

Quantum Diffusion in Solid Helium*

by

André Landesman

Commissariat à L'Energie Atomique
Service de Physique
du Solide et de Résonance Magnétique
Orme des Merisiers
France - 91190 GIF SUR YVETTE

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I. Introduction

We are interested in the motion of a particle in a solid such that: i) its probability density obeys a diffusion equation, and ii) the transfer from site to site is not a thermally activated jump over some barrier but rather a quantum tunneling through that barrier. We shall call such a motion "quantum diffusion". Examples of it in solid helium will be shown. Obviously helium is a good atom for such studies because of its mass. Other particles convenient for quantum diffusion studies include positive muon in an iron or aluminum lattice and solid mixtures of

hydrogen species.

A few facts about solid helium are as follows. Helium behaves quantum mechanically from the point of view of energetics and statistics. The first one is more important. As shown in Figure 1, at moderate pressures, a liquid phase of helium exists to $T = 0$ K. The very existence of a liquid at 0 K is a macroscopic quantum effect. The quantum nature of this system is also demonstrated in the cohesive energy per atom, E_0 , which is well known from experimental thermodynamics. We can write E_0 as the sum of the averages of the kinetic energy (KE) and of the potential energy (PE),

$$E_0 = KE + PE \quad (1)$$

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A very rough evaluation of the kinetic energy of helium in terms of Debye

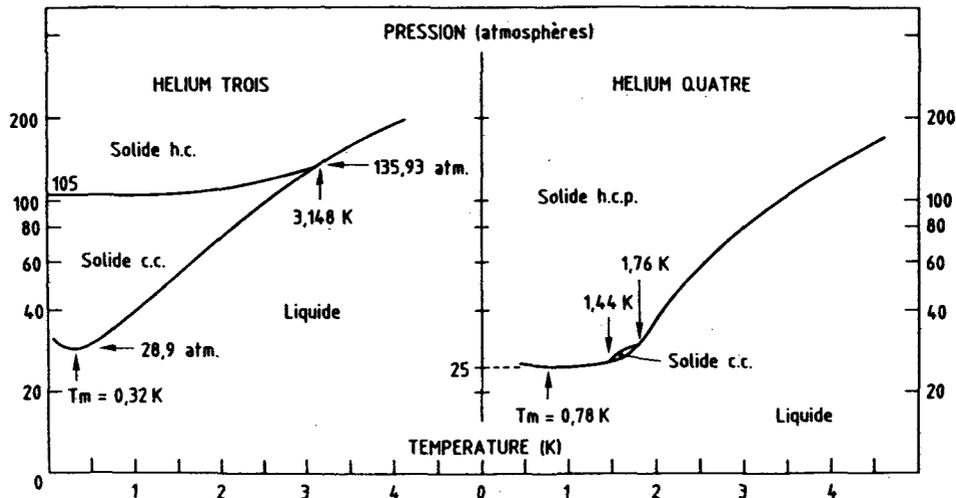


Figure 1. The pressure temperature phase diagram for both isotopes of helium.

temperature θ_D in a system of units where $k_B = 1$ is:

$$KE \sim (9/16) \theta_D . \quad (2)$$

We proceed to evaluate the potential energy for three rare gases, as shown on Table 1, by relating it to E_0 and θ_D . The kinetic energy of helium is comparable to $|PE|$ while for a classical system such as Xe, the kinetic energy is much smaller than the potential energy (in absolute value).

It is also instructive to evaluate the root mean square deviation δ of an atom, again in the Debye approximation (which is a very crude approximation for helium). As is seen in Table 1, this deviation is about ten times as large in helium than in the "extreme classical" rare gas xenon.

Solid helium thus appears as a system with very large zero point motions. Not surprisingly atoms which are as badly localized as they are in helium

are very likely to tunnel. In pure ^3He the Fermi statistics of the atoms, which leads to the effective exchange Hamiltonian necessary to describe the very low temperature magnetic properties of pure solid ^3He has to be considered also (1,2,3). Presently we are only interested in tunneling of dilute point defects. These are either the vacancies in pure ^3He or the isotopic substitutional impurities of ^3He in ^4He - ^3He mixtures. The statistics are not going to play any role.

