London A251, 427 (1959).

[18]It might be argued that prescribing a c-number driving field is inconsistent with a quantum-mechanical treatment of the field and its interaction with the NO. It should be understood, however, that such a prescription merely indicates that the *source* of the driving field is undisturbed by the behavior of the NO, as discussed in detail in several earlier papers on quantum optics: I. R. Senitzky, Phys. Rev. Letters 15, 233 (1965); 16, 619 (1966); Phys. Rev. 155, 1387 (1967). The reaction of the NO on the field is fully taken into account through the coupling of the NO to all the modes, which are referred to as the radiation field, with the word "radiation" sometimes omitted when no ambiguity is possible.

[19]The expression for α thus obtained consists of the uncoupled field (which is α_0) and the reaction of the field due to the presence of the NO. If one regards the field as a loss mechanism or a thermal reservoir, it is easily seen that this derivation is similar, in principle, to that for a more general dissipation mechanism treated in Ref. 3, and also in two later papers: I. R. Senitzky, Phys. Rev. 137, A1635 (1965), Sec. II A; 155, 1387 (1967), Sec. I. The present analysis differs from that of Dillard and Robl (Ref. 8) by the presence of the constant α_2, and also terms which are dropped in the rotating-wave approximation used by them. (This accounts for the fact that they obtain no frequency shift.) $\alpha_1 L_-$ may be regarded as a purely resistive, or dissipative, effect of the field of the NO, while $i\,\alpha_2 L_-$ may be regarded (in the language of circuit theory) as a reactive effect. The expressions for α_1 and α_2 illustrate the fact that the dissipation is mainly a resonant phenomenon, due to the coupling to modes of approximately the same frequency, while the frequency shift is mainly a nonresonant phenomenon, due to the coupling to modes of significantly different frequency.

[20]It is to be noticed that the frequency shift can be written as $m\tilde{\alpha} - \alpha'$, where $\tilde{\alpha}$ and α' are defined by Eqs. (37d) and (74d), respectively. As mentioned in connection with these equations, the frequency shift is determined mainly by terms that are discarded in the use of the rotating-wave approximation. It is found by G. S. Agarwal [Phys. Rev. A 4, 1778 (1971)], who used essentially a Schrödinger-picture description of the system, that the rotating-wave approximation affects the solution significantly only if the initial state of the NO has a well-defined phase. The physical reason for this effect becomes obvious in light of the present discussion. Oscillators with slightly different frequencies will be in much different "states" after a number of cycles if the "states" describe the instantaneous values of the oscillating coordinates, that is, if they describe the phase of the oscillation.

[21]The above expressions for $\langle L_3 \rangle$ are equivalent to those of Dillard and Robl, Ref. 7, who derive, essentially, $\langle L_3 \rangle$ for $n = 2-5$, 9. Their method may appear more complicated because they do not take explicit advantage of the fact that L^2 is a constant of motion.

[22]I. R. Senitzky, Phys. Rev. Letters 19, 1062 (1968).

[23]The amplitude of oscillation of the NO for $\langle L_3 \rangle$ in the neighborhoods of $\pm L_0$ is very small, of course, but—on the one hand—these neighborhoods become relatively smaller as L_0 increases, and—on the other—they are passed through more quickly as the driving field increases.

[24]Leon Kotin (unpublished).

[25]The classical equation for the strong-driving-field case may be recovered by setting these quantities equal to zero, differentiating both sides, and noting that $-\alpha\Omega^2 \int_0^t dt_1 L_3(t_1)$ is equal to $\alpha \dot{L}_3$ up to order α.

[26]I. R. Senitzky, Phys. Rev. 134, A816 (1964).

[27]See, for instance, W. Hurewicz, *Lectures on Ordinary Differential Equations* (Wiley, New York, 1958).

