

Classical and Quantum Rate Theories for Solids*

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(Received 19 December 1967)

A rate formula for defect motion in solids including quantum effects is derived by generalization of the classical equilibrium statistical approach. The development makes use of an interpretation of the canonical density matrix for a harmonic oscillator as an ensemble of oscillators which are in minimum-uncertainty states. The classical limit of the rate formula differs from Vineyard's in the pre-exponential factor. The difference is due to the assumption regarding the degree of mode interaction on the hill of the potential surface. The present derivation assumes no interaction, while Vineyard assumes sufficient interaction to maintain thermal equilibrium on the hill. The derived quantum rate formula includes the effects of quantum statistics but not tunnelling effects. Its low-temperature characteristics are explored for the Debye model.

1. INTRODUCTION

THE theory of rate processes in solids, in the classical regime, has been reviewed recently by Glyde.¹ He discusses the essential equivalence between transition-state theories based on equilibrium statistical mechanics such as that of Vineyard² and the dynamical approach of Rice³ and co-workers.⁴

Of the two methods, the equilibrium statistical approach is simpler and allows the use of more realistic interatomic potentials. The principal purpose of this paper is to present a rate theory which is derived by a generalization of the equilibrium statistical approach to the quantum regime.⁵ The difficulty in the direct generalization of the classical approach is as follows.

In the classical case, thermal equilibrium is described in terms of a canonical probability distribution function $\rho(Q,P)$ whose arguments are the coordinates Q and momenta P of the system. This function may be conceived as giving, at time t_0 , the density of distribution of the members of an ensemble of identical systems in a phase

space Γ . Since the subsequent motion of each member of the ensemble is determined by its position in Γ at time t_0 , the function ρ may be used to compute the average (over the ensemble) rate with which members of the ensemble arrive at a given transition state from which they go on to a neighboring equilibrium state.

In the quantum regime, on the other hand, thermal equilibrium is described generally in terms of a density matrix $M(Q,Q')$ in which both arguments represent coordinates. The difficulty in generalizing the classical equilibrium statistical approach in a straightforward manner is signaled by the loss of the momenta arguments in the ensemble description. It is further reflected in the usual interpretation of an equilibrium quantum ensemble as one whose elements are in stationary quantum states, so that there is no "subsequent motion" of each member of the ensemble as in the classical case.

An early attempt to circumvent this difficulty was made by Wigner.⁶ He reintroduced the momenta into the discussion by presenting a distribution function for an ensemble, whose elements are described by the arguments (Q,P) and whose ensemble average corresponds to the *quantum* expectation value. This ensemble thus represents the quantum but not the thermal aspect of the process, and the thermal averaging must be performed in addition. The difficulty with this approach is in the physical interpretation of the arguments (Q,P) for the elements of the quantum ensemble. In particular, the Wigner distribution function cannot be regarded in the usual statistical ensemble sense since it may take on negative values.

The approach adopted here reintroduces momenta and time evolution in the description of members of the thermal ensemble, leaving unchanged the usual method of calculating quantum expectation values. It exploits the fact that the same density matrix may represent different ensembles, that is, ensembles whose members at a given instant are in a different set of quantum

* Research supported by the U. S. Air Force of Scientific Research under Grant No. AF-AFOSR-228-67.

¹ H. R. Glyde, *Rev. Mod. Phys.* **39**, 373 (1967).

² G. H. Vineyard, *J. Phys. Chem. Solids* **3**, 121 (1957).

³ S. A. Rice, *Phys. Rev.* **112**, 804 (1958).

⁴ Reference should also be made to the older theory of chemical reaction rates which treats in many respects the same type of process. A comprehensive treatment of this subject from various viewpoints and the relationship between them is contained in N. B. Slater [*Theory of Unimolecular Reactions* (Cornell University Press, Ithaca, N. Y., 1959)], hereafter referred to as Slater. Many of the developments in the solid-state theory were preceded by analogous procedures in the chemical theory and the relative lack of communication between the two fields may be due, in part, to the difference in language and emphasis.

⁵ A good discussion of the problem of generalizing rate theories to the quantum regime, as well as some tentative approaches, may be found in Chap. 10 of Slater (Ref. 4). A quantum generalization of the dynamical approach may be found there and, for the solid-state case, in G. Alefeld, *Phys. Rev. Letters* **12**, 372 (1964). The treatments are semiclassical in that the motion of each atom is obtained from the superposition of normal modes whose energy distribution is taken according to quantum theory. Some generalizations of the classical formulas based on equilibrium statistical mechanics also have been made by replacing the partition functions which appear in the classical expressions by their quantum counterparts. See, for example, Slater (Ref. 4); H. S. Johnston and D. Rapp, *J. Am. Chem. Soc.* **83**, 1 (1961); A. D. Le Claire, *Phil. Mag.* **14**, 1271 (1966). However, although such formulas are suggested by analogy, their direct quantum derivation is lacking.

⁶ E. Wigner, *Z. Physik Chem.* **19**, 203 (1933). Further work along these lines has been done by J. E. Moyal, *Proc. Cambridge Phil. Soc.* **45**, 99 (1949); M. S. Bartlett and J. E. Moyal, *ibid.* **45**, 547 (1949). The latter formulation has been used by Slater as a point of departure for a generalization of classical equilibrium statistical rate theory to the quantum regime.

states. For the case of a harmonic oscillator an ensemble may be constructed whose members are in quantum states corresponding to minimum-uncertainty wave packets and for which the density-matrix description is canonical.⁷ The quantum state of a member of the ensemble is thus described at time t_0 completely by giving its quantum means $\bar{Q}(t_0)$, $\bar{P}(t_0)$, and its subsequent time evolution by the functions $\bar{Q}(t)$, $\bar{P}(t)$, which are solutions of the classical equations. This then allows the derivation of a rate formula along the same lines employed in the classical case.⁸

It is not possible, however, to follow a procedure precisely analogous to that followed by Vineyard since the minimum uncertainty ensemble applies only when the harmonic approximation is valid,⁹ and a different approach is developed to accommodate this restriction. In Sec. 2, therefore, we first give a purely classical derivation of the rate formula with this approach. The formula obtained there is the same as the classical limit of the quantum rate formula to be derived subsequently. However, this classical limit differs from Vineyard's formula, and it is desirable to see the sources of these differences in a purely classical framework.

