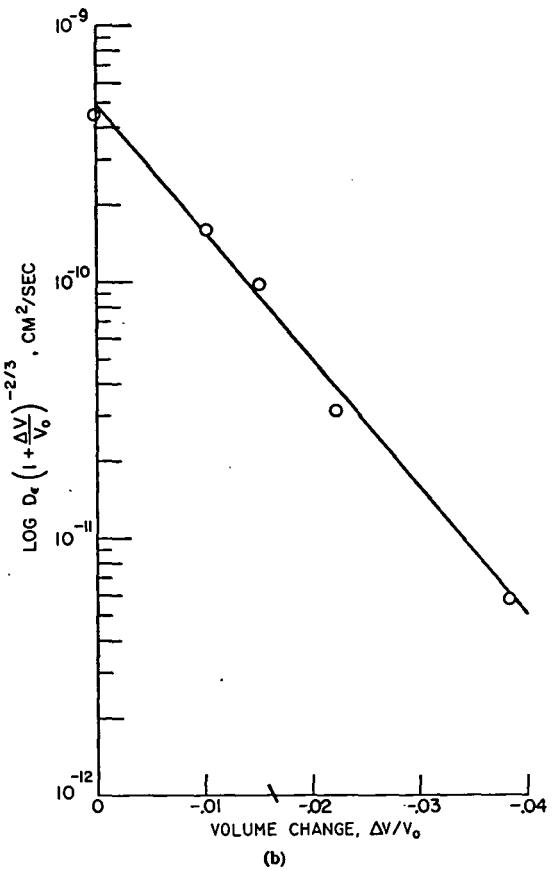
The slopes of the plots are given in Table I, where $a=M/kT$ and aT are shown for the various materials.

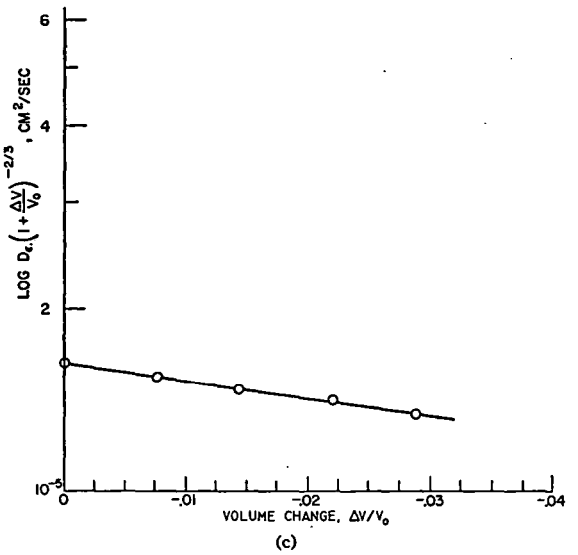
The fact that aT is so much smaller for the liquid metals than for any of the solids including sodium is indicative of the difference in the mechanism of diffusion in liquids and solids. In a liquid, the atoms are not constrained to remain at lattice positions, so that diffusion occurs by a cooperative process involving the migrating atom and its nearest neighbors. Thus, the change in the interatomic forces can be kept to a minimum throughout the diffusion process, and consequently aT would be very low.

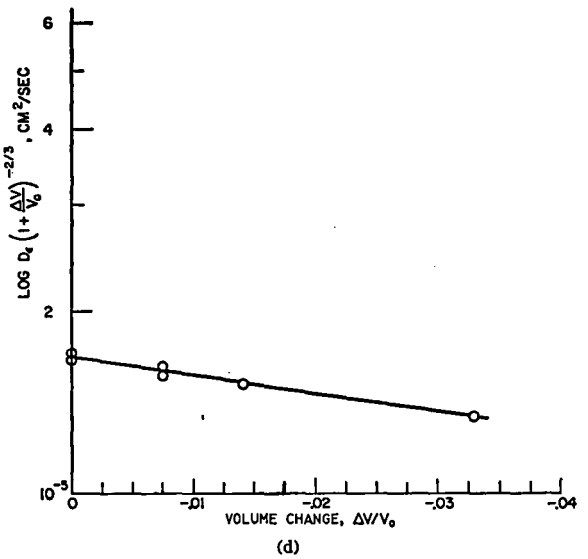
From Eqs. (54) and (59) it is seen that a should be temperature independent. For the self-diffusion of lead for which pressure data are available at two temperatures, the value of a is reasonably constant.

[11] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1925).
[12] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 71 (1948).
[13] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **47**, 347 (1911).
[14] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **58–59**, 166 (1924).
[15] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **74**, 21 (1940).
[16] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **62**, 207 (1927).
[17] Theodore W. Richards and Sylvester Boyer, J. Am. Chem. Soc. **43**, 274 (1921).
[18] T. W. Richards, J. Am. Chem. Soc. **37**, 1643 (1915).









