the coupling between them. We confirm that conventional kinetic equations provide a good description of the intrinsic thermodynamic concentration fluctuations in our archetypal reactive system. The precision of our method can surely be improved and it may be extendable to other indicators such as optical adsorption or Raman scattering. The extremely small numbers of molecules ($\sim 10^4$) needed for a measurement suggest interesting applications in surface physics and biophysics.

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[1]For a review, see H. Z. Cummins and H. L. Swinney, Progr. Opt. 8, 133 (1970); G. B. Benedek, in *Polarisation, Matière et Rayonnement, Livre de Jubilé l'honneur du Professor A. Kastler,* edited by the French Physical Society (Presses Universitaire de France, Paris, 1969), p. 49.

[2]Y. Yeh and R. N. Keeler, J. Chem. Phys. 51, 1120 (1969); Y. Yeh, J. Chem. Phys. 52, 6218 (1970); Y. Yeh and R. N. Keeler, Quart. Rev. Biophys. 2, 315 (1964).

[3]See V. A. Bloomfield and J. A. Benbasat, Macromolecules 4, 609 (1971), and references cited, particularly work of B. J. Berne, H. L. Frisch, Jr., L. Blum, Z. W. Salsburg, and co-workers.

[4]B. A. Newton, in *Metabolic Inhibitors*, edited by R. M. Hochster and J. H. Quastel (Academic, New York, 1963), Vol. 2, p. 285.

[5]J. B. LePecq and C. Paoletti, J. Mol. Biol. 27, 87 (1967).

[6]D. W. Schaefer and B. J. Berne, Phys. Rev. Lett. 28, 475 (1972), have recently observed occupation-number fluctuations of polystyrene spheres by scattering methods.

[7]M. Eigen and L. C. deMaeyer, in *Techniques of Organic Chemistry,* edited by S. L. Friess, E. S. Lewis, and A. Weissberger (Interscience, New York, 1963), Vol. 8, Part II.

[8]J. G. Kirkwood and R. J. Goldberg, J. Chem Phys. 18, 54 (1950).

[9]M. J. Waring, J. Mol. Biol. 13, 269 (1965).

[10]J. Paoletti and J. B. LePecq, J. Mol. Biol. 59, 43 (1971).

[11]L. G. Longsworth, J. Amer. Chem. Soc. 74, 4155 (1952).

[12]D. M. Crothers, private communication.

[13]S. M. Tarr and A. H. Ross, private communication.

Evidence for Isotopic Impuritons in Solid Helium

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Measurements of the spin diffusion coefficient D and the NMR linewidth T_2^{-1} are reported for a ^{3}He impurity in solid ^{4}He at molar volume 21 cm^3. For $x_3 < 3\times10^{-2}$, $Dx_3 = (1.2\pm0.4)\times10^{-11}$ cm^2 sec^{-1}, where x_3 is the fractional impurity concentration, and for $x_3 < 2\times10^{-3}$, $T_2x_3 = (1.1\pm0.3)\times10^{-4}$ sec. These results conform with a model of "impuriton" excitations or "mass fluctuation waves" in which the quasiparticles move like a gas.

In the last few years several workers[1,2] have pointed out that by applying elementary quantum-mechanical ideas to impurities (and other point imperfections) that can tunnel in a solid, one is led to postulate a set of wavelike excitations in which the impurities are delocalized. Isotopic impurity in solid helium is an ideal system in which to search for such excitations because the large zero-point energy of the particles leads to a temperature-independent tunneling frequency J, which for pure solid ^{3}He at low temperatures is about 10^8 sec^{-1} at the melting pressure, decreasing rapidly with increasing pressure.[3]

The question of what properties of the system would be strongly affected by these impurity waves, or "impuritons" as we shall call them, is not a simple one. Since together with phonons, the impuritons are the excitations of the system at low temperatures, formally all physical properties are affected, but in many cases not in a

clear-cut way. For instance[4] the specific heat of a dilute mixture of say ^{3}He in solid ^{4}He should show a term in $x_3(J_{34}/T)^2$, where x_3 is the fractional impurity concentration and J_{34} is the ^{3}He-^{4}He tunneling frequency. However, at a temperature above 1 K the phonon specific heat is much greater, and below 1 K the presence of a short-range interaction of strength K between the impurities leads to an extra term in $(x_3K/T)^2$ and, eventually, to isotopic phase separation which will dominate the impuriton contribution.