II. Vacancies in b.c.c. ^3He

In solid ^3He Schottky type defects of concentration x_V can be thermally excited. The experimental proof of their existence is obtained by X-ray diffraction on crystals held at constant volume (4). As a function of temperature T the variation Δa of the interatomic distance is related to the variation Δx_V of the concentration:

Table 1

Rare gas	Cohesive energy E_0	Kinetic energy $KE \approx \frac{9}{16} \theta_D$	Potential energy PE	Relative r.m.s. derivation $\frac{\delta}{a} = \frac{3}{2} \sqrt{\frac{\hbar}{m\Omega_D a^2}}$
$^3\text{He}(\text{bcc})$	-0.4	11	-11.4	31%
$^4\text{He}(\text{hcp})$	-5.6	15	-20.6	28%
Xe(fcc)	-1928	31	-1959	2.6%

All energies are in K per atom. Helium is considered at the minimum of the melting curve and lattice structure is given in parenthesis. The root mean square deviation δ is evaluated in the Debye approximation as a function of the atomic mass, the Debye frequency $\Omega_D = \theta_D/\hbar$ and the interatomic distance a .

$$\Delta a/a + (\lambda/3) \Delta x_V = 0 \quad (3)$$

This is a well known method for studying vacancies in metals (for example Al). Experiments (4) lead to vacancy concentrations at the melting temperature of the order of

$$x_V^{\text{melt}} \approx 5 \times 10^{-3} ,$$

for molar volumes V between 20.3 and 24.86 cm³. Although this concentration x_V^{melt} is comparable to the concentration at melting observed in some solids (sodium or potassium), it is still somewhat higher than a value compatible with the analysis of the specific heat experiments (5).

Generally speaking the equilibrium concentration of thermally excited vacancies is:

$$x_V = \exp(S_f - \Phi/T) . \quad (4)$$

In equation 4, Φ is the energy of formation and S_f is the entropy of formation. We assume S_f to be very small. Since the vibrational contribution to S_f is probably negligible (note that $T \ll \theta_D$), this is equivalent to assuming that the ground state of a vacancy in bcc ³He is non-degenerate. From X-ray data (4) Φ can be determined. S_f is less well known.

A. NMR Observation of Vacancies

NMR is sensitive to vacancies because they are mobile and lead to an effective jump frequency $1/\tau_r$ for ³He atoms:

$$1/\tau_r = x_V/\tau . \quad (5)$$

In equation 5 the quantity $1/\tau$ is some characteristic frequency for vacancy motion. With NMR, only τ_r can be measured. Several methods to be used in different ranges of temperature were developed (6):

i. the effective spin diffusion coefficient is

$$D = (1/6) a^2/\tau_r \quad (6)$$

whenever x_V is large enough. This coefficient is measured with the method of spin echoes in an applied magnetic field having a nonvanishing gradient.

ii. in the Zeeman-vacancy regime for relaxation by modulation of the dipole-dipole interactions (6,7), the relaxation time T_1 depends on the jump time τ_r . In the high field weak collision limit (Larmor frequency ω much larger than $1/\tau_r$) one has,

$$1/T_1 \approx (8/3) M_2/(\omega^2 \tau_r) , \quad (7)$$

M_2 being the NMR rigid lattice second moment. The temperature range for this mechanism is typically 0.8 to 2 K.

iii. at very low temperatures, spin relaxation is in an exchange-vacancy regime. The bottleneck for the flow of energy occurs between the exchange system and the vacancies, which are in good thermal contact with the phonons. In that "strong" collision regime the intrinsic exchange-lattice relaxation time is:

$$T_{EL} = 2(z-1)\tau_r/z , \quad (8)$$

In equation 8, the coordination number of the bcc lattice, z , equals 8. (This equation assumes the effective exchange Hamiltonian to be an Heisenberg transposition-only Hamiltonian, which is not the case (1,3). The use of a more realistic exchange Hamiltonian however would only lead to a slight variation of the proportionality factor between T_{EL} and τ_r .)

As discussed in reference (7), all the experiments lead to the conclusion that the jump frequency as studied by NMR follows some Arrhenius relation:

$$\tau_r^{-1} = \tau_0^{-1} \exp(-W/T) , \quad (9)$$

where the NMR activation energy W is fairly well determined for the molar volume $V < 23.05$ cm³. In fact for $V = 20$ cm³, where T_{EL} has been studied to 0.45 K (8), the activation energy W is

over approximately ten decades.