We then turn, in Sec. 3, to the development of the concepts and distribution function for a minimum-uncertainty ensemble of harmonic oscillators. With this concept it is then possible to derive, in Sec. 4, the quantum generalization of the rate formula derived classically in Sec. 2 along lines which are completely analogous to the classical derivation. Although it appears that tunnelling may be included in a natural fashion in this framework, we restrict ourselves at present to the case in which tunnelling effects are negligible.¹⁰ The detailed evaluation of the frequency formula must be tied to a given lattice and defect. In Sec. 5, the simplest possible assumptions are made, using the Debye model, to examine the low-temperature form of the result. Conclusions are presented in Sec. 6.

⁷ It has come to the author's attention after the preparation of this paper that these states have been extensively employed in the field of quantum electrodynamics since their introduction by R. J. Glauber [Phys. Rev. **131**, 2766 (1963)], where they are referred to as coherent states. General ensembles of these states are introduced there, including the ensemble corresponding to the canonical density matrix. We have retained the present terminology and the derivation of Sec. 3 since this viewpoint seems better suited to the rate-process study.

⁸ This approach also meets another difficulty in the quantum generalization, that of describing the initially localized state of a member of the ensemble. Another method for accomplishing this purpose has been put forward by J. A. Sussmann [J. Phys. Chem. Solids **28**, 1643 (1967)], who assumes the presence of some external field to produce an asymmetry between two potential wells.

⁹ A similar problem arises in Slater's work based on Moyal's theory; see the remarks following Eq. (48) on p. 219 of Slater (Ref. 4).

¹⁰ The question of tunnelling in rate processes has been treated in many papers, for example, in the paper by Johnston and Rapp (Ref. 5) and that of Sussmann (Ref. 8).

2. CLASSICAL DERIVATION

For the reasons noted in the Introduction, we begin by giving a purely classical derivation of the classical limit of the quantum rate formula which will be derived in Sec. 4.

Let the Hamiltonian of the system be

$$H = \frac{1}{2} \sum_{i=1}^{3N} m_i (\dot{x}_i)^2 + V(x_1, \dots, x_{3N}), \quad (2.1)$$

where m_i are atomic masses (with $m_1 = m_2 = m_3$, $m_4 = m_5 = m_6$, etc.), and where V includes the potential of any externally applied fields.

Introduce reduced-mass coordinates

$$y_i = (m_i)^{1/2} x_i, \quad (2.2)$$

so that H becomes

$$H = \frac{1}{2} \sum_{i=1}^N (\dot{y}_i)^2 + W(y_1, \dots, y_{3N}). \quad (2.3)$$

Let¹¹ $y_i = 0$ ($\mathbf{y} = \mathbf{0}$) correspond to a stable equilibrium configuration which consists of a single defect in an otherwise perfect lattice. Then in the neighborhood of $\mathbf{y} = \mathbf{0}$,

$$W = \frac{1}{2} \sum_{i,j=1}^{3N} W_{ij}^S y_i y_j, \quad \text{where } W_{ij}^S = \left. \frac{\partial^2 W}{\partial y_i \partial y_j} \right|_{\mathbf{y}=\mathbf{0}} \quad (2.4)$$

is a positive-definite matrix. Next let $y_i = d_i$ ($\mathbf{y} = \mathbf{d}$) correspond to the neighboring unstable (saddle-point) configuration of interest. In the neighborhood of $\mathbf{y} = \mathbf{d}$,

$$W = W(\mathbf{d}) + \frac{1}{2} \sum_{i,j=1}^{3N} W_{ij}^U (y_i - d_i)(y_j - d_j), \quad (2.5)$$

where the matrix

$$W_{ij}^U = \left. \frac{\partial^2 W}{\partial y_i \partial y_j} \right|_{\mathbf{y}=\mathbf{d}}$$

has at least one negative eigenvalue. We denote the eigenvalues of $W_{ij}^{S,U}$ by $\lambda_\alpha^{S,U}$, $\alpha = 1, \dots, 3N$ indexed in order of increasing magnitude, and the corresponding eigenvectors by $\mathbf{a}_\alpha^{S,U}$ with components $a_{\alpha i}^{S,U}$ in the y_i coordinate system. Then all the $\lambda_\alpha^S > 0$ and we set $\omega_\alpha = (\lambda_\alpha^S)^{1/2}$ as the frequencies of the normal modes of vibration in the neighborhood of $\mathbf{y} = \mathbf{0}$. We introduce normal coordinates $Q_\alpha^{S,U}$ and momenta $P_\alpha^{S,U}$ in the respective eigenvector directions by equations

$$Q_\alpha^{S,U} = \sum_{i=1}^{3N} a_{\alpha i}^{S,U} y_i, \quad P_\alpha^{S,U} = \dot{Q}_\alpha^{S,U}. \quad (2.6)$$

In order not to encumber the presentation with excessive superscripts, we use the less mnemonic, but simpler,

¹¹ We use throughout notation analogous to $\mathbf{y} = (y_1, \dots, y_{3N})$. The dimension of these vectors vary and are specified when introduced.

notation

$$Q_\alpha = Q_\alpha^S, \quad P_\alpha = P_\alpha^S, \\ q_\alpha = Q_\alpha^U, \quad p_\alpha = P_\alpha^U.$$

For motion in the neighborhood of $\mathbf{y}=0$, the Hamiltonian then takes the form

$$H = \frac{1}{2} \sum_{\alpha=1}^{3N} [(P_\alpha)^2 + \omega_\alpha^2 (Q_\alpha)^2]. \quad (2.7)$$

As to the spectrum of W_{ij}^U , we make the assumption that there is only one negative eigenvalue $\lambda_1^U < 0$. The crest of the potential-energy surface is, therefore, locally tangent to the hyperplane \mathcal{P}_1 through $\mathbf{y}=\mathbf{d}$ and orthogonal to \mathbf{a}_1^U (Fig. 1).

