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Direct measurement of spin diffusion from spin relaxation times in solid ^{3}He

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We show that the spin-diffusion coefficient in solid ^{3}He may be obtained unambiguously from measurements of spin relaxation at low magnetic fields. For long times, the dipolar autocorrelation function decays as $t^{-3/2}$. This follows purely as a consequence of the hydrodynamics of the system. From this we show that the low-frequency form of the dipolar spectral density function is $J(\omega)=J(0)-A\omega^{1/2}$, where the constant A depends on the diffusion coefficient and is independent of the microscopic details of the system. Values of the spin-diffusion coefficient thus obtained are in good agreement with those obtained by conventional means. Moreover this method permits extension to higher densities and lower diffusion coefficients.

I. INTRODUCTION

Solid ^{3}He is a unique model system. The nuclei, with spin-$\frac{1}{2}$, have pure dipole magnetic moments, while the small mass of the atoms together with their Fermi statistics results in significant quantum exchange. From the NMR point of view this represents the simplest (line broadening) interaction, while the exchange, which conventionally is modeled by a spin Hamiltonian, is a "motion" that modulates this interaction.

In the temperature range around 1 K the observed spin-relaxation times are independent of temperature.[1,2] At higher temperatures the motion of thermally activated vacancies becomes important,[3] while at much lower temperatures the exchange excitations lose thermal contact with the surrounding lattice.[4] Within this intermediate-temperature range the spin assembly may be described by a Hamiltonian consisting of three parts: the Zeeman term which gives the energy of interaction between the magnetic dipoles and the externally applied magnetic field, the internuclear dipolar coupling, and the exchange spin Hamiltonian. Thus one has a fully specified quantum-mechanical system which may be treated by the established methods of many-body quantum mechanics.

The special property of this system from the theoretical point of view is that it is much simpler than the usual many-body system since the quantities of interest are the bounded spin variables rather than the unbounded spatial coordinates. Nevertheless there remains sufficient complexity for the system to behave in a truly irreversible way, and following a disturbance, to return to a state of thermal equilibrium. From the experimental standpoint measurements of relevant quantities, such as magnetization, may be made quite directly and unequivocally so that the connection between theory and experiment is unusually direct. It is for these reasons that solid ^{3}He is such a unique system.

II. EXCHANGE AND DIFFUSION

A. Exchange

The purpose of many spin relaxation experiments is to study the motion of the spin-carrying atoms. And in the case of solid ^{3}He this means trying to understand the nature of the exchange Hamiltonian. Although it was proposed quite early on[5] that the exchange process could be rather complex, experimental measurements were often analyzed on the basis of a Heisenberg pairwise exchange of nearest neighbors. It was only with the observation of the low-temperature ordered phases of ^{3}He (Ref. 6) that it was finally accepted that pairwise Heisenberg exchange was an insufficient description for the system. The possibility of zero-point vacancies has been variously proposed[7,8] and although these (together with pairwise exchange) cannot account for all the details of the ordered phases, their existence is still an open question.[8]

Within the framework of the pairwise exchange model there is a single parameter to be determined: the exchange frequency, denoted by J. From experiments one would hope to obtain values for the exchange frequency to see how it varies with density, conventionally expressed as molar volume. It is not the purpose of this paper to discuss exchange in detail and its determination from relaxation-time measurements. Suffice it to say that existing treatments give only the exchange frequency to within a multiplicative constant of the order of unity, being based on various, albeit plausible, approximations. Thus the density dependence is known well but the absolute magnitudes are often scaled so as to agree with determinations from thermal capacity or other measurements.[4]

A more realistic description of the exchange process involves the consideration of interchange cycles involving different numbers of spins. There are a larger number of parameters to be determined, for which conventional NMR relaxation-time measurements are not adequate. All one can obtain is some weighted mean of the strengths of the various exchange processes.[9]

B. Spin diffusion

The purpose of this paper is to consider one of the hydrodynamic consequences of exchange: spin diffusion. In particular we shall be concerned with the connection between spin diffusion and spin relaxation. Regardless of the precise microscopic details of the exchange Hamiltonian, on the long-time scale it will lead to the phenomenon of spin diffusion. That is, a spin inhomogeneity of wave vector $\mathbf{Q}$ will relax exponentially with a time constant DQ^2 in the limit of small $\mathbf{Q}$. Here D is identified as the spin-diffusion coefficient. The relation between D and the exchange parameter(s) has been evaluated for a number of cases[10–12] and, very generally, it takes the form $D = \text{const} \times Ja^2$. J is a frequency characterizing the exchange and a is the interparticle spacing. The dimensionless constant depends on the lattice structure.

The NMR technique of spin echoes[13] is conventionally utilized for the measurement of self-diffusion, with special variants[14] when the diffusion coefficient is very large or very small. Central to the method is the application of a magnetic-field gradient over the specimen, by which means positional information is encoded as phase variations. Using such methods Reich and Garwin[15,16] and Thompson, Hunt, and Meyer[17] have measured the spin-diffusion coefficient in solid ^{3}He over a range of densities corresponding to molar volumes between 21 and 25 cm^3. We emphasize that these measurements, performed in this way, are purely hydrodynamic in nature. That is, the values of the diffusion coefficients so obtained do not depend on any assumptions about microscopic details of the atomic motion such as jump length or hard-core dimension. Typically, in such an experiment, the spin-echo height varies with time t as

$$\exp(-\gamma^2 G^2 D^2 t^3/12) , \tag{2.1}$$

where γ is the magnetogyric ratio of the spins, G is the magnitude of the magnetic-field gradient and D is the diffusion coefficient. For an explanation of the above result treated in the context of this discussion see Refs. 12 and 18. In determining the diffusion coefficient we see that it is only necessary to know the magnitude of the field gradient G.