B. Various Channels for Vacancy Motion

What is the physical mechanism for vacancy motion and what information can be deduced from the jump time τ_f as measured by NMR? We review four possible mechanisms (or channels) for vacancy motion. In each case we ask ourselves: What is the vacancy characteristic frequency and what is the corresponding NMR activation energy W_{NMR} deduced from equations 4 and 5? One has:

$$W_{NMR} = d(\ln\tau_f)/d(1/T) \quad (10)$$

a) Classical diffusion: The motion of the vacancy is a thermally activated jump over a barrier of height Φ_m :

$$1/\tau = \omega_m \exp(-\Phi_m/T) \quad (11a)$$

$$W_{NMR} = \Phi + \Phi_m > \Phi \quad (12a)$$

b) "Incoherent" tunneling diffusion: The vacancy is coupled to a strain field and is somewhat similar to a small polaron. While the vacancy is hopping the phonon quantum numbers are changed (9,10). The corresponding rate is phonon-enhanced and has a temperature dependence given at very low temperatures by:

$$1/\tau \propto T^7 \quad (11b)$$

This channel may have been observed for protons in Ta or for positive muons in Cu. In our case, the corresponding NMR activation energy becomes temperature dependent:

$$W_{NMR} = \Phi + 7T > \Phi \quad (12b)$$

It should be remembered however that experimentally a power law with a high exponent is not always easy to distinguish from the Arrhenius law.

c) "Coherent" tunnel diffusion: If a tunneling particle propagates, while

colliding with phonons, in such a fashion that phonon quantum numbers are conserved in an elementary scattering, the characteristic frequency of the particle is phonon hindered (11,12) and given by

$$1/\tau \approx (\omega_v^2 / \Omega_D) \times (\theta_D/T)^9 \quad (11c)$$

Here ω_v is the tunneling frequency of the particle. Such a mechanism is observed for ^3He in ^4He - ^3He and probably for positive muons in iron or aluminum. The case of a tunneling vacancy in ^3He is special because of the disorder of the ^3He spins in the paramagnetic state (13); strictly speaking the wave vector is not a good quantum number for a vacancy which does not propagate. Collisions such as those described above lead to a diffusion which cannot be called coherent any more for a vacancy. If these collisions are frequent enough, its characteristic frequency is nevertheless given by equation 11c.

$$W_{NMR} = \Phi - 9T < \Phi \quad (12c)$$

d) Pure tunneling motion: The vacancy tunnels and its interaction with phonons is negligible. If it tunnels in ^4He , it forms a band of states, the wave vector being a good quantum number. The diffusion of a tunneling vacancy in ^4He is analogous to that of an electron in a metal: it is coherent and the diffusion constant D_v is equal to an average group velocity times a mean free path. If a vacancy tunnels in ^3He , because of the disorder of the spins (13), its diffusion is incoherent and the diffusion

$$D_v \approx \omega_v a^2.$$

As shown in reference (14) for ^3He spins a vacancy-induced spin diffusion constant D can be defined. By using the moment approximation to evaluate the hydrodynamic limit to the behavior of the spin-spin correlation function (14), it is found to be

$$D = (1/6) A \omega_v a^2 \chi_v,$$

where $A = 5.2$. By use of equation 6, the prefactor τ_0 in equation 9 is seen to be independent of temperature leading to

$$W_{\text{NMR}} = \Phi \quad (12d)$$

C. Discussion

In equations (12) the quantity on the left side is an NMR observable while the right-side quantity is the energy of formation obtained by X-ray scattering (4). The activation energies obtained in the two experiments are shown in Figure 2. The values are very close. It should be noted however that it is hard to evaluate the error of the X-ray data. In view of the observed agreement, the channel (d) model seems to be the most likely mechanism.

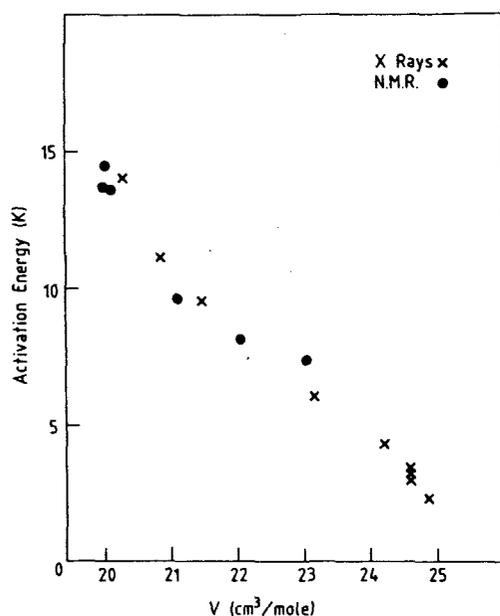


Figure 2. Vacancy activation energy as a function of molar volume; X-ray data are from reference (4) and NMR data are from reference (7).