Usually (e.g., in the derivation of Vineyard²) specification of the potential-energy function W is limited to the matrices W_{ij}^S and W_{ij}^U and, in fact, only to their eigenvalues. For the present derivation we need an additional assumption about the nature of W . We assume the existence of a second hyperplane \mathcal{P}_0 (Fig. 1) parallel to \mathcal{P}_1 with the following properties:

(i) Until the system, starting from the neighborhood of $\mathbf{y}=0$, crosses \mathcal{P}_0 , its motion is governed by the Hamiltonian of Eq. (2.7).

(ii) There exists a critical momentum μ such that if (and only if) $p_1 > \mu$ when crossing \mathcal{P}_0 the system will continue on to \mathcal{P}_1 and to the next stable equilibrium configuration.

We now consider an ensemble of identical defects in thermal equilibrium at temperature T . A collection of defects in the same crystal, if sufficiently dilute so that no interaction between them takes place, is a good approximation to such a conceptual ensemble. An observation of the state of all defects at a given instant [classically this means the determination of the coordinates and momenta (\mathbf{Q}, \mathbf{P}) for each] would find most of the defects in their respective valleys with relatively few (at low temperatures) on the hill between hyperplanes \mathcal{P}_0 and \mathcal{P}_1 . The latter we neglect. We assume that those members of the ensemble found in the valley will be found to be canonically distributed, that is, with

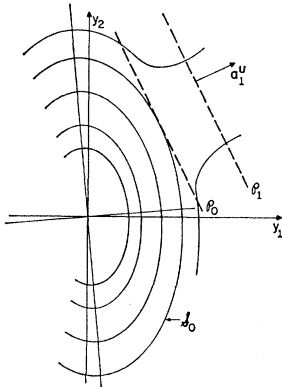


FIG. 1. Schematic diagram of potential-energy contours. \mathcal{P}_1 is hyperplane through saddle point at $\mathbf{y}=\mathbf{d}$ orthogonal to unstable localized mode vector \mathbf{a}_1^U . \mathcal{P}_0 is parallel to \mathcal{P}_1 and tangent to the constant-energy surface \mathcal{S}_0 . It is assumed that the harmonic approximation is valid in the region including the stable equilibrium configuration at the origin until the plane \mathcal{P}_0 is reached.

distribution function

$$\rho(\mathbf{Q}, \mathbf{P}) = \mathcal{C} e^{-H(\mathbf{Q}, \mathbf{P})/kT}, \quad (2.8)$$

with $H(\mathbf{Q}, \mathbf{P})$ given by Eq. (2.7). To determine the normalization constant \mathcal{C} , we integrate this function ρ over all of phase space¹² to obtain the usual result

$$\mathcal{C} = \frac{\prod_{\alpha=1}^{3N} \omega_\alpha}{(2\pi kT)^{3N}}. \quad (2.9)$$

In order to determine the average rate f at which elements of this ensemble will cross \mathcal{P}_0 with the requisite momentum $p_1 > \mu$, we express the distribution function $\rho(\mathbf{Q}, \mathbf{P})$ in terms of the variables \mathbf{q}, \mathbf{p} . The relationships between these variables are

$$Q_\alpha = \sum_{\beta=1}^{3N} A_{\alpha\beta} q_\beta, \quad P_\alpha = \sum_{\beta=1}^{3N} A_{\alpha\beta} p_\beta \quad (2.10)$$

or

$$\mathbf{Q} = \mathbf{A}\mathbf{q}, \quad \mathbf{P} = \mathbf{A}\mathbf{p},$$

where \mathbf{A} is the orthogonal matrix with elements

$$A_{\alpha\beta} = \mathbf{a}_\alpha^S \cdot \mathbf{a}_\beta^U = \sum_{i=1}^{3N} a_{\alpha i}^S a_{\beta i}^U, \quad (2.11)$$

$$\rho(\mathbf{q}, \mathbf{p}) = \mathcal{C} \exp - \left[\sum_{\alpha, \beta=1}^{3N} (B_{\alpha\beta} p_\alpha p_\beta + C_{\alpha\beta} q_\alpha q_\beta) \right], \quad (2.12)$$

where

$$B_{\alpha\beta} = (2kT)^{-1} \sum_{\delta=1}^{3N} A_{\delta\alpha} A_{\delta\beta} \quad (2.13)$$

and

$$C_{\alpha\beta} = (2kT)^{-1} \sum_{\delta=1}^{3N} \omega_\delta^2 A_{\delta\alpha} A_{\delta\beta}.$$

Since \mathbf{A} is an orthogonal matrix, it is clear that $\mathbf{B} = (2kT)^{-1} \mathbf{I}$, where \mathbf{I} is the identity matrix. However, we retain the designation \mathbf{B} for use in the subsequent quantum generalization.

In terms of $\rho(\mathbf{q}, \mathbf{p})$, the average rate f defined above may be written as

$$f = \int_{\mu}^{\infty} p_1 d p_1 \int_{\Omega_0} \rho(\mathbf{q}, \mathbf{p}) \prod_{\alpha=2}^{3N} d q_\alpha d p_\alpha, \quad (2.14)$$

where Ω_0 is the subspace, $q_1 = \eta$, $-\infty < q_\alpha < \infty$, $-\infty < p_\alpha < \infty$, $\alpha = 2, \dots, 3N$, and where we have set $q_1 = \eta$ as the equation of \mathcal{P}_0 . It may be expressed in terms of integrals over all coordinates and momenta by use of the Dirac

¹² Strictly speaking, in carrying out this normalization, we should omit the hill regions, both because we are considering only what fraction of those defects in the valley escape and because H is not given by Eq. (2.7) on the hills. At low temperatures, however, the contribution of the hill region is negligible with either value of H so that the procedure adopted introduces negligible error.