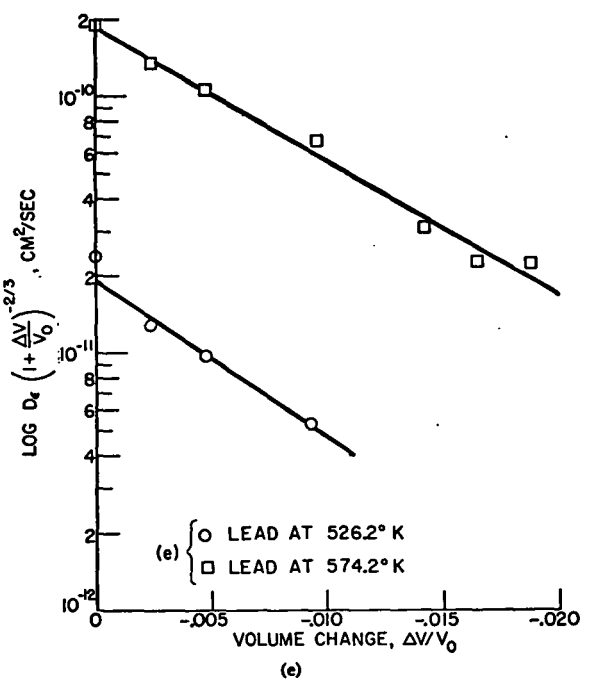
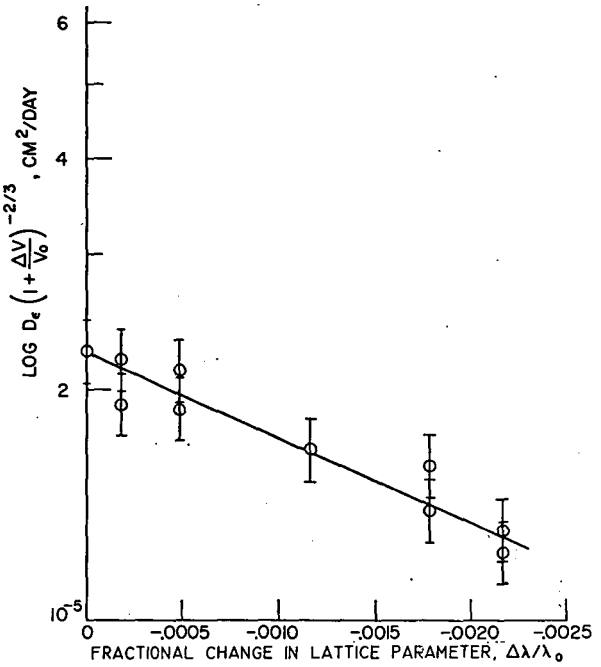
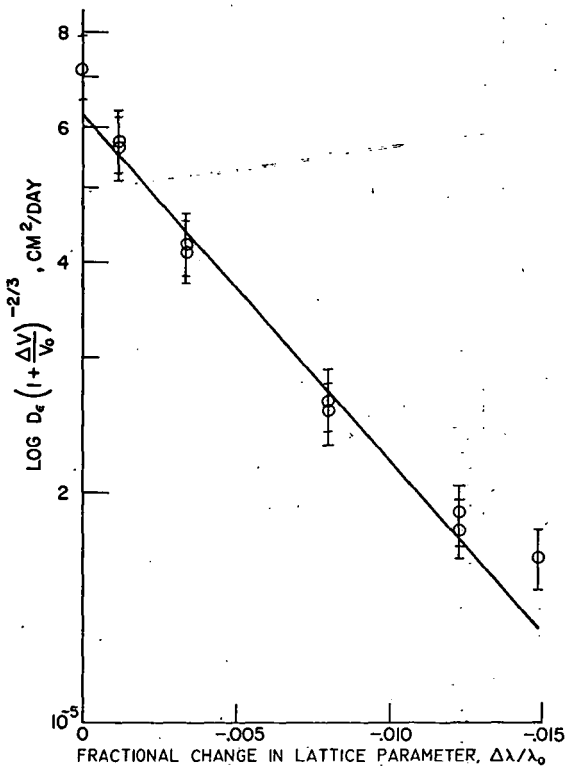


FIG. 1. Variation of $\log[D_s(1+\Delta V/V_0)^{-\frac{1}{3}}]$ plotted against volume change ($\Delta V/V_0$) for self-diffusion of various elements. (a) Sodium at 363°K [see enclosed graph]. (b) White phosphorous at 314°K. (c) Liquid mercury at 303°K. (d) Liquid gallium at 303°K. (e) Lead at 526.2°K—o ; Lead at 574.2°K—□.