We can then evaluate the tunneling

frequency by using the prefactor τ_0 . The result is

$$\hbar\omega_V = 40 \text{ mK}, \quad (13)$$

for $20 \text{ cm}^3 < V < 23.05 \text{ cm}^3$ (7). If a positive value for S_f were used, this figure would be an upper limit only for the tunneling frequency. If at the temperature of the NMR experiments, only the bottom state of the vacancy band were populated, the vacancy concentration would be effectively less than $\exp(-\Phi/T)$ and the estimate (13) would then become a lower limit.

It has to be pointed that the analysis (5) of the specific heat measurements leads to a tunneling frequency which is about ten times larger than the above estimate (13). At the present time it is not easy to explain the reason for this discrepancy. A more complete analysis of spin relaxation through narrow band vacancies is needed, as well as a thorough investigation of the effect of strain fields.

Note that the channel (a) seems to apply to a vacancy in the hcp ^3He , where the inequality equation 12a holds (7).

III. Isotopic impurities of ^3He in h.c.p. $^4\text{He} - ^3\text{He}$

Due to the zero-point motion discussed in the introduction, an isotopic impurity can exchange site with a host atom in a transposition. In fact, this exchange might well happen with two host atoms, in a three-body cyclic permutation, as argued in the case of an ortho impurity in the h.c.p. solid hydrogen (15). We do not have to discuss the microscopic physics of the impurity exchange since no qualitative effect is different for a permutation of a ^3He impurity with either one or two host atoms. It is assumed that a ^3He atom is transferred to a neighboring lattice site with a phenomenological tunneling frequency J ; J will be typically of the order of 10^{-5} K.

One isolated ^3He atom in the crystal propagates freely. Its eigenstates, analogous to the vacancy waves in ^4He ,

called impuritons (16,17), form a band of states with a width $16hJ$. The root mean square velocity of an impuriton over the band is

$$\bar{v} = \sqrt{12}Ja \quad (14)$$

Two ^3He atoms separated by a vector R_{jk} are two point defects, each one surrounded by a strain field. These two strain fields interact and this elastic interaction decreases asymptotically with R_{jk}^{-3} . In an infinite crystal the interaction is non vanishing if the sound velocity is anisotropic or if the local strain around one impurity is anisotropic. In our case, the asymptotic form for the interaction could be written as

$$E_{jk}^{33} = (a/R_{jk})^3 \{V_0(1-3\cos^2\zeta)/2+\dots\} \quad (15)$$

In equation 15, ζ is the angle between R_{jk} and the trigonal axis of the crystal and V_0 is an energy typically one thousand times larger than J .

A. The Impuriton Gas

In low concentration these impurities may be thought of as a gas, similar to the case of electrons in a metal.

1. Collision between Impurities.

The scattering of two narrow band particles through a potential, such as given by equation 15, is a difficult problem. A dimensionality argument (17) leads to a cross section,

$$\sigma = \pi b^2 \quad (16)$$

where b is some effective interaction radius related to the mean square value hU_0 of the anisotropic elastic interaction (15):

$$b = a(U_0/16J)^{1/3} \quad (17)$$

Note that equation 16 can be written as

$$\sigma \propto (\bar{v})^{-2/3} \quad ,$$

which agrees with the well known fact

that the cross section for collision of gaseous molecules having dipolar moments depends on $T^{-1/3}$.

The mean free path for impuritons is

$$l = (1/\sigma) a^3/x\sqrt{2} \quad ,$$

where x is the concentration of ^3He atoms. Kinetic theory leads to a diffusion constant for impurity atoms

$$D = (1/3)\bar{v}l = (1.65Ja^2/x)(J/U_0)^{2/3} \quad (18)$$

It should be noted that D is measurable by NMR (see Section II-A-i) and also that it can be much larger than Ja^2 . If D is much larger than Ja^2 , the diffusion is coherent, as opposed, for instance, to an incoherent ordinary spin diffusion.

If the impuritons are considered to form a gas, the density of this gas must be sufficiently low so that only two-particle collisions are occurring. In other words: $l \gg b$, which leads to

$$x \ll J/U_0 \quad (19)$$

In section III-C the situation of ^3He concentration larger than the limit set by equation 19 is considered.

2. Impuriton-phonon Scattering

At finite temperatures phonons are scattered off the impurities. This is why a pure crystal has a larger thermal conductivity than an impure one. The problem can be analyzed exactly (12), only the final result is given here. When impuritons collide with phonons more often than with other impuritons, the ^3He diffusion constant becomes:

$$D = 1.3 \times 10^{-4} (J^2 a^2 / S^2 \Omega_D) (\theta_D/T)^3 \quad (20)$$

where S is some coupling constant which can be deduced from the analysis of thermal conductivity measurements in $^4\text{He} - ^3\text{He}$. Equation 20 is essentially the same as the result of equation 11c; note, however, that we still have a coherent diffusion for ^3He atoms. Equation 20 was established by introducing a Kubo type memory function

which can be integrated exactly and is not based on a moment approximation.