delta function $\delta(x)$ and the unit step function, $U(x)=1$ for $x>0$, $U(x)=0$ for $x<0$, as follows:

$$f = \mathcal{C} I_p \times I_q, \quad (2.15)$$

where

$$I_p = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \times [\exp(-\sum_{\alpha,\beta=1}^{3N} B_{\alpha\beta} \dot{p}_\alpha \dot{p}_\beta)] \dot{p}_1 U(\dot{p}_1 - \mu) \prod_{\alpha=1}^{3N} d\dot{p}_\alpha, \quad (2.16)$$

$$I_q = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \times [\exp(-\sum_{\alpha,\beta=1}^{3N} C_{\alpha\beta} q_\alpha q_\beta)] \delta(q_1 - \eta) \prod_{\alpha=1}^{3N} dq_\alpha.$$

Both of these integrals may be evaluated by using a formula of Schlömilch as generalized by Rice.¹³ The results are

$$I_p = \frac{1}{2} R_B \left[\frac{\pi^{3N-1}}{|B|} \right]^{1/2} e^{-\mu^2 / R_B^2}, \quad (2.17)$$

$$I_q = \frac{1}{R_C} \left[\frac{\pi^{3N-1}}{|C|} \right]^{1/2} e^{-\eta^2 / R_C^2},$$

where $|B|$, $|C|$ are the determinants of \mathbf{B} , \mathbf{C} , $R_B = (B_{11}^{-1})^{1/2}$, $R_C = (C_{11}^{-1})^{1/2}$, with $B_{\alpha\beta}^{-1}$, $C_{\alpha\beta}^{-1}$ the elements of the matrices inverse to \mathbf{B} and \mathbf{C} . With the definitions of the matrices of \mathbf{B} and \mathbf{C} , we find

$$|B| = (2kT)^{-3N}, \quad |C| = (2kT)^{-3N} \prod_{\alpha=1}^{3N} \omega_\alpha^2, \quad (2.18)$$

$$R_B^2 = 2kT, \quad R_C^2 = 2kT \sum_{\alpha=1}^{3N} A_{\alpha 1}^2 \omega_\alpha^{-2}.$$

When the component quantities as given in Eqs. (2.9), and (2.15)–(2.18) are combined, the formula for f becomes

$$f = \frac{\omega_e}{2\pi} \exp\left(-\frac{\mu^2 + \omega_e^2 \eta^2}{2kT}\right), \quad (2.19)$$

where we have introduced the notation

$$\omega_e = \left(\sum_{\alpha=1}^{3N} A_{\alpha 1}^2 \omega_\alpha^{-2} \right)^{-1/2}. \quad (2.20)$$

The exponent of Eq. (2.19) may be given a further interpretation. Consider the hyperplane \mathcal{O}_0 previously introduced (Fig. 1). It will be tangent to one of the

constant-energy surfaces \mathcal{S}_0 with the equation

$$\frac{1}{2} \sum_{\alpha=1}^{3N} \omega_\alpha^2 Q_\alpha^2 = W_0. \quad (2.21)$$

If use is now made of the fact that \mathcal{O}_0 is also normal to \mathbf{a}_1^U and that its equation is also $q_1 = \eta$, it may be verified that

$$\frac{1}{2} \omega_e^2 \eta^2 = W_0. \quad (2.22)$$

We have also assumed that a momentum μ in the \mathbf{a}_1^U direction will carry the system from any point on \mathcal{O}_0 over the crest \mathcal{O}_1 . This implies a constant change ΔW in energy between corresponding points on \mathcal{O}_0 and \mathcal{O}_1 (that is, points which differ only in their q_1 coordinates). Since the constant-energy surfaces of the form of Eq. (2.21) are convex, it is clear that the point of tangency of \mathcal{O}_0 to \mathcal{S}_0 corresponds to an energy minimum and, therefore, that the corresponding point on \mathcal{O}_1 is the saddle point. It follows that Eq. (2.19) can be written also in the form

$$f = \frac{\omega_e}{2\pi} e^{-W_1/kT}, \quad (2.23)$$

where W_1 is the energy difference between the saddle point and stable equilibrium configurations. The frequency formula obtained by Vineyard is, in the present notation,

$$f = \frac{1}{2\pi} \frac{\prod_{\alpha=1}^{3N} \omega_\alpha}{\prod_{\beta=2}^{3N} (\lambda_\beta^U)^{1/2}} e^{-W_1/kT}, \quad (2.24)$$

and it is seen that they differ in the multiplying frequency factor.

The difference between the two results may be ascribed to the different assessment of the extent of mode interaction on the hill (between planes \mathcal{O}_0 and \mathcal{O}_1 in the present model). Vineyard assumes that a typical member of the ensemble continues to experience sufficient mode interaction in the time it spends on the hill so that the ensemble characteristics correspond to thermal equilibrium on the hill right up to plane \mathcal{O}_1 . Therefore, the details of the transition region between valley and hill are erased and do not enter into his rate formula. In the present derivation, we assume that the passage over \mathcal{O}_1 is determined by conditions at \mathcal{O}_0 , i.e., no subsequent interaction. The inner products $A_{\alpha 1} = \mathbf{a}_\alpha^S \cdot \mathbf{a}_1^U$ are measures of the effectiveness of energy transfer¹⁴ from the stable modes to the direction \mathbf{a}_1^U that carries the system over the crest. These inner products appear therefore

¹⁴ The transfer of energy from stable to unstable modes was found to play a significant role also in the study of dislocation motion in a crystal model; see J. H. Weiner and W. T. Sanders, Phys. Rev. **134**, A1007 (1964); J. H. Weiner, *ibid.* **136**, A863 (1964); **139**, A442 (1965).

¹³ S. O. Rice, Bell Syst. Tech. J. **24**, 58 (1945). Reprinted in *Selected Papers on Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, Inc., New York, 1954), p. 209.

as weighting factors to give the equivalent frequency we obtained here.¹⁵ The two assessments of the extent of mode interaction on the hill thus represent two extremes, with further analysis and experiment necessary to determine where specific real systems lie relative to them.¹⁶

3. MINIMUM-UNCERTAINTY ENSEMBLE

We start by considering, in this section, a single harmonic oscillator with Hamiltonian

$$H_0(Q,P) = \frac{1}{2}(P^2 + \omega^2 Q^2)$$

in thermal equilibrium with a reservoir at T .