NMR properties of a ^{3}He impurity in ^{4}He might be expected to provide the clearest demonstration of the existence of impuritons since the spin diffusion coefficient D and the relaxation times T_1 and T_2 are all controlled by the impurity motion. However, as we now show, T_2 measurements will not distinguish clearly between impurity waves and the random-walk motion of impurities. T_1 measurements in the appropriate frequency region are of value. However, D is the parameter which will most clearly indicate the existence of impuritons. We begin by discussing the behavior of D, T_2, and T_1 for the case of random-walk motion and the case of impuriton motion (i.e., free-particle-like behavior).

1. Random walk.—For random walk motion in which an impurity jumps a lattice spacing a every J_{34}^{-1} sec, we have

$$D \sim J_{34}a^2.$$

For T_2 we may use the expression $T_2^{-1} = \langle \omega_{loc}^2 \rangle \tau$, where $\langle \omega_{loc}^2 \rangle$ is the mean square dipole field seen by a ^{3}He atom and τ is the correlation time for the field fluctuations. Clearly, $\tau \sim J_{34}^{-1}$ and $\langle \omega_{loc}^2 \rangle \sim \hbar^2\gamma^4 x_3/a^6$ if we assume a random distribution of impurities (this effectively ignores any interactions between impurities). Hence

$$1/T_2 \sim \hbar^2\gamma^2 x_3/a^6 J_{34}.$$

Resing and Torrey[5] have carried out this calculation more carefully and they also obtain for T_1

$$1/T_1 \sim \hbar^2\gamma^4 x_3 J_{34}/a^6\omega^2$$

for the Larmor frequency $\omega_0 \gg J_{34}$.

2. Impuriton motion.—For impuriton motion, Widom and Richards[6] have discussed the diffusion coefficient in detail. For the region where scattering is caused by the impuriton-impuriton interaction, which is assumed to have a range of R, we have from a simple kinetic-theory approach

$$D \sim v\lambda,$$

where v is the wave velocity and is $\sim J_{34}a$, and the mean free path λ is $\sim a^3/x_3R^2$. Hence

$$D \sim J_{34}a^4/R^2x_3.$$

For T_2 we assume that we have to calculate the effects of two-particle collisions which take place incoherently at an average frequency of τ_{coll}^{-1}. In each collision the spin transverse magnetization dephases by $\Delta\varphi$. Hence

$$1/T_2 = \langle \Delta\varphi^2 \rangle / \tau_{coll},$$

with

$$\langle \Delta\varphi^2 \rangle \sim \frac{\hbar^2\gamma^4}{R^6} \frac{R^2}{(J_{34}a)^2} \text{ and } \tau_{coll} \sim \frac{D}{J_{34}^2 a^2};$$

therefore,

$$1/T_2 \sim \hbar^2\gamma^4 x_3/R^2a^4J_{34}.$$

T_1 is more difficult to calculate but one can say[7] that in the limit of low x_3, where only two-particle collisions are considered, the spectral density of dipole field fluctuations, $J(\omega)$ ($\sim 1/T_1$), falls to zero at twice the impuriton band thickness[6] which is $\sim zJ_{34}$, where z is the number of nearest neighbors.

At frequencies much greater than zJ_{34}, an effective contribution to $J(\omega)$ may be expected to come from ^{3}He-^{3}He tunneling (at frequency J_{33}), particularly at high x_3.

The predictions of the two models are summarized in Table I which includes, for comparison, the results for a ^{3}He Boltzmann gas.[8]

The only previously published data[9] on very dilute ^{3}He-^{4}He mixtures are of T_2 and T_1 at high frequencies. Reproducible results were obtained at $x_3 = 0.01$ and 0.02, but at lower x_3 large scatter on the data prevents quantitative analysis. As explained above, T_2 data are ambiguous in deciding between the two models of impurity mo-

TABLE I. Theoretical predictions for the behavior of NMR linewidths and spin diffusion coefficients of ^{3}He impurities in solid ^{4}He.

	^{3}He impurity, random jump	^{3}He impurity, impuritons	^{3}He gas
D	$J_{34}a^2$	$\frac{J_{34}a^4}{R^2x_3}$	$\left(\frac{k_BT}{m}\right)^{1/2}\frac{1}{\rho R^2}$
$\frac{1}{T_2}$	$\frac{\hbar^2\gamma^4x_3}{J_{34}a^6}$	$\frac{\hbar^2\gamma^4x_3}{J_{34}a^4R^2}$	$\left(\frac{m}{k_BT}\right)^{1/2}\frac{\hbar^2\gamma^4\rho}{R^2}$
$\frac{D}{T_2}$	$\frac{\hbar^2\gamma^4x_3}{a^4}$	$\frac{\hbar^2\gamma^4}{R^4}$	$\frac{\hbar^2\gamma^4}{R^4}$

tion, and it is not clear that the T_1 results relate to ^{3}He-^{4}He tunneling since the data points join smoothly onto results for high x_3, where they are interpreted as yielding measurements of J_{33}.