B. The Experimental Behavior of the Diffusion Constant

When measured by the method of spin echoes in an inhomogeneous magnetic field, the diffusion constant D (for a given molar volume) has a typical behavior shown on Figure 3, for three different ^3He concentrations. Three different regimes can be defined.

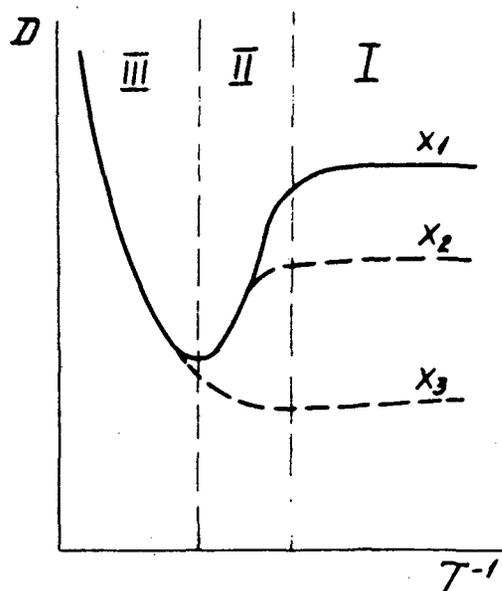


Figure 3. Temperature dependence of the diffusion constant at different concentrations in $^4\text{He} - ^3\text{He}$ (17).

In the regime I, the mechanism for D is not a $^3\text{He}-^4\text{He}$ transposition but goes through thermally excited vacancies, more or less like in the section II

above. Vacancies in ^4He are numerous enough in that regime to show up when T is higher than about 1.4 K.

In the intermediate regime II, D is a decreasing function of T and depends slightly on concentration when it is low enough. Here one observes the impuriton-phonon scattering discussed in Section II-A-2. This is illustrated in Figures 4 and 5. The latter shows a plot of D^{-1} versus T^3 which confirms rather well the power law of equation 20. For the corresponding molar volume of $V = 21 \text{ cm}^3$ the Debye temperature is $\theta_D = 26 \text{ K}$. The coupling constant $S^2 = 0.17$ is deduced from the thermal conductivity data. This enables us to evaluate the $^3\text{He}-^4\text{He}$ exchange frequency:

$$J \approx 5 \times 10^6 \text{ s}^{-1} \quad (21)$$

In the regime III, D is a decreasing function of x , independent of T . This regime is established well below 1 K. Now the diffusion at low temperatures, such that impuriton-phonon scattering is negligible, should be discussed at higher ^3He concentration, such that x is high enough to violate the gas criterion given by equation 19.

C. The Dense Fluid of Impurities

When x is large enough, an impurity really interacts with the elastic fields of many impurities simultaneously and tunnels in the mean elastic field gradient of all the impurities of the crystal. This can be calculated (18) by the method of Anderson and Margenau, which was used also for the NMR linewidth in a dilute system (Abragam Chapter IV) as well as for the relaxation time of ortho hydrogen impurities in parahydrogen (19). The result is

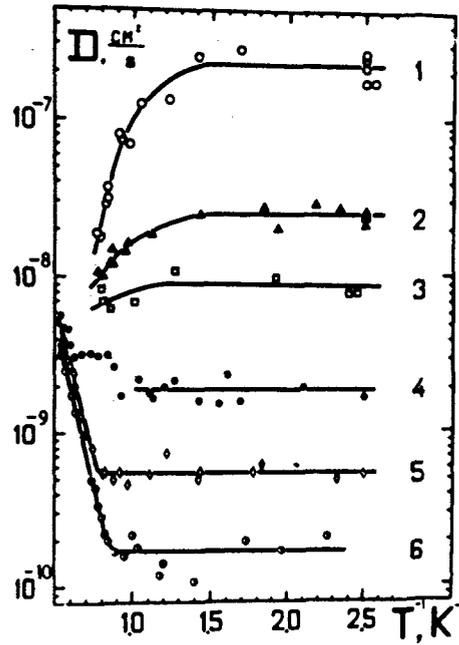


Figure 4. Temperature dependence of the diffusion constant in ${}^4\text{He} - {}^3\text{He}$ for different concentrations and molar volumes (21):