The density matrix $M(Q,Q')$ corresponding to a canonical ensemble is

$$M(Q,Q') = D \sum_{n=0}^{\infty} e^{-\beta n} \psi_n(Q) \psi_n(Q'), \quad (3.1)$$

where

$$\beta = \frac{\hbar\omega}{kT}, \quad D = 1 - e^{-\beta}, \quad (3.2)$$

and $\psi_n(Q)$ is the wave function of the oscillator in the n th eigenstate with energy $(n + \frac{1}{2})\hbar\omega$. The density matrix may be regarded as representing an ensemble of oscillators in these pure states. We are not, however, confined to this viewpoint and we show next that the same density matrix, Eq. (3.1), may also be regarded as representing a suitably defined ensemble of oscillators whose elements at time $t=t_0$ are in quantum states that correspond to minimum-uncertainty wave packets. The wave functions $f(Q,t_0)$ for the latter states are of the form

$$f(Q,t_0) = (2\pi\sigma)^{-1/4} \exp\left[\frac{i}{\hbar}\bar{P}_0 Q - \frac{(Q - \bar{Q}_0)^2}{4\sigma}\right], \quad (3.3)$$

where $\bar{Q}_0 = \bar{Q}(t_0)$ and $\bar{P}_0 = \bar{P}(t_0)$ denote the quantum expectations of these quantities in this state and $\sigma = \hbar(2\omega)^{-1}$. Then the wave packet remains minimum in the course of time and at time t we have, within a phase factor,

$$f(Q,t) = (2\pi\sigma)^{-1/4} \exp\left[\frac{i}{\hbar}\bar{P}Q - \frac{(Q - \bar{Q})^2}{4\sigma}\right], \quad (3.4)$$

¹⁵ The inner products $\mathbf{a}_\alpha^S \cdot \mathbf{a}_\beta^U$ describe only the relative orientation of valley and saddle point. Still more extensive description of what is referred to in the chemical literature as the reaction path are possible. Discussion of motion along this path in terms of curvilinear coordinates may be found for the chemical problem, from both the classical and quantum viewpoints in R. A. Marcus, *J. Chem. Phys.* **45**, 4493 (1966); **45**, 4500 (1966); a classical treatment for the solid-state problem appears in J. H. Weiner, *Phys. Rev.* **152**, 597 (1966).

¹⁶ Reference should be made here to the computer-simulation results of J. H. Weiner and W. F. Adler [*Phys. Rev.* **144**, 511 (1966)] in which the observed jump frequencies for a particular crystal model agreed reasonably well (within the limits of uncertainty imposed by the nature of the computer simulation) with the Vineyard formula. Further work along these lines with a variety of model parameter is projected.

where $\bar{Q} = \bar{Q}(t)$ and $\bar{P} = \bar{P}(t)$ are again the quantum expectations of these quantities and satisfy the classical equations¹⁷ corresponding to $H_0(\bar{Q}, \bar{P})$ with the initial conditions \bar{Q}_0, \bar{P}_0 . With the notation¹⁸

$$Q = (\hbar/\omega)^{1/2} q, \quad P = (\hbar\omega)^{1/2} p, \quad (3.5)$$

the wave function may be rewritten as

$$f(q,t) = (2\pi\sigma)^{-1/4} \exp[i\bar{p}q - \frac{1}{2}(q - \bar{q})^2] \quad (3.6)$$

and may be expanded in terms of the eigenstates $\psi_n(Q)$ as

$$f(q,t) = \exp\left\{-\left[\frac{1}{4}(\bar{q}^2 + \bar{p}^2) - \frac{1}{2}i\bar{p}\bar{q}\right]\right\} \times \sum_{n=0}^{\infty} \frac{(\bar{q} + i\bar{p})^n}{(n!)^{1/2} 2^{n/2}} \psi_n(q). \quad (3.7)$$

Let

$$\xi = \frac{1}{2}(\bar{p}^2 + \bar{q}^2) = H_0(\bar{Q}, \bar{P})/\hbar\omega. \quad (3.8)$$

We see that ξ is constant since \bar{Q} and \bar{P} are governed by the classical equations corresponding to $H_0(\bar{Q}, \bar{P})$, and we may write

$$\bar{q} + i\bar{p} = (2\xi)^{1/2} e^{i\theta}, \quad (3.9)$$

where $\theta(t)$ is the phase angle for the classical oscillator motion executed by (\bar{q}, \bar{p}) . We introduce the notation $f(q; \xi, \theta)$ for the wave function at a given instant of time whose mean values \bar{q}, \bar{p} correspond then to the values ξ, θ . In this notation Eq. (3.7) takes the form

$$f(q; \xi, \theta) = \exp\left\{-\frac{1}{2}\xi(1 + i \sin 2\theta)\right\} \times \sum_{n=0}^{\infty} \frac{\xi^{n/2} e^{in\theta}}{(n!)^{1/2}} \psi_n(q). \quad (3.10)$$

We now consider an ensemble of oscillators whose quantum states at a given instant correspond to Eq. (3.10) with values of ξ , $0 \leq \xi < \infty$ and θ , $0 \leq \theta < 2\pi$ suitably distributed according to an ensemble distribution function $\rho(\xi, \theta)$. This ensemble will be equivalent to the canonical ensemble of Eq. (3.1) if

$$\int_0^{2\pi} d\theta \int_0^\infty d\xi \rho(\xi, \theta) f(q; \xi, \theta) f^*(q'; \xi, \theta) = M(q, q'). \quad (3.11)$$

We start by assuming that $\rho(\xi, \theta) = (2\pi)^{-1} \rho(\xi)$, i.e., that the phase angles θ are uniformly distributed. Equation (3.11) then becomes

$$\int_0^\infty d\xi \rho(\xi) e^{-\xi} \sum_{n=0}^{\infty} \frac{\xi^n}{n!} \psi_n(q) \psi_n(q') = M(q, q'). \quad (3.12)$$

Comparison of Eqs. (3.1) and (3.12) shows that $\rho(\xi)$

¹⁷ See, for example, A. Messiah, *Quantum Mechanics* (North-Holland Publishing Co., Amsterdam, 1964), Vol. I, p. 446.