C. Field gradient

Since the accuracy and reliability of diffusion measurements made by this method relies on a good knowledge of the field gradient, we digress slightly to consider this further.

If a uniform magnetic-field gradient is applied perpendicular to the axis of a cylindrical specimen (a common geometry; others can be treated similarly) then the envelope of the free-induction decay may be shown to be proportional to

$$\frac{J_1(aG\gamma t)}{aG\gamma t} ,$$

where $J_1(x)$ is the first-order Bessel function and a is the radius of the cylinder. This result provides a method for finding the field gradient from the free-induction decay: essentially by imaging the field distribution. Either one may fit to the above function or simply locate the zeros.

The validity of the above result is based on a number of assumptions, some questionable in a realistic situation. In particular it requires the following:

(1) A truly cylindrical chamber with flat ends and nonrounded corners.

(2) The field gradient precisely perpendicular to the cylinder axis.

(3) Elimination of baseline errors; this is particularly important in determination of zeros in a demodulated free-induction decay.

(4) The field gradient over the specimen should be uniform.

(5) Homogeneous sensitivity of the NMR receiver coil.

The first three items have been discussed adequately in the literature.[19]

Item (4) concerning uniformity of the field gradient is likely to be problemmatic only in confined spaces where the gradient coil is close to the specimen. There are two aspects to this problem. So long as the gradient variation does not change too wildly[20] the spin-echo relaxation will still follow the familiar cubic decay. But now, in the decay function equation (2.1), the square of the gradient is simply replaced by its mean-square value. The effect is not so simple, however, on the free-induction-decay shape. This would have to be calculated numerically from a knowledge of the field profile of the gradient. The problem introduced then is not in the actual measurements but in the calibration process.

We now turn to item (5), the homogeneous sensitivity of the receiver coil. Here we require that a precessing spin in any part of the specimen chamber will induce the same voltage in the coil. While this is true for an infinitely long solenoid, it becomes decreasingly so for shorter coils, particularly when they are wound closely around the specimen. In a realistic calculation of the free-induction signal it is necessary to take this position-dependent sensitivity into account. By symmetry, contours of constant sensitivity will be on-axis circles. And such a circle of spins, of radius a, will produce a magnetization proportional to

$$-2\frac{J_2(aG\gamma t)}{a} ,$$

where $J_2(x)$ is the second-order Bessel function. This expression must now be integrated over a sensitivity function for the coil. Fortunately this function may be found in a relatively straightforward, if cumbersome way by application of the reciprocity theorem.[21] Numerical integration would then follow. The disadvantage is that now the dimensions of the receiver coil enter into the discussion, and the result can no longer be expressed in analytic form.

The result of the above discussion is to demonstrate that although the conventional spin-echo method for studying diffusion does give a purely hydrodynamic measurement, nevertheless the precise values for D rely on an accurate determination of the applied magnetic-field gradient, which is not necessarily a trivial problem.

III. SPIN RELAXATION

As discussed in Sec. II A, measurements of spin-relaxation times are performed in solid ^{3}He, primarily, to gain an understanding of the exchange interaction and its strength. Analysis of experimental data in this way requires a knowledge of the internuclear dipolar autocorrelation function or, equivalently, its Fourier transform, the dipolar spectral density function. Unfortunately, such a many-body function usually may not be calculated accurately so that approximate forms are often used. Thus for the bcc phase of solid ^{3}He it is conventionally taken that the spectral density function has an approximately exponential form.

The approach of this paper is different. We shall be concerned directly with the effects of spin diffusion on the relaxation. Thus it is the hydrodynamics that are of concern, and using this approach one can obtain results requiring no approximation procedures or assumptions. One conclusion will be the extraction of spin-diffusion coefficients from relaxation-time data. This will be shown to be a purely hydrodynamic measurement, depending on no microscopic details of the atomic behavior and with no adjustable parameters.

A. Dipolar autocorrelation function

Information about the relaxation processes is contained in the dipolar autocorrelation functions. These may be written in the form[22]

$$G_m(t)=\frac{6\pi\hbar^2\gamma^4}{5N}\sum_{i<j}\frac{Y_2^{-m}(\Omega_{ij}(0))Y_2^m(\Omega_{ij}(t))}{r_{ij}^3(0)r_{ij}^3(t)} , \tag{3.1}$$

where we use the conventional notation.[11] The sum is over the particles in the system and Ω is the orientation of the line joining the ith and the jth particle with respect to the static magnetic field. In a true Hamiltonian approach to the problem the vectors $\mathbf{r}=(r,\Omega)=(r,\theta,\Phi)$ have a time variation induced by a motion Hamiltonian: the full many-body problem. One way of circumventing this difficulty is to replace the summation over particles by an integral over space with an appropriate distribution function:

$$\sum_{i,j}\to\alpha\int d\mathbf{r}_0\int d\mathbf{r}\,P(\mathbf{r},\mathbf{r}_0,t)g(\mathbf{r}_0) . \tag{3.2}$$

Here $P(\mathbf{r},\mathbf{r}_0,t)$ is the probability that a pair of particles, initially of separation $\mathbf{r}_0$ will, after a time t, be separated by $\mathbf{r}$. And $\alpha g(\mathbf{r}_0)$ gives the probability that at time $t=0$ a pair of particles will be found with that initial separation $\mathbf{r}_0$; $g(r)$ is the radial distribution function and α is the spin density.

For diffusive motion $P(\mathbf{r},\mathbf{r}_0,t)$ may be found by solution of a diffusion equation (with the appropriate boundary conditions). There have been a number of approaches to the phenomenon of spin relaxation along these lines.