Curve	$V (\text{cm}^3)$	x
1	20.95	6×10^{-5}
2	20.95	5.2×10^{-4}
3	20.95	1.2×10^{-3}
4	20.7	2.5×10^{-3}
5	20.7	7.5×10^{-3}
6	20.7	2.17×10^{-2}

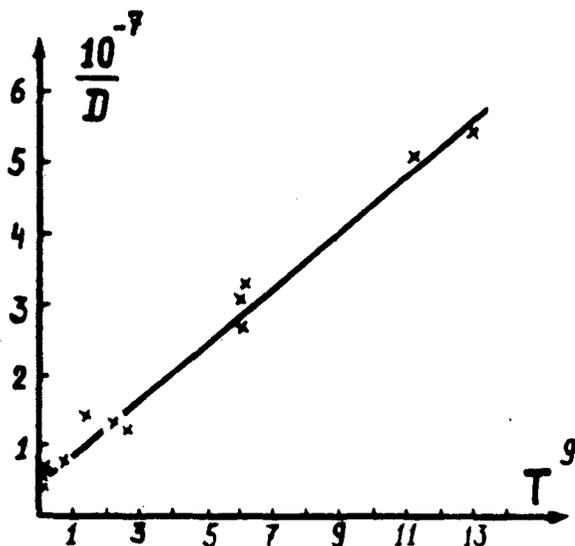


Figure 5. Temperature dependence of the diffusion constant exhibiting the impuriton-phonon collisions (22) (regime II: $V = 21 \text{ cm}^3$, $x = 6 \times 10^{-5}$).

$$D = \frac{0.47Ja^2}{x^{4/3}} \left(\frac{J}{U_0} \right) \quad (22)$$

Note that the average elastic field gradient is indeed proportional to $U_0 x^{4/3}$. The main difference between a dense fluid and a gas is the difference in power laws. The data in the regime III are given in Figure 6. In this figure D vs x is plotted for two different molar volumes. It is impossible to conclude whether the power law is -1 or -4/3, however.

D. A Direct Determination of the ^3He - ^4He Transposition Frequency

An experiment in which the tunneling frequency J could be observed with no interference of the much larger elastic interaction U_0 is needed. This is

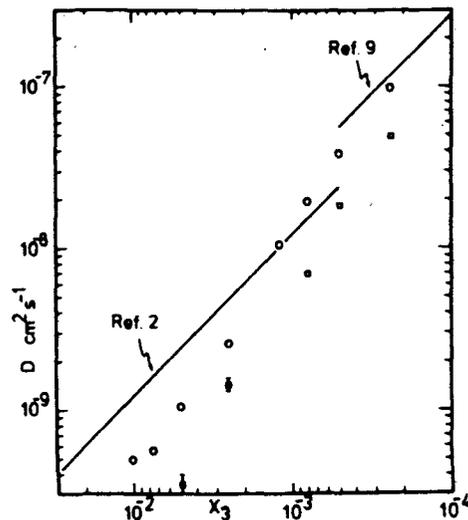


Figure 6. Concentration dependence of the diffusion constant in the low temperature plateau (23) (regime I: circles are for $V = 20.95 \text{ cm}^3$, squares are for $V = 20.7 \text{ cm}^3$).

provided by the possibility of a coherent propagation of a two dimensional quasiparticle formed by a cluster of two nearest neighbor ^3He atoms (17,20). Suppose this cluster or this $(^3\text{He})_2$ molecule, remains in the basal plane of the hcp crystal. All vectors joining nearest neighbor sites are crystallographically equivalent. Consequently they correspond to identical elastic interactions. If the "molecule" moves in that plane and in such a manner that the interatomic distance is conserved, the elastic interaction remains constant and one has a free privileged tunneling. Of course, this is possible only if the concentration is low enough that the other impurities can be neglected. For such a motion, the tunneling Hamiltonian can be diagonalized. The density of states for these two dimensional excitations is shown in Figure 7.