¹⁸ This notation is used only in this section.

must satisfy the equation

$$\int_0^\infty e^{-\xi} \xi^n \rho(\xi) d\xi = n! D e^{-\beta n}, \quad \text{for } n=0, 1, 2, \dots \quad (3.13)$$

This integral equation is readily solved by rewriting the right-hand side by use of the integral representation of the Γ function:

$$\begin{aligned} n! e^{-\beta n} &= \Gamma(n+1) e^{-\beta n} = \int_0^\infty (e^{-\beta y})^n e^{-y} dy \\ &= b \int_0^\infty \xi^n e^{-b\xi} d\xi, \end{aligned} \quad (3.14)$$

where $b = e^\beta$. Comparison of Eqs. (3.13) and (3.14) then shows that

$$\rho(\xi) = D b e^{-(b-1)\xi} = (b-1) e^{-(b-1)\xi} = c e^{-c\xi}, \quad (3.15)$$

where $c = b-1 = e^\beta - 1$. We next express the distribution function $\rho(\xi, \theta) = (2\pi)^{-1} \rho(\xi)$ in terms of \bar{Q}, \bar{P} ,

$$\begin{aligned} \rho(\bar{Q}, \bar{P}) &= \frac{\partial(\xi, \theta)}{\partial(\bar{Q}, \bar{P})} \rho(\xi, \theta) = \hbar^{-1} \rho(\xi, \theta) \\ &= \frac{c}{2\pi\hbar} \exp\left\{-\frac{c(\bar{P}^2 + \omega^2 \bar{Q}^2)}{2\hbar\omega}\right\}. \end{aligned} \quad (3.16)$$

The function $\rho(\bar{Q}, \bar{P})$ can be regarded as describing the distribution of the ensemble over a phase space with coordinates (\bar{Q}, \bar{P}) in a completely analogous fashion to the classical case. This is possible for the case of the harmonic oscillator since the specification that elements of the ensemble are in minimum-uncertainty states at time t_0 insures that this will be true for all subsequent times and then the values of the quantum means (\bar{Q}, \bar{P}) of an element at time t are sufficient to completely define its state.

4. QUANTUM DERIVATION OF RATE FORMULA

We next make use of the distribution function $\rho(\bar{Q}, \bar{P})$ to derive a quantum generalization of the rate formula of Eq. (2.19). The notation follows Sec. 2 as closely as possible with superposed bars employed to denote quantum means of the coordinates and momenta.

The previous assumptions regarding the topography of the potential-energy function W apply here as well. The discussion just prior to Eq. (2.8) is again relevant except that the observation of the state of all the defects at a given instant must now be interpreted from the quantum viewpoint; the best that can be done is to determine the state of each with minimum uncertainty and to measure the quantum means $\bar{Q}_\alpha, \bar{P}_\alpha$ in this state. The distribution function valid in the valley is then obtained by composition of that of Eq. (3.16).

$$\rho'(\mathbf{Q}, \mathbf{P}) = \mathcal{C}' \exp\left\{-\sum_{\alpha=1}^{3N} c_\alpha (2\hbar\omega_\alpha)^{-1} (\bar{P}_\alpha^2 + \omega_\alpha^2 \bar{Q}_\alpha^2)\right\}, \quad (4.1)$$

where

$$c_\alpha = \exp\frac{\hbar\omega_\alpha}{kT} - 1, \quad \mathcal{C}' = (2\pi\hbar)^{-3N} \prod_{\alpha=1}^{3N} c_\alpha.$$

Primes (ρ' and \mathcal{C}') are used in Eq. (4.1) *et seq.* to denote entities analogous to those without primes in the classical derivation of Sec. 2. When this notation is employed it also implies that the limits of the quantum entities as $\hbar \rightarrow 0$ are the corresponding classical entities.

We assume that the distribution ρ' applies up to and including the hyperplane \mathcal{O}_0 , i.e., that the states of the elements of the ensemble are sufficiently localized relative to the size of the transition region to the hill Hamiltonian beyond \mathcal{O}_0 so that the motion of the mean coordinates \bar{Q}, \bar{P} are not affected until after that plane is crossed. The distribution ρ' may be used therefore to determine the rate at which the mean values will cross \mathcal{O}_0 and to do so it is again convenient to convert from \mathbf{Q}, \mathbf{P} coordinates to \mathbf{q}, \mathbf{p} coordinates by means of Eq. (2.10). Then the mean values $\bar{\mathbf{q}}, \bar{\mathbf{p}}$ will be related to $\bar{\mathbf{Q}}, \bar{\mathbf{P}}$ by the same equations and ρ' assumes the form

$$\rho'(\bar{\mathbf{q}}, \bar{\mathbf{p}}) = \mathcal{C}' \exp\left\{-\sum_{\alpha,\beta=1}^{3N} (B_{\alpha\beta}' \bar{p}_\alpha \bar{p}_\beta + C_{\alpha\beta}' \bar{q}_\alpha \bar{q}_\beta)\right\}, \quad (4.2)$$

where

$$B_{\alpha\beta}' = \frac{1}{2\hbar} \sum_{\delta=1}^{3N} c_\delta \omega_\delta^{-1} A_{\delta\alpha} A_{\delta\beta}, \quad (4.3)$$

$$C_{\alpha\beta}' = \frac{1}{2\hbar} \sum_{\delta=1}^{3N} c_\delta \omega_\delta A_{\delta\alpha} A_{\delta\beta}. \quad (4.4)$$