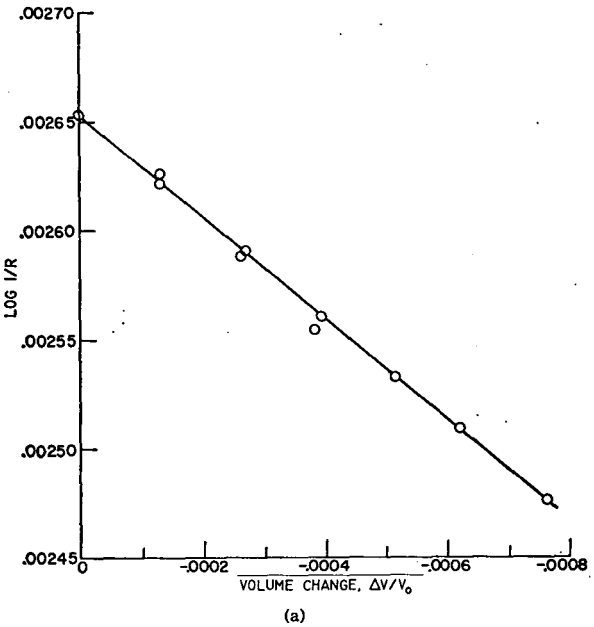


(a)

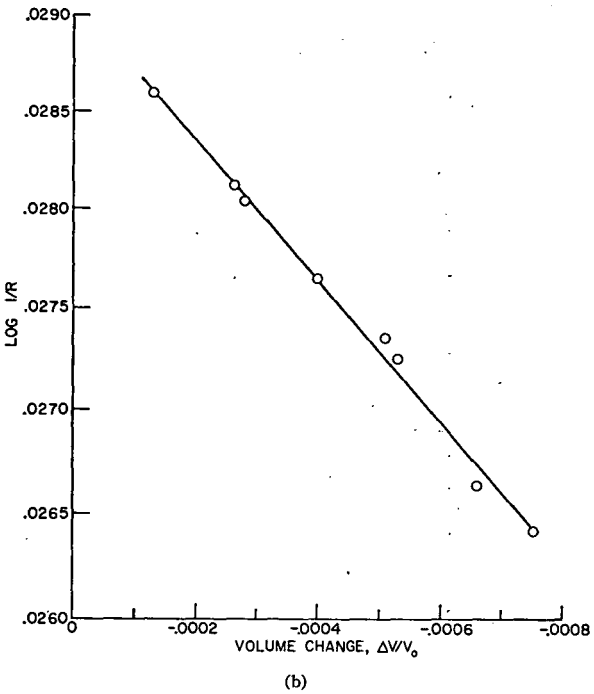


(b)

FIG. 2. Variation of $\log[D_\epsilon(1+\Delta V/V_0)^{-\frac{2}{3}}]$ plotted against fractional change in lattice parameter $\Delta\lambda/\lambda_0$ for self-diffusion in zinc. (a) Zinc at 580°K, perpendicular to c axis. (b) Zinc at 580°K, parallel to c axis.



(a)



(b)

FIG. 3. Variation of $\log(1/R)$ plotted against volume change $\Delta V/V_0$ for mobility of silver at 573°K. (a) Silver chloride. (b) Silver bromide.

Activation Volume

The activation volume is ordinarily calculated from the relation

$$\Delta V^\ddagger = \left[\frac{\partial(\Delta G)}{\partial P}\right]_T = -kT\left[\frac{\partial[\ln(D/\alpha\lambda^2\nu^*)]}{\partial P}\right]_T, \quad (60)$$

TABLE I. Comparison of values of aT for various solids.

Solid	Temperature, T (°K)	a	aT
Sodium	363	27.9	10 130
Zinc ($\perp$)	580	86.6	50 230
Zinc ($\parallel$)	580	34.7	20 130
Mercury (liquid)	303	6.5	1970
Gallium (liquid)	303	6.5	1970
Silver in silver chloride	573	91.9	52 660
Silver in silver bromide	573	128.0	73 340
Lead	526	139.9	73 590
Lead	574	121.5	69 740

where P is the pressure and ΔG refers to the Gibbs free-energy changes for vacancy formation and for the formation of the activated state configuration. This free-energy change is calculated from the measured diffusion coefficient as a function of pressure. It follows from Eq. (58) that (60) may be written

$$\Delta V^{\ddagger}=-kT\left[\frac{(M/kT)\partial(\Delta V/V_0)}{\partial P}\right]_T$$

$$=-akT\left[\frac{\partial(\Delta V/V_0)}{\partial P}\right]_T. \quad (61)$$

Since

$$\left[\frac{\partial(\Delta V/V_0)}{\partial P}\right]_T=-\beta,$$

where β is the compressibility, the activation volume defined by (61) can be calculated from the simple formula

$$\Delta V^{\ddagger}=a\beta kT. \quad (62)$$

Table II presents values of the activation volume calculated from Eq. (62) at atmospheric pressure for those systems for which data are available.