B. Different approaches

Torrey[23] considered various jump models for atomic motion and he also treated the hydrodynamic limiting case of diffusion. In arriving at his results, however, he made a number of approximations. He assumed a uniform spin distribution and regarded the atoms as hard spheres. Thus he approximated $g(r)$ by a step function:

$$g(r)=\begin{cases}0, & r<a\\ 1, & r>a .\end{cases} \tag{3.3}$$

The boundary conditions on the relative diffusion were taken into account only at the initial and the final configuration, not during the motion; he simply excluded the volume $|\mathbf{r}|<a$ from the integrals over $\mathbf{r}_0$ and $\mathbf{r}$. Hubbard[24] showed that Torrey's continuum-model result could be integrated analytically to give the dipolar spectral density in closed form. This is frequently referred to in the literature as "model A."

Both Hwang and Freed[25] and Ayant *et al.*[26] treated the boundary condition on the colliding particles in a more realistic way. Their calculations, also, gave the spectral density functions in analytic form. The main qualitative difference was in the asymptotic high-frequency behavior. Torrey's model led to a $\omega^{-3/2}$ law whereas with correct (hard-sphere) boundary conditions, referred to as "model B," the high-frequency decay became ω^{-2}. We note incidentally that neither asymptotic form is physically correct, since the diffusion description of particle motion is not appropriate in this limit; the microscopic details of the motion are paramount here. In particular the principle of microscopic reversibility must be respected. As discussed in another context,[27] the high-frequency spectral density must decay exponentially or faster. Asymptotic behavior as above may seem to appear in some systems as a result of widely separated time scales, but clearly at much higher frequencies this must break down.

The dipolar interaction falls off quite rapidly with separation, decreasing as r^{-6}. Thus an important effect comes from near neighbors. Now the radial distribution function peaks significantly above its mean, large-distance, value at the next-neighbor position. This means that there are on average more near neighbors than the uniform distribution would imply. And this will therefore have an influence on the observed relaxation behavior. The effect of this was considered by Harmon and Muller,[28] although clearly no analytic solution was possible.

Unfortunately there is a further problem with the probabilistic approach. At time t the probability of finding a particle at position r is given by

$$\alpha\int d\mathbf{r}_0P(\mathbf{r},\mathbf{r}_0,t)g(\mathbf{r}_0) .$$

Accepting that $g(\mathbf{r}_0)$ is the radial distribution function, we know that this distribution should remain constant in time; the integral should evaluate to $\alpha g(\mathbf{r})$, the same function. Unfortunately if $P(\mathbf{r},\mathbf{r}_0,t)$ follows from a diffusion equation then the final distribution in the above integral tends to a uniform density at long times. Huang and Freed[25] take $P(\mathbf{r},\mathbf{r}_0,t)$ as a solution of the Smoluchowski equation, which includes an effective pair interaction of the particles $U(r)$, related to $g(r)$ by

$$g(r)=\exp[-U(r)/kT] .$$

This ensures that the density distribution remains as $g(r)$.

C. Long-time behavior of $G(t)$: Qualitative treatment

In all that follows we shall adopt the probabilistic description, common to all four models discussed in the previous section. Thus taking the expression for the dipolar autocorrelation function, Eq. (3.1), we rewrite this as an integral according to the recipe of Eq. (3.2), which gives

$$G_m(t)=\frac{3\pi\alpha\hbar^2\gamma^4}{5}\int\int P(\mathbf{r},\mathbf{r}_0,t)\frac{Y_2^{-m}(\Omega_0)Y_2^m(\Omega)}{r_0^3r^3}\times g(\mathbf{r}_0)\,d\mathbf{r}_0\,d\mathbf{r} . \tag{3.4}$$

The time dependence of this expression is contained in the propagator $P(\mathbf{r},\mathbf{r}_0,t)$. And if we are interested in the long-time behavior of $G(t)$, then we must examine how the propagator behaves for long times. Now for large t, $P(\mathbf{r},\mathbf{r}_0,t)$ behaves in a diffusive manner. That is, it tends to the diffusion propagator

$$P_d(\mathbf{r},\mathbf{r}_0,t)=(8\pi Dt)^{-3/2}\exp(-|\mathbf{r}-\mathbf{r}_0|^2/8Dt) .$$

Fortunately the exponential is a function of *inverse* powers of time. So the long-time behavior is given by the small argument expansion of the exponential function. And in particular the limiting long-time form is

$$P_d(t\rightarrow\infty)\rightarrow(8\pi Dt)^{-3/2} .$$

We conclude that for any motion which becomes diffusive at long times, in this limit the propagator has a $t^{-3/2}$ behavior as in the above expression. Substituting this into Eq. (3.4) we obtain the long-time behavior of $G(t)$. We note that this result is independent of the precise nature of the particle motion. In this limit the only quantity relevant to the motion is the diffusion coefficient D.

$$G_m(t\rightarrow\infty)\rightarrow\frac{3\pi\alpha\hbar^2\gamma^4}{5}\frac{1}{(8\pi Dt)^{3/2}}\int\int\frac{Y_2^{-m}(\Omega_0)Y_2^m(\Omega)}{r_0^3r^3}\times g(\mathbf{r}_0)d\mathbf{r}_0d\mathbf{r} . \tag{3.5}$$

An important point to observe about this expression is that the autocorrelation function varies as $t^{-3/2}$ at long times; it does not decay exponentially as most semiquantitative[29] treatments argue. We now examine this in more detail.