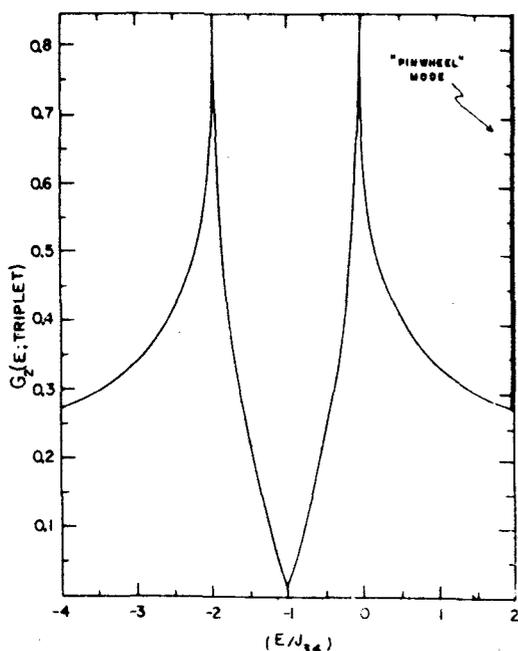


Figure 7. Density of states for the spin triplet $(^3\text{He})_2$ two-dimensional quasiparticle confined to hexagonal planes is plotted as a function of energy (24).

These excitations modulate the intramolecular dipole-dipole interaction leading to a relaxation mechanism which is dominant when the Larmor frequency is related to the energy difference between the bands of Figure 7. As a result, T_1 versus field experiment, at a given concentration, shows dips shown in Figure 8. These dips occur at frequencies which do not depend on x ; they are more pronounced at lower concentrations.

This contribution to the relaxation rate has been calculated theoretically (20) and the result is illustrated by Figure 9, which shows relaxation maxima occurring at $\omega = 2.5J$ and $\omega = 5J$. By fitting this result to the data of Figure 8, at $V = 21 \text{ cm}^3$, the following J is obtained:

$$J \approx 4 \times 10^6 \text{ s}^{-1}, \quad (23)$$

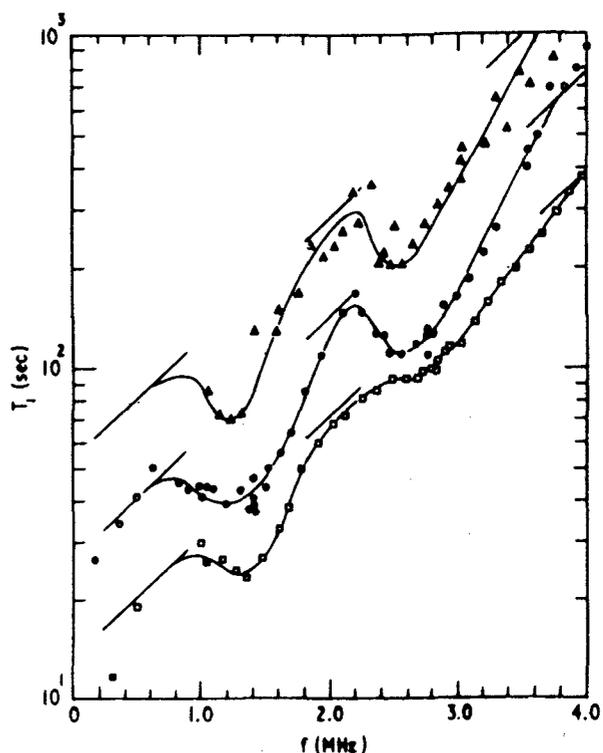


Figure 8. The spin lattice relaxation time T_1 in $^4\text{He} - ^3\text{He}$ as a function of frequency for three concentrations (25) (squares: $x = 10^{-3}$; circles: $x = 5 \times 10^{-4}$; triangles: $x = 2.5 \times 10^{-4}$; $V = 21 \text{ cm}^3$, $T = 0.53 \text{ K}$).

which is fairly close to the estimate (21).

One might question however whether the tunneling frequency deduced from the experiments shown in Figure 8 is indeed the same as the one which determines the diffusion. It could be argued that the phenomenon determining the experiments of Figure 8, is not a $^3\text{He}-^4\text{He}$ transposition but a more complicated permutation involving two ^3He atoms and one ^4He atom. We assume that these various tunneling frequencies are very similar, so that we can indeed use the result of equation 23 to analyze the data of Figure 6 quantitatively as follows.