CONCLUSIONS

A statistical mechanical theory was developed that relates the diffusion coefficient to strain in terms of the atomic properties of the system. The theory makes the following statements:

1. For diffusion as a function of hydrostatic pressure, the diffusion coefficient is an exponential function of the volume strain.

2. The rate of change of the diffusion coefficient with strain is related to the interatomic forces. The relation is explicit enough that the variation of the diffusion coefficient with pressure can be interpreted in terms of the interatomic potential-energy functions of the material.

3. For diffusion under hydrostatic pressure, the activation volume can be calculated from the compressibility and the rate of change of the diffusion coefficient with volume strain.

In every case for which data are available, these conclusions are in agreement with experiment.

The general framework of the theory provides a basis for understanding the effect of strain on diffusion in terms of the atomic properties of the system and should provide a valuable tool for comparing diffusion rates for different states of strain, as well as for investigating the mechanism of diffusion.

TABLE II. Activation volumes for self-diffusion of various solids at 1 atmosphere calculated from Eq. (62).

Solid	Temperature, T (°K)	Activation volume, $\Delta V^{\ddagger}$ (cc/g-atom)
Sodium	363	12.3
Phosphorous (white)	314	71.7
Zinc ($\perp$)	580	3.0
Zinc ($\parallel$)	580	8.3
Mercury (liquid)	303	0.62
Gallium (liquid)	303	0.62
Silver in silver chloride	573	10.3
Silver in silver bromide	573	13.7
Lead	526	13.9
Lead	574	12.0

APPENDIX

The Vacancy Concentration Formula

Consider a canonical ensemble containing X member systems, each system being a crystal containing N atoms and l vacancies. Let E_j^l be the jth energy level of a system containing l vacancies and let Ω_j^l be the corresponding degeneracy. Then the number of systems containing l vacancies is

$$N_l=X\frac{\sum_j \Omega_j^l \exp(-E_j^l/kT)}{Z}, \quad (A1)$$

where Z is the total partition function for the ensemble.

The number of vacancies in the ensemble is

$$N_v=\sum_l lN_l, \quad (A2)$$

and the number of atoms in the ensemble is

$$N_A=N\sum_l N_l. \quad (A3)$$

The atomic fraction of vacancies is given by $n_v=N_v/(N_a+N_v)$. Since $N_v \ll N_a$, n_v is given by the ratio of Eqs. (A2) to (A3) to an excellent approximation, and therefore

$$n_v=\sum_l lQ_l/(N\sum_l Q_l), \quad (A4)$$

where Q_l is defined by

$$Q_l=\sum_j \Omega_j^l \exp(-E_j^l/kT). \quad (A5)$$

Q_l is the partition function of a system containing l vacancies.

Carrying out the division in (A4) and retaining only the leading term give

$$n_v = (1/N)Q_1/Q_0, \tag{A6}$$

which is an excellent approximation, since the energy of formation of a vacancy is of the order of 1 ev, and therefore the higher terms in the series are very small. Q_0 is the partition function of a perfect crystal and Q_1 is the partition function of a crystal containing a vacancy.

In the semiclassical approximation,

$$\frac{Q_1}{Q_0} = (N+1)\int\cdots\int e^{-\psi_v/kT}\prod_j dp_j dq_j \Big/ \int\cdots\int e^{-\psi_0/kT}\prod_j dp_j dq_j, \tag{A7}$$

where $\psi_v = \psi_v(p,q)$ is the energy of a crystal containing a vacancy and $\psi_0 = \psi_0(p,q)$ is the energy of a perfect crystal. The integrations are carried out over all values of the momenta and coordinates p_j and q_j. The factor $(N+1)$ arises from the fact that N indistinguishable atoms can be placed in $(N+1)$ numbered lattice sites in $(N+1)$ ways so that Q_1 is proportional to $(N+1)$.

Combining Eqs. (A6) and (A7) gives

$$n_v = \int\cdots\int e^{-\psi_v(p_j,q_j)/kT}\prod_j dp_j dq_j \Big/ \int\cdots\int e^{-\psi_0(p_j,q_j)/kT}\prod_j dp_j dq_j, \tag{A8}$$

where unity has been neglected relative to N.

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