D. Long-time behavior of $G(t)$: Quantitative treatment

We turn to an explicit calculation of the behavior of the dipolar autocorrelation function. The diffusion propagator $P(\mathbf{r},\mathbf{r}_0t)$ is first expressed as a Fourier integral:

$$P(\mathbf{r},\mathbf{r}_0,t)=\frac{1}{(2\pi)^3}\int\exp(-2k^2Dt)\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_0)]d\mathbf{k} . \tag{3.6}$$

The next few steps follow closely those described by Torrey.[30] The complex exponentials are expanded as

$$\exp(i\mathbf{k}\cdot\mathbf{r})=4\pi\left[\frac{\pi}{2kr}\right]^{1/2}\sum_{m,l}i^lY_l^{m*}(\Omega)Y_l^m(\Omega')\times J_{l+1/2}(kr) ,$$

where Ω' is the orientation of the vector $\mathbf{k}$ and J is a Bessel function. These expansions are substituted into Eq. (3.6), which is substituted into Eq. (3.4) for $G(t)$. Then exploiting the orthogonality properties of the spherical harmonics we finally obtain the expression

$$G(t)=\frac{3\pi\alpha\hbar^2\gamma^4}{5}\int_0^\infty k\exp(-2k^2Dt)\left\{\int_0^\infty\frac{J_{5/2}(kr)}{r^{3/2}}dr\right\}\left\{\int_0^\infty\frac{J_{5/2}(kr)}{r^{3/2}}g(r)dr\right\}dk . \tag{3.7}$$

The two integrals in the curly brackets are similar, except that the second contains the radial distribution function. Note also that there is no longer a dependence on the "spin-flip" index m, a consequence of the rotational invariance of the diffusive propagator.

In order to investigate the time dependence of $G(t)$ we change variables in the k integral, substituting

$$x=\sqrt{2Dt}\,k .$$

This gives

$$G(t)=\frac{3}{5}\frac{\pi\alpha\hbar^2\gamma^4}{2Dt}\int_0^\infty x\exp(-x^2)\left\{\int_0^\infty\frac{J_{5/2}(xr/\sqrt{2Dt})}{r^{3/2}}dr\right\}\left\{\int_0^\infty\frac{J_{5/2}(xr/\sqrt{2Dt})}{r^{3/2}}g(r)dr\right\}dx , \tag{3.8}$$

and taking note of the t^{-1} prefactor, we now focus attention on the Bessel function integrals.

Our intention is to demonstrate that the long-time behavior of $G(t)$ is determined solely by diffusion and that it is independent of any microscopic details. To this end we introduce a length d such that for distances r greater than d, the diffusion description of the motion is valid. The Bessel function integrals can then be expressed as a sum of two parts. For $r<d$ details of the motion and configuration may be important while for $r>d$ only diffusion need be considered. By the same token, for $r>d$ the radial distribution function in the second integral may be neglected.

Making the further substitution

$$y=\frac{x}{\sqrt{2Dt}}r\ ,$$

the first Bessel integral is the sum of "internal" and "external" parts:

$$\{\dots\}=\frac{x^{1/2}}{(2Dt)^{1/4}}\left[\int_0^{xd/\sqrt{2Dt}}\frac{J_{5/2}(y)}{y^{3/2}}dy+\int_{xd/\sqrt{2Dt}}^{\infty}\frac{J_{5/2}(y)}{y_{5/2}}dy\right]$$

and the integrals may be evaluated as

$$\int_0^{xd/\sqrt{2Dt}}\frac{J_{5/2}(y)}{y^{3/2}}dy=\frac{J_{3/2}(xd/\sqrt{2Dt}\,)}{xd/\sqrt{2Dt}} \tag{3.9}$$

and

$$\int_{xd/\sqrt{2Dt}}^{\infty}\frac{J_{5/2}(y)}{y^{5/2}}dy=\frac{1}{3}\left[\frac{2}{\pi}\right]^{1/2}-\frac{J_{3/2}(xd/\sqrt{2Dt}\,)}{xd/\sqrt{2Dt}}\ . \tag{3.10}$$

For long times we may expand these:

$$\frac{1}{3}\left[\frac{2}{\pi}\right]^{1/2}\frac{1}{20}\frac{x^2d^2}{Dt}-\dots,\quad\text{for } r<d \tag{3.11}$$

and

$$\frac{1}{3}\left[\frac{2}{\pi}\right]^{1/2}\left[1-\frac{1}{20}\frac{x^2d^2}{Dt}+\dots\right],\quad\text{for } r>d\ . \tag{3.12}$$

Considering the diffusion regime $r>d$, as stated above, the structure factor $g(r)$ may be ignored since it is unity except at very short distances. In this regime, then, the two Bessel function integrals of Eq. (3.8) are the same and they are given by expression (3.10), with long-time expansion, expression (3.12). Thus the pure diffusion contribution to $G(t)$ may be expressed as

$$G_d(t)=\frac{3}{5}\frac{\pi\alpha\hbar^2\gamma^4}{(2Dt)^{3/2}}\int_0^{\infty}x^2\exp(-x^2)\left[\frac{1}{3}\left[\frac{2}{\pi}\right]^{1/2}+O(t^{-1})\right]^2dx\ . \tag{3.13}$$

This gives the long-time asymptotic behavior. Observe that the leading time is in $t^{-3/2}$ and that this term is independent of the precise magnitude of the distance d.

Turning now to the inner region $r<d$, we observe from expression (3.11) that the time dependence of the integral, Eq. (3.9), has a leading term in t^{-1}. Now we must consider the function $g(r)$ that appears in the second set of curly braces of Eq. (3.8). Because of the functional form of $g(r)$, this will have the effect of *reducing* the value of the integral compared with that of the first set of curly braces of Eq. (3.8), evaluated above in expression (3.11). Deviation of the propagator $P(\mathbf{r},\mathbf{r}_0,t)$ from pure diffusion may be considered similarly. The time decay of this term must be t^{-1} or faster. The conclusion is that the contribution to $G(t)$ from the region $r<d$ will have a leading term in $t^{-5/2}$.