The rate f' at which elements of the ensemble will cross \mathcal{O}_1 and go on to the next valley may be written as

$$f' = \int_0^\infty \bar{p}_1 d\bar{p}_1 \int_{\bar{\Omega}_0} K(\bar{\mathbf{q}}, \bar{\mathbf{p}}) \rho'(\bar{\mathbf{q}}, \bar{\mathbf{p}}) \prod_{\alpha=2}^{3N} d\bar{q}_\alpha d\bar{p}_\alpha, \quad (4.5)$$

where $\bar{\Omega}_0$ is the subspace, $\bar{q}_1 = \eta$, $-\infty < \bar{q}_\alpha < \infty$, $-\infty < \bar{p}_\alpha < \infty$, $\alpha = 2, \dots, 3N$. Equation (4.5) may be interpreted as integrating over the rates at which a system arrives at \mathcal{O}_0 with mean values $(\bar{\mathbf{q}}, \bar{\mathbf{p}})$ (and therefore, under our assumptions, with known wave-packet characteristics) multiplied by the transmission coefficient $K(\bar{\mathbf{q}}, \bar{\mathbf{p}})$ or probability that it will go on to the next valley. This quantum aspect of the process, tunnelling, could be included readily in the above framework if it could be assumed that $K(\bar{\mathbf{q}}, \bar{\mathbf{p}}) = K(\bar{p}_1)$. However, this question requires further investigation and here we use for $K(\bar{\mathbf{q}}, \bar{\mathbf{p}})$ its classical limit

$$\lim_{\hbar \rightarrow 0} K(\bar{\mathbf{q}}, \bar{\mathbf{p}}) = U(\bar{p}_1 - \mu), \quad (4.6)$$

where $U(x)$ is the unit step function previously introduced. Then the preceding classical derivation, Eqs. (2.12)–(2.19), applies here as well with the quantities

\mathcal{C} , \mathbf{B} , and \mathbf{C} replaced by \mathcal{C}' , \mathbf{B}' , and \mathbf{C}' . The relevant values of Eq. (2.18) are

$$|B'| = (2\hbar)^{-3N} \prod_{\alpha=1}^{3N} c_{\alpha} \omega_{\alpha}^{-1}, \quad |C'| = (2\hbar)^{-3N} \prod_{\alpha=1}^{3N} c_{\alpha} \omega_{\alpha},$$

$$R_{B'}^2 = 2\hbar \sum_{\delta=1}^{3N} c_{\delta}^{-1} \omega_{\delta} (A_{\delta 1})^2, \quad (4.7)$$

$$R_{C'}^2 = 2\hbar \sum_{\delta=1}^{3N} (c_{\delta} \omega_{\delta})^{-1} (A_{\delta 1})^2.$$

The resulting frequency f' is

$$f' = \frac{\omega_e'}{2\pi} \exp \left[- \left(\frac{\mu^2}{R_{B'}^2} + \frac{\eta^2}{R_{C'}^2} \right) \right], \quad (4.8)$$

where $\omega_e' = R_{B'} R_{C'}^{-1}$.

5. LOW-TEMPERATURE LIMIT IN DEBYE APPROXIMATION

We have considered the high-temperature limit, Eq. (2.19), of the quantum frequency formula, Eq. (4.8), in Sec. 2. It is clear that a detailed analysis of its low-temperature predictions would be tied in with details of the phonon dispersion relations for a given crystal and of the nature of the unstable localized mode associated with motion over the saddle point. In this section we estimate the nature of the low-temperature behavior on the basis of the simplest possible assumptions.

We treat the case of an atom in a simple Bravais lattice which moves into an adjacent vacancy. The atom positions are denoted by integer triples $(l_1, l_2, l_3) = \mathbf{l}$ in the usual manner, with $\mathbf{l} = \mathbf{0}$ denoting the migrating atom. The unstable mode \mathbf{a}_1^U is taken to be as localized as possible, namely,

$$\mathbf{a}_1^U = v \delta_{\mathbf{l}, \mathbf{0}}, \quad (5.1)$$

where $(v_1, v_2, v_3) = \mathbf{v}$ is a unit vector in the jump direction.

The modes \mathbf{a}_{α}^S of the perfect lattice are considered next.¹⁹ A Debye model is assumed, that is, these modes are identified with those in an isotropic elastic continuum. A portion of the lattice, a cube with center at $\mathbf{l} = \mathbf{0}$ containing N atoms, with periodic boundary conditions is considered. The allowed wave vectors \mathbf{q}_{α} , $\alpha = 1, \dots, N$ are then taken as uniformly distributed in the Debye sphere of radius \mathcal{D} . For each value of \mathbf{q} , we may choose two polarization vectors orthogonal to \mathbf{v} and one equal to \mathbf{v} . The latter modes may be written in the form

$$\mathcal{C}' v \begin{pmatrix} \cos \\ \sin \end{pmatrix} q_{\alpha 1} l_1 \begin{pmatrix} \cos \\ \sin \end{pmatrix} q_{\alpha 2} l_2 \begin{pmatrix} \cos \\ \sin \end{pmatrix} q_{\alpha 3} l_3, \quad (5.2)$$

with \mathbf{q}_{α} , $\alpha = 1, \dots, \frac{1}{3}N$ those in the first octant \mathcal{D}_1 of the

¹⁹ Actually \mathbf{a}_{α}^S should be taken as the modes of the lattice including the vacancy. We make this approximation here since at low temperatures only long-wavelength modes will be effective and these are little affected by the vacancy.

Debye sphere, where \mathcal{C}' is a normalization constant. Therefore,

$$A_{\alpha 1} = \mathbf{a}_{\alpha}^S \cdot \mathbf{a}_1^U = \mathcal{C}' \text{ or } 0 \quad (5.3)$$

depending on whether \mathbf{a}_{α}^S is nonzero or zero at $\mathbf{l} = \mathbf{0}$. Since \mathbf{a}_1^U is a unit vector and the \mathbf{a}_{α}^S are orthonormal, we have the relation

$$\sum_{\alpha=1}^{3N} A_{\alpha 1}^2 = \sum'_{\alpha} A_{\alpha 1}^2 = 1, \quad (5.4)$$

where in the second sum all zero values of $A_{\alpha 1}^2$ are omitted so that it can be regarded as a sum over constant quantities. The latter sum can be replaced therefore by an integral over \mathcal{D}_1 of a constant function $F(\mathbf{q}) = F$ so that