Quantum Theory of Diffusion with Application to Solid Helium

Allan Widom* and M. G. Richards
School of Mathematical and Physical Sciences,
University of Sussex, Brighton, Sussex, England
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A quantum theory of diffusion is presented and applied to the diffusion of isotopic impurities in solid helium. For temperatures much less than the Debye temperature Θ and much more than the impurity exchange temperature $\hbar J/k_B$, it is shown that the diffusivity is given by $D = (Ja^4/\sigma^* x)$. The effective cross section σ^* for the scattering of two mobile impurity atoms is of the order of a square lattice spacing a^2, and the mole fraction x of the impurity atoms is assumed to obey $(\hbar J/k_B\Theta)(T/\Theta)^7 \ll x \ll 1$. Observation of the concentration dependence $D \propto 1/x$ would constitute strong evidence of quantum mobility, which has been of considerable theoretical interest in recent years.

I. INTRODUCTION

In the limit of low temperatures, where thermally activated diffusion is virtually zero, the conventional picture of a crystalline solid is one of atoms immobile on equilibrium lattice sites.

This picture cannot be precisely correct. For low concentrations of impurity atoms a simple counting argument shows that a macroscopic degeneracy would exist at zero temperature leading to an entropy of solid solution in violation of the third law of thermodynamics.[1] This apparent

macroscopic ground-state degeneracy is split by (i) static lattice forces due to zero-point phonon oscillations which lead to phase separation of the impurities or, at the very least, strong statistical correlations in the positions of the impurity atoms, and (ii) quantum mobility,[2] i.e., a quantum process by which substitutional (interstitial) impurity atoms exchange (tunnel) onto a neighboring lattice site. From the viewpoint of the third law of thermodynamics, quantum mobility is of prime importance in reducing impurity configuration entropy and in preventing a disordered metastability.

Quantum solids (e. g., helium) with relatively large zero-point phonon oscillations should exhibit prominent quantum mobility.[3] This is apparent by the ease with which isotopic impurity atoms phase separate in crystalline helium.

Here we examine the diffusivity of isotopic impurities in solid helium. Let J be the exchange frequency of the impurity, Θ the Debye temperature of the host crystal, and a the lattice spacing. In the concentration (i.e., mole fraction) range

$$(\hbar J/k_B \Theta)(T/\Theta)^7 \ll x \ll 1 \tag{1}$$

and temperature range

$$(\hbar J/k_B) \ll T \ll \Theta, \tag{2}$$

we show that the diffusivity is given by

$$D = (Ja^4/\sigma^* x), \tag{3}$$

where σ^* is an effective cross section for the scattering of two quantum mobile impurities. For isotopic impurities with short range host crystal distortions σ^* will be of order a^2.

Observation of the concentration dependence $D \propto 1/x$ confirms the general picture of quantum mobility as well as measures the exchange- (or tunneling-) energy bandwidths $\propto \hbar J$.

II. QUANTUM DIFFUSION

Let us imagine that the wave functions for a crystal with an impurity localized at site $\vec{l}$ are known. Let n represent the quantum numbers which describe the phonon oscillations of the crystal. Then we have

$$|n\vec{l}\rangle = \text{(localized impurity wave functions)}, \tag{4a}$$

$$E_n(\vec{l}) = \text{(localized impurity energy levels degenerate with respect to } \vec{l}). \tag{4b}$$

We further suppose that overlap integrals have been taken into account to the extent that $|n\vec{l}\rangle$ are orthonormal wave functions,

$$\langle n_f \vec{l}_f | n_i \vec{l}_i \rangle = \delta_{fi}. \tag{5}$$

Since the localized wave functions $|n\vec{l}\rangle$ are not quite eigenfunctions of the true Hamiltonian H, there will be small transition-matrix elements

$$V_{fi} = \langle n_f \vec{l}_f | (H - E_i) | n_i \vec{l}_i \rangle, \tag{6}$$

leading to diffusion. The transition rate between initial and final quasiequilibrium lattice sites is given by Fermi's Golden Rule,

$$W(\vec{l}_f - \vec{l}_i) = \sum_{n_f} \sum_{n_i} p_i \left(\frac{2\pi}{\hbar}\right) |V_{fi}|^2 \delta(E_f - E_i), \tag{7}$$

where the initial phonon states have been thermally averaged and the final phonon states have been summed.