In the above calculation we have demonstrated that the leading term in the asymptotic expansion of $G(t)$ varies as $t^{-3/2}$ and that this term is independent of the structure function $g(r)$ and the microscopic details of the dynamics. The long-time behavior of $G(t)$ is thus found to vary as

$$G(t)\sim\frac{\hbar^2\gamma^4\alpha\sqrt{\pi}}{60\sqrt{2}}\frac{t^{-3/2}}{D^{3/2}}+O(t^{-5/2})\ . \tag{3.14}$$

We note parenthetically that using a procedure similar to that described above in arriving at Eqs. (3.9) and (3.10), it is possible to obtain an exact expression for the dipolar autocorrelation function in the case of the so-called model A. We find that $G(t)$ may be expressed as a generalized hypergeometric function[31]

$$\frac{G(t)}{G(0)}=\frac{1}{6\sqrt{\pi}}\left[\frac{\tau_0}{t}\right]^{3/2}{}_3F_3\left[2,\frac{5}{2},\frac{3}{2};\frac{5}{2},\frac{5}{2},4;-\frac{\tau_0}{t}\right],$$

where we have introduced the zero-time value of $G(t)$,

$$G(0)=\frac{1}{5}\hbar^2\gamma^4\frac{\pi\alpha}{a^3}$$

and a correlation time τ_0, the time taken for a particle to diffuse a hard-core distance a:

$$\tau_0=a^2/2D\ .$$

From the expansion of the hypergeometric function we may express $G(t)$ as a series

$$\frac{G(t)}{G(0)}=\frac{3}{\sqrt{\pi}}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)}{(2k+3)(k+3)!}\left[\frac{\tau_0}{t}\right]^{k+3/2},$$

whose first few terms may be written as

$$G(t)\sim\frac{\hbar^2\gamma^4\alpha\sqrt{\pi}}{20\sqrt{2}}\left[\frac{1}{3}\frac{t^{-3/2}}{D^{3/2}}-\frac{1}{20}\frac{a^2t^{-5/2}}{D^{5/2}}+\dots\right].$$

The leading term is identical with that obtained from the general argument above, and we see that the second term, in $t^{-5/2}$, depends on the hard core dimension a: one of the "microscopic details" of the system. Any model, which may include a realistic radial distribution function and a more appropriate description of particle motion, so long as it leads to diffusive behavior at long times, will give the same value for the leading term in the above expression. Clearly the other, higher-order, terms will depend on the specific details of the model as will the initial value $G(0)$. These assertions are supported by explicit calculations for the more sophisticated models[24–26,28] discussed in Sec. III B.

E. The dipolar spectral density function

The relaxation times in an NMR experiment are given in terms of the spectral density functions: Fourier transforms of the autocorrelation function. In particular we have

$$\begin{aligned} \frac{1}{T_1} &= J_1(\omega)+4J_2(2\omega) \; , \\ \frac{1}{T_2} &= \tfrac{3}{2}J_0(0)+\tfrac{5}{2}J_1(\omega)+J_2(2\omega) \; , \\ \frac{1}{T_{1\rho}} &= \tfrac{3}{2}J_0(2\omega_1)+\tfrac{5}{2}J_1(\omega)+J_2(2\omega) \end{aligned} \tag{3.15}$$

for spin-lattice relaxation, spin-spin relaxation, and spin-lattice relaxation in the rotating frame. Here ω_1/γ is the magnitude of the rotating frame magnetic field and

$$J_n(\omega)=\int_{-\infty}^{\infty} G_n(t)\exp(i\omega t)dt \; .$$

Given the autocorrelation function for a particular model it is possible (at least formally) to obtain the spectral density function through Fourier transformation. Alternatively one may start from the specification of the system and attempt to obtain the spectral density directly. Thus Hubbard[24] treated the above diffusion model (model A), obtaining the following expression for $J(\omega)$:

$$\begin{aligned} J(\omega)=G(0)6\tau_0 u^{-5}\{u^2-2+[(u^2+4u+2)\cos(u) \\ +(u^2-2)\sin(u)] \\ \times\exp(-u)\} \; , \end{aligned} \tag{3.16}$$

where

$$u=(2\omega\tau_0)^{1/2} \; .$$

This result for $J(\omega)$ may be expanded as a power series. The first few terms are

$$\begin{aligned} J(\omega)=6G(0)\tau_0 \Bigg[\frac{2}{15}-\frac{\sqrt{2}}{18}(\omega\tau_0)^{1/2}+\frac{\sqrt{2}}{90}(\omega\tau_0)^{3/2} \\ -\frac{4}{567}(\omega\tau_0)^{5/2}+\dots \Bigg] \; , \end{aligned} \tag{3.17}$$

and we have an ascending series in fractional powers of frequency. It is worth pointing out that this, also, is contrary to the assumption implicit in some semiquantitative models, that $J(\omega)$ must be smooth at the origin. In fact its singular behavior there is a necessary consequence of hydrodynamics.

As when considering $G(t)$ we shall now eliminate the quantities $G(0)$ and τ_0 in favor of the diffusion coefficient and the hard-core dimension. We then write $J(\omega)$ as

$$\begin{aligned} J(\omega)=\frac{2}{25}\frac{\pi\alpha}{D}\hbar^2\gamma^4 a^{-1}-\frac{1}{30}\frac{\pi\alpha}{D}\hbar^2\gamma^4\left[\frac{\omega}{D}\right]^{1/2} \\ +\frac{1}{300}\frac{\pi\alpha}{D}\hbar^2\gamma^4 a^2\left[\frac{\omega}{D}\right]^{3/2} \\ -\frac{1}{945}\frac{\pi\alpha}{D}\hbar^2\gamma^4 a^3\left[\frac{\omega}{D}\right]^{2}+\dots \; . \end{aligned} \tag{3.18}$$

We observe that the term in $\omega^{1/2}$ is independent of a. This is no accident. This term is purely hydrodynamic: independent of model. This is supported by the various models of Sec. III B all having the same term in $\omega^{3/2}$ even though the other terms will in general differ. We shall prove that this is a general result by showing that it follows from the asymptotic expansion for $G(t)$.