The measurements reported here were carried out at 0.53 K using an NMR spin-echo method[10] to measure D, T_1, T_2, and the susceptibility (to determine x_3). A frequency of 5 MHz was chosen as a compromise between large signals with long T_1's and shorter T_1's with weak signals. A small cylindrical sample chamber 0.4 cm in diameter and 0.4 cm long was used to allow gradients G of up to 60 G cm^{-1} to be applied without requiring too large a bandwidth to amplify the resulting narrow echos. The use of a pulsed gradient facility which we are preparing will obviate the need for such a small sample and allow gradients of up to 1000 G cm^{-1} to be applied.

The samples were formed by the blocked capillary method and were all estimated to be 21.0 ± 0.1 cm^3 molar volume, though no strain gauge was used to check this. The measurements of T_2 and D were made using the expression

$$h(2\tau) = h(0)\exp[-2\tau/T_2 - \gamma^2\hbar^2G^2D(2\tau)^3/12]$$

for the echo height at time 2τ after applying a $\frac{1}{2}\pi$ pulse at time 0 and a π pulse at time τ. T_1 measurements were made by observing the echo recovery at t following the previous $\frac{1}{2}\pi$-π sequence, using

$$h(t) = h(\infty)[1-\exp(-t/T_1)]\exp(-2\tau/T_2)$$

for $t, T_1 \gg \tau, T_2$.

The concentration of impurity is proportional to $h(\infty)$ which is found by extrapolating $h(t)$ back to $t=0$ and $\tau=0$. These measured x_3 values never differed from the concentration in the gas used for sample formation by more than 25%.

Figure 1 shows D, the spin-diffusion coefficient of the ^{3}He impurity, as a function of x_3, the fractional impurity content. The solid line represents

$$D = 1.2\times10^{-11}/x_3 \text{ cm}^2 \text{ sec}^{-1}.$$

Figure 2 shows the results for T_2 as a function of x_3. In both cases the temperature is 0.53 K and the frequency 5 MHz. The solid line represents

$$T_2 = 1.1\times10^{-4}/x_3 \text{ sec}.$$

A point taken under similar conditions by Greenberg, Tomlinson, and Richardson[9] is indicated. Their data for $x<0.01$ fall mostly above that reported here but with large scatter and uncertainty in the x_3 values.

The results for x_3 less than about 2×10^{-3} are consistent with the impuriton model though it is noticeable that a lower x_3 is required for the onset of the predicted behavior for D than for T_2. This may be because to scatter an impuriton, momentum transfer is required (and as we shall show, the range of the impuriton-impuriton interaction is $\sim a$), while it is the longer range dipole field that dephases the transverse magnetism, thus contributing to $1/T_2$. Hence as x_3 falls, one

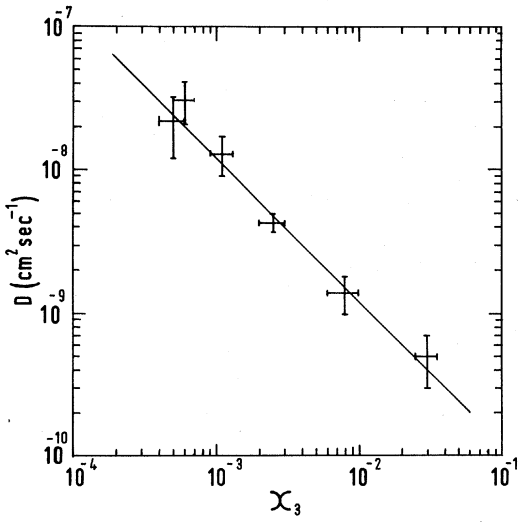

FIG. 1. Spin diffusion coefficient D of ^{3}He impurity in solid ^{4}He versus x_3, the mole fraction of ^{3}He. Temperature, 0.53 K; sample molar volume, 21 cm^3; operating frequency, 5 MHz. $D \propto 1/x_3$ is characteristic of the impuriton model. The line drawn is $Dx_3 = 1.2 \times 10^{-11}$ cm^2 sec^{-1}.

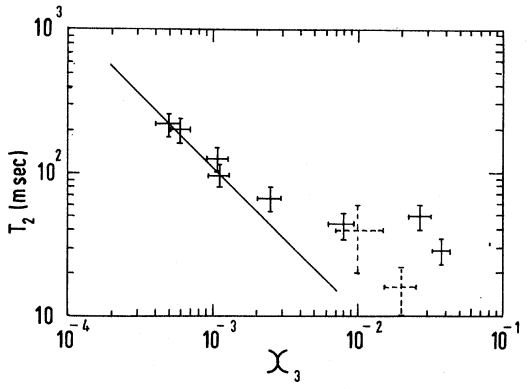

FIG. 2. Transverse relaxation time T_2 of ^{3}He impurity in solid ^{4}He versus x_3, the mole fraction of ^{3}He. Operation conditions, same as in Fig. 1. Dashed error bars, taken from Ref. 9. Straight line, $T_2x_3 = 1.1\times10^{-4}$ sec.

will enter the two-particle region for D before doing so for T_2. It is also clear that one must work at x_3 below about 2×10^{-3} if J_{34} is to be deduced from T_2 measurements using either of the models summarized in Table I.