The diffusivity is now given by[4]

$$D = \frac{1}{6} \frac{\langle \vec{\Delta}^2 \rangle}{\tau_d} = \frac{1}{6} \sum_{\vec{\Delta}} W(\vec{\Delta}) \vec{\Delta}^2. \tag{8}$$

Equations (7) and (8) imply

$$D = \frac{\pi}{3\hbar} \sum_{if} p_i |\vec{l}_f - \vec{l}_i|^2 |V_{fi}|^2 \delta(E_f - E_i). \tag{9}$$

In order to write Eq. (9) in a more conventional form, we defined a lattice position operator by

$$l_{op} |n\vec{l}\rangle = \vec{l} |n\vec{l}\rangle \tag{10}$$

and a diffusional velocity operator by

$$\vec{v} = (i/\hbar)[H, \vec{l}_{op}]. \tag{11}$$

Equations (6), (10), and (11) imply

$$|\vec{l}_f - \vec{l}_i|^2 |V_{fi}|^2 = \hbar^2 |\langle n_f \vec{l}_f | \vec{v} | n_i \vec{l}_i \rangle|^2; \tag{12}$$

hence

$$D = \frac{1}{3} \pi \hbar \sum_{if} p_i |\langle f | \vec{v} | i \rangle|^2 \delta(E_f - E_i). \tag{13}$$

Equation (13) is a Kubo formula,[5]

$$D = \frac{1}{3} \text{Re} \int_0^\infty \langle \vec{v}(t) \cdot \vec{v}(0) \rangle dt, \tag{14}$$

in a not-too-disguised form. At first sight it would appear that Eq. (14) is well known. However, $\vec{v}$ defined in Eqs. (10) and (11) is not the usual velocity operator $-i\hbar\vec{\nabla}/m$. The point is that the impurity oscillations, which contribute to the finite frequency power spectrum of velocity fluctuations, are not relevant to diffusion which is a measure of the zero-frequency part of the power spectrum.

III. QUANTUM MOBILITY

The theory in Sec. II can be improved for the purposes of this paper by taking into account, from the start, that the degeneracy of the levels $E_n(\vec{l})$ with respect to $\vec{l}$ is split by the exchange (or tunneling) process into energy bands $E_n(\vec{k})$. Equation (4) should now read[2]

$$|n\vec{k}\rangle = \text{(mobile impurity wave function)}, \tag{15a}$$

$$E_n(\vec{k}) = \text{(mobile impurity energy band)}. \tag{15b}$$

The localized and mobile wave functions are connected by the Bloch expansions

$$|n\vec{k}\rangle = (1\sqrt{N}) \sum_{\vec{l}} e^{i\vec{k}\cdot\vec{l}} |n\vec{l}\rangle ,$$ (16)

which preserve orthogonality [Eq. (5)],

$$\langle n_f \vec{k}_f | n_i \vec{k}_i \rangle = \delta_{fi} .$$ (17)

It is not diffucult to prove the group-velocity formula

$$\langle n\vec{k}| \vec{v} | \Psi \rangle \simeq \frac{1}{\hbar} \frac{\partial E_n(\vec{k})}{\partial \vec{k}} \langle n\vec{k}| \Psi \rangle ,$$ (18)

given that $|n\vec{k}\rangle$ are approximate eigenstates of the true Hamiltonian H. Equation (14) now reads

$$D = \frac{1}{3\hbar^2} \sum_{n\vec{k}} e^{[F - E_n(\vec{k})]/k_B T} \left| \frac{\partial E_n(\vec{k})}{\partial \vec{k}} \right|^2$$
$$\times \mathrm{Re} \int_0^\infty \langle n\vec{k}| \exp\left(-\frac{it}{\hbar} [H - E_n(\vec{k})] \right) |n\vec{k}\rangle dt .$$ (19)

The integrand on the right-hand side of Eq. (19) represents the decay amplitude of the mobile state $|n\vec{k}\rangle$; hence the integral represents the lifetime of the state $|n\vec{k}\rangle$.