F. Watson's lemma

The autocorrelation function $G(t)$ and the spectral density function $J(\omega)$ are related by Fourier transformation. There are many properties of Fourier-transform pairs which are well known. Knowledge of one function permits evaluation of the other (at least in principle). A feature of one function will manifest itself in the behavior of the dual function. Thus derivatives at the origin of the time function are related to moment integrals of the frequency function. What may be called "local" features of the time function are in this way related to what may be called "global" features of the frequency function.

There are also relations involving coefficients of asymptotic expansions. Kubo[32] has given some examples of these. Considering, for example, an asymptotic expansion in inverse powers of time and a conventional power series expansion in ω of the dual function, there is a relation between the coefficient of ω^n and the coefficient of $1/t^{n+1}$. It is quite straightforward to derive this by repeatedly integrating by parts the Fourier-Laplace integral relating $J(\omega)$ to $G(t)$. Here, by contrast, local features of the time function are being related to local features of the frequency function.

Unfortunately the above method is not directly applicable in the present case. We are involved with expansions containing *fractional* powers. Here the usual machinery of Taylor expansion and differentiation, and integration by parts, are of no use. Nevertheless the basic physical ideas must still apply, and it turns out that there continues to be a relation between the coefficient of ω^n and the coefficient of $1/t^{n+1}$ even for nonintegral n. To demonstrate the plausibility of this we start from the Fourier-Laplace relations between $J(\omega)$ and $G(t)$

$$J(\omega)=2\,\mathrm{Re}\int_0^{\infty} G(t)\exp(i\omega t)dt \; , \tag{3.19a}$$

$$G(t)=\frac{1}{\pi}\,\mathrm{Re}\int_0^{\infty} J(\omega)\exp(-i\omega t)d\omega \; , \tag{3.19b}$$

which apply since both $G(t)$ and $J(\omega)$ are real and even functions, and these expressions hold for the *magnitudes* of t and ω. We use an integral identity that is essentially the definition of the gamma function, valid for noninteger n:

$$\int_0^\infty x^{n-1}\exp(-\mu x)dx=\frac{1}{\mu^n}\Gamma(n)\ . \tag{3.20}$$

Making the substitution $x\to\omega$ and $\mu\to it$, and taking the real part of our result we obtain

$$\begin{aligned}\mathrm{Re}\int_0^\infty \omega^{n-1}\exp(-i\omega t)d\omega&=\mathrm{Re}\frac{1}{(it)^n}\Gamma(n)\\ &=\cos(n\pi/2)\Gamma(n)/t^n\ ,\end{aligned} \tag{3.21}$$

which may be compared with Eq. (3.19a) above. This indicates that if $G(t)$ has a term in t^{-n} then this leads to a term in ω^{n-1} for the spectral density function $J(\omega)$, the coefficients being proportional. Thus the relation does indeed generalize to noninteger n. This result, of course, includes the result for integer n, however, we note that for terms where n is an odd integer the constant of proportionality is zero.

For the case of $n=\frac{3}{2}$, it then follows, since $\Gamma(\frac{3}{2})=\sqrt{\pi}/2$ and $\cos(3\pi/4)=-1\sqrt{2}$, that the term $a/t^{3/2}$ in $G(t)$ corresponds to a term $-2(2\pi)^{1/2}a\omega^{1/2}$ in $J(\omega)$.

The rigorous mathematical treatment of the above result for series expansions is embodied in what is known as Watson's lemma.[33] This states that if a function $F(x)$ has an expansion

$$F(x)=\sum_{s=0}^{\infty}a_s x^{(s+\lambda-\mu)/\mu}$$

then its Laplace transform (variable t) may be expressed by the asymptotic series

$$\sum_{s=0}^{\infty}\Gamma\left[\frac{s+\lambda}{\mu}\right]a_s t^{-(s+\lambda)/\mu}\quad \text{as } t\to\infty\ ,$$

where s, λ, and μ are positive integers. There are convergence conditions on the result that we do not need to consider here. Fundamentally, the lemma tells us that there is a relation between the coefficients of the small argument expansion and those of the large argument asymptotic expansion of the dual function. Some terms are lost in going from the Laplace transform to the Fourier transform, on taking the real part of a complex quantity; for integer-only expansions all are lost for the cosine transform pair (the odd-integer n case above).

The consequence of Watson's lemma for the problem in hand is that the coefficient of $\omega^{1/2}$ may be found directly from the asymptotic expansion of $G(t)$, from the coefficient of the $1/t^{3/2}$ term. And since we showed that that term was purely hydrodynamic and model independent, then the same must follow for the $\omega^{1/2}$ term. It is thus a general result that at low frequencies the spectral density function deviates from its zero-frequency value by a term in the *square root* of the frequency. We have

$$J(\omega)=J(0)-\frac{1}{30}\frac{\pi\alpha}{D}\hbar^2\gamma^4\left[\frac{\omega}{D}\right]^{1/2}+\dots\ . \tag{3.22}$$

Although the value of $J(0)$ depends somewhat on the microscopic details of the motion, the coefficient of $\omega^{1/2}$ does not. This term alone (as is its time domain counterpart) is determined solely by macroscopic-hydrodynamic quantities.

