

Reprinted from THE PHYSICAL REVIEW, Vol. 121, No. 4, 982-991, February 15, 1961  
 Printed in U. S. A.

## Effect of Static Strains on Diffusion

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(Received September 16, 1960; revised manuscript received November 7, 1960)

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<sup>1</sup> and large hydrostatic pressures may decrease the self-diffusion coefficient by as much as an order of magnitude.<sup>2-5</sup>

The theory of the effect of pressure on diffusion has been examined on the basis of the dynamic theory of diffusion.<sup>6,7</sup> 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<sup>8</sup> 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-

<sup>1</sup> T. Liu and H. G. Drickamer, *J. Chem. Phys.* **22**, 312 (1954).

<sup>2</sup> Norman H. Nachtrieb, Wright Air Development Center Technical Report No. 55-68 (unpublished).

<sup>3</sup> J. Petit and N. H. Nachtrieb, *J. Chem. Phys.* **24**, 1027 (1956).

<sup>4</sup> W. Jost and G. Nehlep, *Z. physik. Chem.* **34**, 348 (1936).

<sup>5</sup> Norman H. Nachtrieb, Henry A. Resing, and Stuart A. Rice, *J. Chem. Phys.* **31**, 135 (1959).

<sup>6</sup> Stuart A. Rice, *Phys. Rev.* **112**, 804 (1958).

<sup>7</sup> Stuart A. Rice and Norman H. Nachtrieb, *J. Chem. Phys.* **31**, 139 (1959).

<sup>8</sup> 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

$$D = \alpha \lambda^2 n \Gamma, \quad (1)$$

where  $D$  is the diffusion coefficient,  $\lambda$  is the lattice parameter,  $n$  is the concentration of carrier defects,  $\Gamma$  is the jump frequency, and  $\alpha$  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<sup>8</sup> is used, in which the jump frequency is given in terms of these integrals by

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

where  $k$  is Boltzmann's constant,  $T$  is the temperature, and  $\varphi$  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  $\sigma$  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  $\varphi$  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<sup>9</sup> in an analysis of the statistical mechanics of crystal

lattices. Thus, the potential energy in Eq. (2) is given by

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

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

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

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

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

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

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

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:

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

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

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

<sup>9</sup> Max Born, Proc. Cambridge Phil. Soc. 36, 160 (1940).