Our final result for the diffusivity can be written in the compact form

$$D = \frac{1}{3\hbar^2} \left\langle \left| \frac{\partial E}{\partial \vec{k}} \right|^2 \tau_{\vec{k}} \right\rangle .$$ (20)

In order to calculate D one needs to compute the energy bands and the lifetimes of the mobile impurity atoms.

IV. MOBILE-STATE LIFETIMES

In the temperature range of Eq. (2) the impurities should move as a Boltzmann "gas" of particles in a quantum mobile band $E(\vec{k})$. The impurity lifetimes are due to (i) scattering off phonons, and (ii) scattering off each other. Hence we write

$$\tau_k^{-1} = (\tau_k^{ph})^{-1} + (\tau_k^{imp})^{-1} .$$ (21)

Let $\langle \vec{k}\vec{Q}\lambda | t_{ph} | f \rangle$ be the scattering matrix element for an impurity in state $\vec{k}$ and a thermally excited phonon in state $\vec{Q}\lambda$ to be scattered into a final state f; then

$$(\tau_k^{ph})^{-1} = \frac{2\pi}{\hbar} \sum_{\vec{Q}\lambda} \bar{n}_{\vec{Q}\lambda} \sum_f |\langle \vec{k}\vec{Q}\lambda | t_{ph} | f \rangle|^2$$
$$\times \delta(E(k) + \hbar\omega_{\vec{Q}\lambda} - E_f) .$$ (22)

Using the optical theorem (unitarity), Eq. (22) reads

$$(\tau_k^{ph})^{-1} = \frac{2}{\hbar} \sum_{\vec{Q}\lambda} \bar{n}_{\vec{Q}\lambda} \mathrm{Im} \langle \vec{k}\vec{Q}\lambda | t_{ph} | \vec{k}\vec{Q}\lambda \rangle .$$ (23)

The imaginary part of the forward scattering am-

plitude is proportional to the total cross section. For phonons scattering off point defects this is well known[6] to obey

$$\mathrm{Im} \langle \vec{k}\vec{Q}\lambda | t_{ph} | \vec{k}\vec{Q}\lambda \rangle \propto Q^4 \quad \text{as} \quad Q \to 0 .$$ (24)

Thermally averaging over initial phonon occupation numbers

$$\bar{n}_{Q\lambda} = [\exp(\hbar\omega_{Q\lambda}/k_B T) - 1]^{-1}$$ (25)

leads to

$$[\tau_k^{ph}]^{-1} \propto J(T/\Theta)^7, \quad T \ll \Theta .$$ (26)

The lifetime due to scattering off other impurities is calculated in a similar manner:

$$[\tau_k^{imp}]^{-1} = \frac{2\pi}{\hbar} \sum_{\vec{k}'f} \bar{n}_{\vec{k}'} \cdot |\langle \vec{k}\vec{k}' | t_i | f \rangle|^2$$
$$\times \delta(E(\vec{k}) + E(\vec{k}') - E_f) ,$$ (27)

where possible spin indices have not been included to avoid a certain amount of algebraic ceremony. The optical theorem implies

$$(\tau_k^{imp})^{-1} = \frac{2}{\hbar} \sum_{\vec{k}'} \bar{n}_{\vec{k}'} \cdot \mathrm{Im} \langle \vec{k}\vec{k}' | t_i | \vec{k}\vec{k}' \rangle .$$ (28)

In the temperature range of Eq. (2), $\bar{n}_k$ is approximately constant and proportional to x. In the concentration range of Eq. (1) the phonon-induced lifetime [Eq. (26)] is large compared to the impurity-induced lifetime [Eq. (28)]. We then write [Eq. (20)]

$$D = \frac{1}{3\hbar^2} \left\langle \left| \frac{\partial E}{\partial \vec{k}} \right|^2 [\tau_k^{imp}] \right\rangle = Ja^4/\sigma^* x ,$$ (29)