The expressions for T_1 and T_2 in the low-frequency limit, and for $T_{1\rho}$ in the high-ω_0, low-ω_1 limit are then

$$\begin{aligned}\frac{1}{T_1(\omega)}&=\frac{1}{T_1(0)}-\frac{(1+4\sqrt{2})}{30}\frac{\pi\alpha\hbar^2\gamma^4}{D^{3/2}}\omega^{1/2}+\dots\ ,\\ \frac{1}{T_2(\omega)}&=\frac{1}{T_2(0)}-\frac{(5+2\sqrt{2})}{60}\frac{\pi\alpha\hbar^2\gamma^4}{D^{3/2}}\omega^{1/2}+\dots\ ,\\ \frac{1}{T_1\rho(\omega_1)}&=\frac{1}{T_1\rho(0)}-\frac{\sqrt{2}}{20}\frac{\pi\alpha\hbar^2\gamma^4}{D^{3/2}}\omega_1^{1/2}+\dots\ .\end{aligned} \tag{3.23}$$

IV. ANALYSIS OF EXPERIMENTAL DATA

A. Extraction of diffusion coefficients

It follows from the treatment in the previous sections that the low-frequency behavior of the relaxation times is characterized by a $\omega^{1/2}$ variation. And whenever this behavior is observed the diffusion coefficient may be obtained directly from the data without any knowledge of the microscopic aspects of the system. For solid ^{3}He the relaxation-time equations may be written in terms of measured quantities as

$$\frac{V_m\ (\mathrm{cm}^3)}{T_1\ (\mathrm{ms})}=\mathrm{const}-2.019\times10^{-3}\frac{1}{D^{3/2}}[f_0\ (\mathrm{MHz})]^{1/2}\ , \tag{4.1}$$

$$\frac{V_m\ (\mathrm{cm}^3)}{T_2\ (\mathrm{ms})}=\mathrm{const}-1.187\times10^{-3}\frac{1}{D^{3/2}}[f_0\ (\mathrm{MHz})]^{1/2}\ , \tag{4.2}$$

where the diffusion coefficient D is in units of cm^2 s^{-1} and V_m is the molar volume.

We have analyzed available relaxation-rate data by plotting them on an $f^{1/2}$ scale. At lower molar volumes only the lower-frequency points follow the linear asymptote, but at higher molar volumes, where the diffusion is more rapid, more of the points fall on the limiting straight line. Some typical plots are shown. In Fig. 1 we show T_1 measurements for a molar volume of 20.1 cm^3.[34] We see that the first four points follow the $\omega^{1/2}$ law very

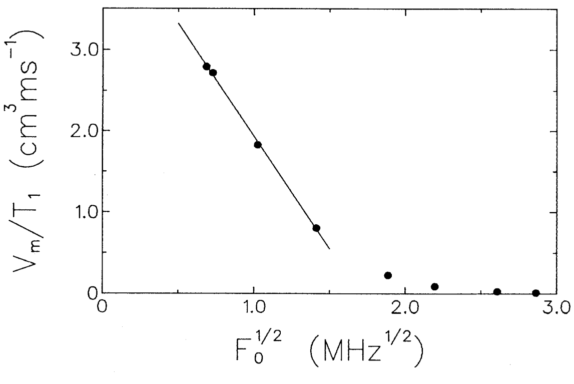

FIG. 1. T_1 for molar volume 20.1 cm^3.

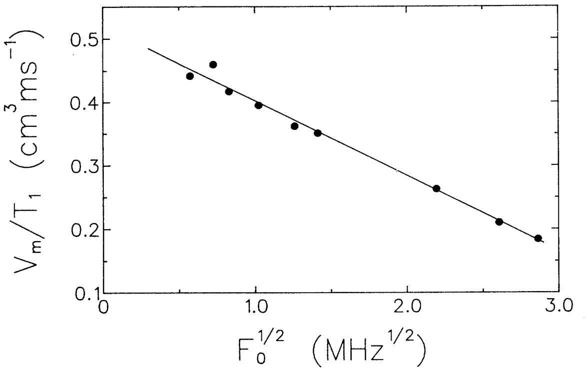

FIG. 2. T_1 for molar volume 22.1 cm^3.

well but the points at higher frequencies start deviating quite rapidly. In Fig. 2 we show T_1 data for a molar volume of 22.1 cm^3.[34] Here all points are seen to follow the straight line. And in Fig. 3 we show T_2 data at the same molar volume.

Analysis of the data was performed by fitting a straight line through those points following the visibly linear law, using a least-squares method. From the slope of the lines the diffusion coefficient was obtained using Eqs. (4.1) and (4.2). In Table I we give T_1 data from Richardson, Hunt, and Meyer,[34] while Table II shows the data extracted from Richards, Hutton, and Giffard.[1] In Table III we show T_2 data[34] analyzed similarly.

TABLE I. T_1 data, Richardson, Hunt, and Meyer (Ref. 34).

Molar volume V_m (cm^3)	Slope $V_m/(T_1f^{1/2})$	Diff. coeff. D (cm^{2}s^{-1})
20.1	2.763	1.75×10^{-9}
20.4	2.612	1.82×10^{-9}
21.3	0.4293	6.05×10^{-9}
21.8	0.169	1.13×10^{-8}
22.1	0.118	1.43×10^{-8}
22.4	0.1099	1.50×10^{-8}
23.8	0.01665	5.28×10^{-8}
24.1	0.0153	5.58×10^{-8}
24.6	5.402×10^{-3}	1.12×10^{-7}

B. Comparison with conventional measurements

We compare the values for the diffusion coefficient, obtained above, with those found from the conventional measurements using spin echoes in a magnetic-field gradient.[13] Two sets of measurements have been published: those of Thompson, Hunt, and Meyer[17] and those of Reich.[16] In Fig. 4 we have plotted the values of D obtained by both methods against molar volume. The filled points have been obtained, by the above analysis, from relaxation-time measurements. The open points are from conventional measurements. The agreement between measurements made in these two different ways is most gratifying. Although different, both techniques are purely hydrodynamic and so they should, fundamentally, give the same values. The good agreement is indicative that the dipolar autocorrelation function has a long-time tail of the form presented above and that the method of analysis is therefore appropriate.