$$F = (\rho^3 \mathcal{U}_1)^{-1}, \quad (5.5)$$

where ρ is the (constant) density of nonzero values of $A_{\alpha 1}$ in the sphere and $\mathcal{U}_1 = \frac{1}{8} \pi \mathcal{D}^3$ is one-eighth the volume of the Debye sphere. We may now express $R_{B'}^2$ and $R_{C'}^2$ in Eqs. (4.7) as integrals over \mathcal{D}_1 :

$$R_{B'}^2 = 2\hbar \rho \int_{\mathcal{D}_1} \frac{\omega(\mathbf{q}) F dq_1 dq_2 dq_3}{c(\mathbf{q})} = \frac{2\hbar}{\mathcal{U}} \int_{\mathcal{D}_1} \frac{\omega(\mathbf{q}) dq_1 dq_2 dq_3}{c(\mathbf{q})}, \quad (5.6)$$

$$R_{C'}^2 = 2\hbar \rho \int_{\mathcal{D}_1} \frac{F dq_1 dq_2 dq_3}{\omega(\mathbf{q}) c(\mathbf{q})} = \frac{2\hbar}{\mathcal{U}_1} \int_{\mathcal{D}_1} \frac{dq_1 dq_2 dq_3}{\omega(\mathbf{q}) c(\mathbf{q})}.$$

In the Debye model, $\omega(\mathbf{q}) = C\mathbf{q}$. The integrals may be evaluated in spherical coordinates in the usual manner. The final results are

$$R_{B'}^2 = 6 \left(\frac{T}{\Theta} \right)^3 kT \int_0^{\Theta/T} \frac{z^3 dz}{e^z - 1}, \quad (5.7)$$

$$R_{C'}^2 = \frac{6\hbar^2}{k\theta} \left(\frac{T}{\Theta} \right)^2 \int_0^{\Theta/T} \frac{z dz}{e^z - 1},$$

where the Debye temperature $\Theta = \hbar C \mathcal{D} k^{-1}$.

At low temperatures, $T \ll \Theta$, the upper limit of the integral may be taken as infinite. The corresponding approximations for Eqs. (5.7) are

$$R_{B'}^2 \approx \frac{2}{3} \pi^4 k \Theta^{-3} T^4, \quad (5.8)$$

$$R_{C'}^2 \approx \pi^2 \hbar^2 k^{-1} \Theta^{-3} T^2.$$

The corresponding approximate frequency factor ω_e' of Eq. (4.8) is then

$$\omega_e' \approx \left(\frac{2}{3} \right)^{1/2} \pi k \hbar^{-1} T.$$

Also, if we recall that μ represents the momentum required to surmount the hill classically, it appears from Eqs. (4.8) and (5.8) that it is this part of the process which is rate controlling at low temperatures rather than η which is a measure of the energy required to reach the hill. These equations also indicate that the apparent activation energy of the process becomes

infinite as $T \rightarrow 0$. This reemphasizes the need to consider the tunnelling process at very low temperatures.

6. CONCLUSIONS

The principal purpose of this paper has been the derivation of a rate formula for defect motion in solids based on equilibrium quantum statistics. This was done by making use of an interpretation of the canonical density matrix for a harmonic oscillator as an ensemble of oscillators which are in minimum-uncertainty states. This interpretation leads to a probability distribution function defined on a phase space of quantum means of coordinates and momenta and bears a close resemblance to the classical picture.

The classical limit of the derived quantum rate formula has a frequency factor which does not agree with

that of Vineyard. The difference is due to the assumptions regarding mode interaction on the hill of the potential surface. Vineyard's derivation² assumes sufficient interaction to maintain equilibrium there; the present derivation assumes no interaction. This may have some relevance for observed anomalous isotope effects (see Le Claire⁵ and Glyde¹), but this question has not been examined here.

The low-temperature behavior of the quantum rate formula has been examined for a Debye model. The analysis indicates that the frequency factor $\omega_e' \sim T$ for $T \ll \Theta$, with Θ the Debye temperature and that the apparent activation energy of the process becomes infinite as $T \rightarrow 0$. Tunnelling has not been included in the present derivation but it appears that it should be possible to do so within the same framework.

Electrical Conduction in *n*-Type Cadmium Sulfide at Low Temperatures*

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(Received 12 April 1967; revised manuscript received 13 September 1967)

Measurements of the Hall mobility and electrical conductivity of *n*-type CdS were made between 1.8 and 294°K. Both Ohmic and non-Ohmic regions were studied at low temperatures. In these undoped crystals, a donor level of 0.021 eV, believed due to excess Cd, was found. Below 22°K, charge transport by impurity conduction was observed. The electric field dependence of the conduction-band mobility was found to be caused by hot-electron effects and the acoustoelectric effect. Good agreement between hot-electron theory and experiment was obtained when ionized-impurity as well as acoustic-phonon scattering were included in the theory. To obtain satisfactory agreement between theory and experiment, electron-phonon interactions via deformation and piezoelectric potentials were included. In the impurity-conduction region, variations of the Hall mobility with electric field were shown to be caused by the hot-electron behavior of the conduction-band electrons.

I. INTRODUCTION

SEVERAL investigators¹⁻⁸ have made Hall-effect measurements on *n*-type CdS at low temperatures. Their results¹⁻⁶ indicate that with decreasing tempera-

ture, the mobility increases, reaches a maximum in the neighborhood of 30°K, and then decreases rapidly. The Hall constant increases with decreasing temperature until the temperature of the mobility maximum is reached. At lower temperatures the Hall constant saturates or decreases with decreasing temperature. The rapid decrease in mobility has been interpreted as being due to either ionized-impurity scattering or impurity conduction.⁹

Measurements of the Hall effect at high electric fields⁸ have shown the existence of the acoustoelectric effect which limits the drift velocity of the electrons to the sound velocity. Thus, hot-electron effects¹⁰ are not observable. Measurements of the electric field dependence of the electrical conductivity at low temperatures

* Research reported in this paper was sponsored by the U. S. Army Research Office (Durham) under Contract No. DA31-124-ARO(D)-84 and the U. S. Army Engineer Research and Development Laboratories under Contract No. DA44-009-AMC-1276(T).

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