where we define the exchange frequency J via

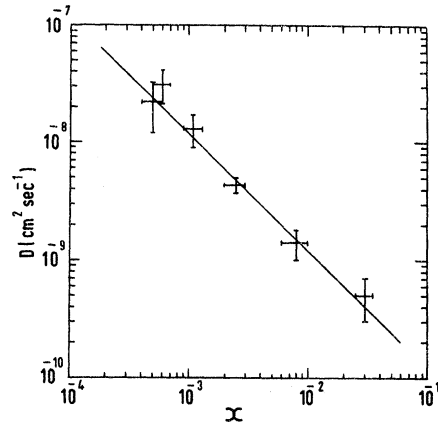FIG. 1. Spin diffusion coefficient D of ^{3}He impurity in solid ^{4}He vs x, the mole fraction of ^{3}He. The temperature of the sample is 0.53 K and the molar volume 21 cm^3. The Larmor frequency is 5 MHz. The data points are from Richards et al. (Ref. 7), and the solid line represents $Dx = 1.2 \times 10^{-11}$ cm^2 sec^{-1}.

$$\left\langle \left| \frac{\partial E}{\partial \vec{k}} \right|^2 \right\rangle = z\hbar^2 J^2 a^2 , \qquad T \gg \hbar \; J/k_B \tag{30}$$

as a measure of the mobility band thickness, and σ^* as an appropriately averaged total cross section for the scattering of two mobile impurities.

V. CONCLUSION

We may estimate the range of validity of Eq. (29) by taking[3] in Eq. (1) $J \sim 10^7$ sec^{-1} (the value for ^{3}He-^{3}He tunneling in pure ^{3}He of the same lattice spacing) and $\Theta = 30$ K. This leads to the condition 10^{-16} T^7 $\ll x \ll 1$, which is easily satisfied for, say, $T \sim 1$ K and $x \sim 10^{-2}$. If the dependence $D \propto 1/x$ is observed,

then strong evidence for the above theory would be available.

In Fig. 1 we show some recent data[7] for spin diffusion in dilute solutions of ^{3}He impurities in solid ^{4}He. Without the concept of quantum mobility or "gaslike" behavior for the impurity subsystem, it would be very difficult to explain the observed concentration dependence of D.

Further information on impurity motion is obtainable from NMR relaxation times T_1 and T_2. Theoretical calculations of the dipole field fluctuations necessary to explain NMR relaxation are quite subtle. They are presently being carried out and will be reported elsewhere.

*Permanent address: Physics Department, Northeastern University, Boston, Mass.

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Stimulated Thermal Scattering of Picosecond Laser Pulses*

S. S. Rangnekar and R. H. Enns

Department of Physics, Simon Fraser University, Burnaby 2, British Columbia, Canada

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A theoretical calculation of the stimulated thermal scattering of picosecond laser pulses by common liquids is presented. The calculation is made for the experimental configuration of Mack. The behavior of the first-order diffraction spots is studied in detail by varying liquid and laser parameters. A comparison with Mack's observations is made.

I. INTRODUCTION

In this paper we present a theory of the stimulated thermal scattering of picosecond laser pulses for the experimental configuration of Mack.[1,2] In Mack's experiment a train of picosecond laser pulses derived from a mode-locked ruby laser is sent through a beam splitter creating two beams, one much weaker than the other. The two beams are then sent through a colored liquid at a small angle to each other. The transmitted beams are then studied either photographically or electronically. In addition to the two original beams, additional beams are generated in the colored liquid. This is because the mechanism of thermal deposition creates a diffraction grating in the region where the original two beams overlap. Shortly thereafter, Scarlet[3] performed a similar experiment using two beams of equal in-

tensity. In his experiment he pointed out the different behavior of the scattered beams depending upon whether saturable or nonsaturable dyes were used to color the host liquid.

Theoretically, we shall restrict ourselves here to Mack's type of experiment involving nonsaturable dyes and incident weak and strong beams. Experimentally, of course, it is just as easy to create two beams of equal intensity. The theoretical problem is much more difficult to solve, however, because one can no longer neglect depletion of the strong beam by the other beams. Although Mack himself gave a brief theoretical discussion of his experimental results he did not actually carry out any quantitative calculation following the development of the fields, initial plus scattered, through the pulse train. A systematic quantitative comparison of theory and experiment was not made. The first attempt to carry out a