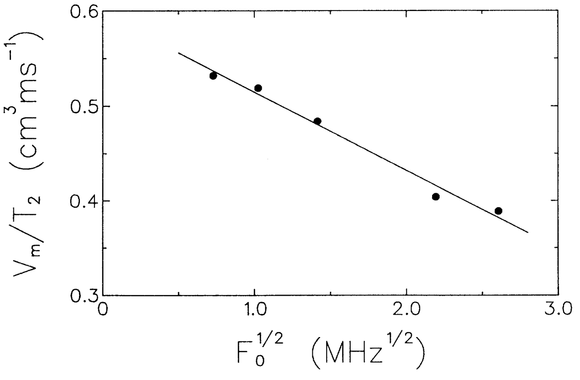

FIG. 3. T_2 for molar volume 22.1 cm^3.

While the conventional method for measuring diffusion gives reliable values at the lower densities, we see that as the density increases, for molar volumes below 23 cm^3, there is already considerable dispersion in the data points. The method becomes difficult for smaller values of D. And there are no points for molar volumes of 21 cm^3 or less; the diffusion is too slow. However the present method is perfectly adequate, giving good values for molar volumes down to 20 cm^3. And this could easily be extended to higher densities, into the hcp phase, using rotating frame measurements of $T_1\rho$.

In Fig. 4 we also show a solid line. This is the diffusion coefficient as calculated from the effective pairwise exchange frequency[10] for the bcc lattice:

$$D=4.12(J/2\pi)a^2\ , \tag{4.3}$$

where the values of J are found from the formula of Panczyk and Adams:[35]

$$\frac{J}{2\pi}=13.67\left[\frac{V_m}{24}\right]^{18.13}\ \text{MHz}\ . \tag{4.4}$$

The line is seen to follow the data quite well. This agreement is, however, more interesting since now some microscopical considerations are involved.

The validity of both Eqs. (4.3) and (4.4) relies on the assumption that only pairwise (and three-particle) exchange processes are involved. To the extent that higher-order excitations are involved the equations may be regarded as

TABLE II. T_1 data, Richards, Hatton, and Giffard (Ref. 1).

Molar volume V_m (cm^3)	Slope $V_m/(T_1f^{1/2})$	Diff. coeff. D (cm^{2}s^{-1})
20.0	1.56	2.56×10^{-9}
20.6	1.104	3.22×10^{-9}
21.05	0.4396	5.95×10^{-9}
23.0	0.0341	3.27×10^{-8}

TABLE III. T_2 data, Richardson, Hunt, and Meyer (Ref. 34).

Molar volume V_m (cm^3)	Slope $V_m/(T_2 f^{1/2})$	Diff. coeff. D (cm^{2}s^{-1})
20.1	1.393	1.94×10^{-9}
20.4	0.9341	2.53×10^{-9}
21.3	0.2663	5.84×10^{-9}
21.8	0.0824	1.28×10^{-8}
22.1	0.0585	1.60×10^{-8}
22.4	0.0408	2.04×10^{-8}
24.1	6.04×10^{-3}	7.28×10^{-8}
24.6	1.0875×10^{-2}	4.92×10^{-8}

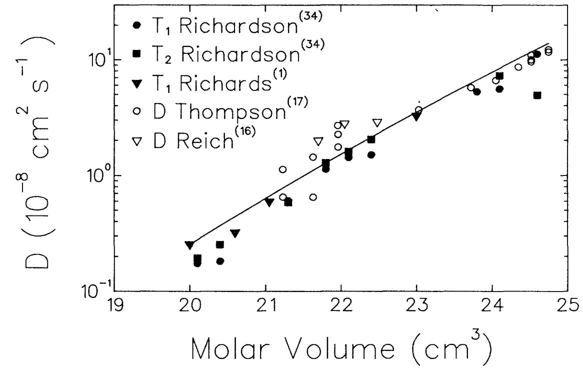

FIG. 4. Diffusion coefficient as a function of molar volume.

referring to an "effective" pair exchange frequency—possibly different for each equation.

The derivation of Eq. (4.3) relating D to the exchange frequency relies on a number of assumptions about the shape of a spin-correlation function. Cowan, Mullin, and Nelson[12] have shown how bounds may be established for such results, and following that method one finds that while Eq. (4.3) is the likely result, the value of D must fall within the interval

$$2.97(J/2\pi)a^2 < D < 4.94(J/2\pi)a^2 .$$

However previous measurements of D by spin echoes have supported the result in Eq. (4.3).

The relation between J and the molar volume, Eq. (4.4) also relies on details of a microscopical calculation. Panczyk and Adams obtained their result from measurements of the exchange frequency contribution to the pressure at constant volume. Their analysis involves a high-temperature expansion of the pressure found from the partition function, a quantity of microscopic origin. However, here again, their result is in good agreement with measurements of J made in other ways.[4]

V. CONCLUSION

We have shown that for low frequencies the dipolar spectral density function has the form $J(\omega)=J(0)-A\omega^{1/2}$. This is a consequence of the hydrodynamic behavior of the system at long times; the constant a is a function of the diffusion coefficient, but it is independent of the microscopic details of the system. We have analyzed spin relaxation-time measurements in the bcc phase of solid ^{3}He, obtaining values for the diffusion coefficient in this way. These results are in good agreement with conventional measurements, and they extend to higher densities where measurements were previously unavailable. The results are also in good agreement with D values inferred from exchange frequency measurements. This is evidence that it is the quantum exchange which is responsible for the diffusion. The method is suited to the measurements of slow diffusion through studies of $T_{1\rho}$.

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