To obtain the range R we compare experimental and theoretical values for D/T_2:

$$(D/T_2)_{\text{expt}} = (1.1\pm0.4)\times10^{-7}\ \text{cm}^2\ \text{sec}^{-2}.$$

This leads to $R\sim3.7\times10^{-8}$ cm, which is the lattice spacing appropriate to a molar volume of 21 cm^3. We are thus led to assume that the impuriton-impuriton interaction is short ranged, as expected from lattice-distortion calculations[11] but not as has been previously assumed.[1,12]

The D/T_2 values may be compared with D/T_1 in ^{3}He gas at 4 K, which has recently been measured.[13,14] In this case $\omega_0\tau\ll1$, where $\tau\sim10^{-12}$ sec is the correlation time and

$$(D/T_1)_{\omega_0\to0} = (D/T_2)_{\omega_0\to0} = (10D/3T_2)_{\omega_0\to\infty}.$$

The experimental value of D/T_1 is $(3\pm1)\times10^{-7}$ cm^2 sec^{-2} which is, within error, equal to $\frac{10}{3}$ times the D/T_2 reported here. Thus we again obtain $\sim10^{-15}$ cm^2 for the scattering cross section; in this case, however, we know that this value is approximately correct and so we gain some confidence in our kinetic theory model.

Using $R\approx a$, we now obtain $J_{34}\sim10^4$ sec^{-1} from D. This value is about $10^{-3}J_{33}$, where J_{33} is the ^{3}He-^{3}He tunneling frequency in pure solid ^{3}He at the same sample molar volume.[3] This result will be modified somewhat when the accuracy of the theory is improved but it is clear that if our impuriton model is correct then $J_{34}\ll J_{33}$, which conflicts with the usual assumption[2] that $J_{34}\sim J_{33}$.

The T_1 data that we have at 5 MHz are not presented here because we are not convinced that the dominant spin-lattice relaxation process is ^{3}He-^{4}He tunneling under our experimental conditions. Miyoshi *et al.*[15] and Greenberg, Tomlinson, and Richardson[9] have shown that for $x_3\geq0.01$ and $\omega_0/2\pi>1$ MHz, T_1 is controlled by ^{3}He-^{3}He tunneling. We believe that at 5 MHz this may still be true down to even lower x_3 values. To look for the characteristic effects on T_1 of ^{3}He-^{4}He tunneling one has to work at $x_3<10^{-3}$ and $\omega_0\sim zJ_{34}$, a region which we are currently investigating.

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[1]A. F. Andreev and L. M. Lifshitz, Zh. Eksp. Teor. Fiz. 56, 2057 (1969) [Sov. Phys. JETP 29, 1107 (1969)].

[2]R. A. Guyer and L. I. Zane, Phys. Rev. Lett. 24, 660 (1970).

[3]M. G. Richards, Advan. Mag. Res. 5, 305 (1971).

[4]M. Bernier and A. Landesman, J. Phys. (Paris), Suppl. 32, C5a-213 (1971).

[5]H. A. Resing and H. C. Torrey, Phys. Rev. 131, 1102 (1963).

[6]A. Widom and M. G. Richards, Phys. Rev. A 6, 1196 (1972).

[7]A. Widom, to be published.

[8]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford Univ. Press, Oxford, England, 1961), p. 302.

[9]A. S. Greenberg, W. C. Thomlinson, and R. C. Richardson, Phys. Rev. Lett. 27, 179 (1971), and to be published.

[10]H. Y. Carr and E. M. Purcell, Phys. Rev. 94, 630 (1954).

[11]H. R. Glyde, Phys. Rev. 177, 202 (1969).

[12]R. A. Guyer, R. C. Richardson, and L. I. Zane, Rev. Mod. Phys. 43, 532 (1971).

[13]K. Luszczynski, R. E. Norberg, and J. E. Opfer, Phys. Rev. 128, 186 (1962).

[14]R. Chapman and M. G. Richards, to be published.

[15]D. S. Miyoshi, R. M. Cotts, A. S. Greenberg, and R. C. Richardson, Phys. Rev. A 2, 870 (1970).