For $V = 20.95 \text{ cm}^3$, we consider the

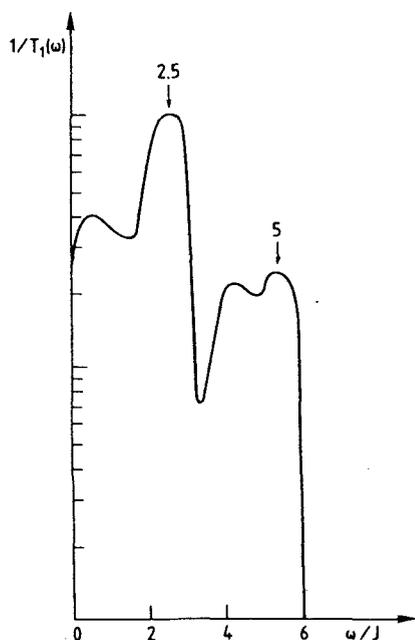


Figure 9. Spectral density histogram in arbitrary units for spin-lattice relaxation due to coherent tunneling of $(^3\text{He})_2$ molecules in ^4He (20).

lower concentration studied ($x = 2.5 \times 10^{-4}$) for which the measured D is 10^{-7} cm^2/s . With equation 18 in the impuriton gas regime we find

$$J/U_0 = 1.5 \times 10^{-4} \approx 0.6x$$

and with equation 22 (dense fluid of impurities) we find

$$J/U_0 = 6 \times 10^{-4} \approx 2.4x.$$

Apparently this concentration $x=2.5 \times 10^{-4}$ is approximately the transition concentration between the impuriton gas regime and the dense fluid regime. Indeed, for $x > 5 \times 10^{-4}$ the data of Figure 6 for $V = 20.95$ cm^3 fit the equation 22 fairly well with $J/U_0 \approx 4 \times 10^{-4}$ or $\hbar U_0 = 8 \times 10^{-2}$ K.

Other interesting aspects about quantum diffusion in $^4\text{He} - ^3\text{He}$ systems are the values of the relaxation x . Also several theoretical problems regarding quantum diffusion remain to

be solved. The solution of these problems is relevant not only to the solid helium but also to other situations where quantum diffusion is observed.

REFERENCES

- ¹A. Landesman, *J. Phys. (Paris)* **39**, C6-1305 (1978).
- ²D. Osheroff, *Physica*, LT16 Conference (1981).
- ³M. Cross, *Physica*, LT16 Conference (1981).
- ⁴S. M. Heald, Ph.D. Dissertation, University of Illinois (1976) and R. O. Simmons (private communication).
- ⁵J. H. Hetherington, *J. Low Temp. Phys.* **32**, 173 (1978).
- ⁶A. Landesman, *Ann. de Physique (Paris)*, **9**, 69 (1975).
- ⁷N. Sullivan, G. Deville, and A. Landesman, *Phys. Rev.* **B11**, 1858 (1975).
- ⁸R. B. Giffard, D. Phil. Dissertation, University of Oxford (1968).
- ⁹C. P. Flynn and A. M. Stoneham, *Phys. Rev.* **B1**, 3966 (1970).
- ¹⁰A. M. Stoneham, *J. Phys. F*, **2**, 417 (1972).
- ¹¹Yu. Kagan and M. I. Klinger, *Zh. Eksp. Teor. Fiz.* **70**, 255 (1976).
- ¹²A. Landesman, *J. Low Temp. Phys.* **30**, 117 (1978).
- ¹³W. F. Brinkman and T. M. Rice, *Phys. Rev.* **B2**, 1324 (1970).
- ¹⁴A. Landesman, *J. Low Temp. Phys.* **17**, 365 (1974).
- ¹⁵J. M. Delrieu and N. Sullivan, *Phys. Rev.* **B23**, 3197 (1981).
- ¹⁶R. A. Guyer and L. I. Zane, *Phys. Rev. Letters*, **24**, 660; 1325E (1970).
- ¹⁷A. F. Andreev, *J. Phys. (Paris)*, **39**, C6-1257 (1978).
- ¹⁸A. Landesman and J. M. Winter, LT13 Conference, Boulder, Colorado, (1972).
- ¹⁹C. C. Sung, *Phys. Rev.* **167**, 271 (1968).
- ²⁰W. J. Mullin, R. A. Guyer, and H. A. Goldberg, *Phys. Rev. Letters* **35**, 1007 (1975).
- ²¹B. N. Eselson, V. A. Mikheev, V. N. Grigoriev, and N. P. Mikhin, *J. Phys. (Paris)* **39**, C6-119 (1978).
- ²²V. A. Mikheev, B. N. Eselson, V. N. Grigoriev, and N. P. Mikhin, *Fiz. Nizk.*

Temp. 3, 385 (1977).

²³A. R. Allen, M. G. Richards, and J. Schratte, J. Phys. (Paris) 39, C6-113 (1978).

²⁴J. E. Sacco and A. Widom, Phys.

Rev. B17, 204 (1978).

²⁵M. G. Richards, J. H. Smith, P. S. Tofts, and W. J. Mullin, Phys. Rev. Letters 34, 1545 (1975).