

varies between  $-\pi/2$  and  $\pi/2$ . Taking these values as limits of integration on  $\phi$ , we obtain for the scattering probability into the zone  $d(\Delta\theta_z)$

$$\omega(\Delta\theta_z)d(\Delta\theta_z) = (\pi/2)e^4E^{-2}d(\Delta\theta_z)(\Delta\theta_z)^{-3}. \quad (D15)$$

This is the pure coulomb result.

The scattering probability in the magnetic case tacitly assumed one particle/cm<sup>2</sup>-sec in the direction of

the magnetic field incident on the scatterer. The scattering probability in the coulomb case assumed one particle/cm<sup>2</sup>-sec in the direction of the velocity incident on the scatterer. Since the assumption in the coulomb description is the equivalent of  $E_z^{1/2}/E^{1/2}$  particles/cm<sup>2</sup>-sec in the direction of the magnetic field, the value for this situation should be a factor of  $E_z^{1/2}/E^{1/2}$  lower than the magnetic value.

## Spin Diffusion in Gases at Low Temperatures\*†

V. J. EMERY

*Department of Physics, University of California Berkeley, California*

(Received 30 August 1963)

It is shown that the first approximation to the spin-diffusion coefficient  $D$  of a gas at low temperatures involves a scattering cross section for distinguishable particles only, so that  $D$  is different from the self-diffusion coefficient  $D_0$ . Quantum symmetry effects show up in the second approximation to  $D$  but the correction to the first approximation is small. The theoretical values of  $D$  for gaseous hydrogen and gaseous He<sup>3</sup> agree quite well with experimental results.

### I. INTRODUCTION

RECENTLY, nuclear magnetic resonance experiments have been used to measure the spin-diffusion coefficient  $D$  in gaseous hydrogen<sup>1,2</sup> between 20 and 55°K, and<sup>3</sup> in gaseous He<sup>3</sup> between 1.7 and 4.2°K. In these experiments, it is usually assumed that  $D$  is identical with the self-diffusion coefficient<sup>4</sup>  $D_0$  of the gas and that the nuclear spin is merely a label which allows the diffusion to be observed. However, it turns out that the values<sup>5,6</sup> of  $D_0$  given by the Chapman-Enskog theory of transport processes are systematically smaller than the experimental values of  $D$ , and that they lie outside the limits of experimental error.

The object of this paper is to show that, in fact,  $D_0$  is not the quantity measured in these experiments and that an appropriate expression for  $D$  reproduces the experimental results quite well. The distinction between  $D_0$  and  $D$  arises only in those situations in which it is necessary to treat the scattering of particles quantum mechanically. For a two-component gas at

the temperatures under consideration, the coefficient of diffusion of component 1 relative to component 2 is given by<sup>4</sup>

$$D_{12} = \frac{3}{8nm} \frac{kT}{\Omega_{12}^{(1,1)}}, \quad (1)$$

where  $T$  is the temperature,  $k$  is Boltzmann's constant,  $n$  the total number density, and  $m$  the mass of the particles (assumed to be the same for each component). Quantum mechanical effects enter through  $\Omega_{12}^{(1,1)}$  which is a special case of

$$\Omega_{12}^{(n,t)} = \left(\frac{kT}{\pi m}\right)^{1/2} \int_0^\infty d\gamma e^{-\gamma^2} \gamma^{2t+3} Q_{12}^{(n)}(\gamma), \quad (2)$$

where  $\gamma^2$  is the relative kinetic energy of the pair of particles divided by  $kT$ , and

$$Q_{12}^{(n)} = \frac{\pi}{\gamma} \left(\frac{m}{kT}\right)^{1/2} \int_0^\pi dx \sin x (1 - \cos^n x) \alpha_{12}(\gamma, x). \quad (3)$$

$\alpha_{12}(\gamma, x)$  is proportional to the differential cross section for scattering of a particle from component 1 by a particle from component 2 at a relative kinetic energy  $\gamma^2 kT$ .  $x$  is the scattering angle.

The self-diffusion coefficient  $D_0$  is defined as the limit of  $D_{12}$  when components 1 and 2 become identical, and  $\alpha_{12}(\gamma, x)$  is taken to be proportional to the properly symmetrized differential cross section for the scattering of identical particles. Thus, for example, in pure orthohydrogen, the particles have nuclear spin  $I=1$  and rotational angular momentum  $J=1$ , and  $D_0$  has

\* This work was carried out while the author was a summer visitor at Brookhaven National Laboratory, Upton, New York.

† Work done under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup> A. Hartland and M. Lipsicas, *Phys. Letters* **3**, 212 (1963).

<sup>2</sup> A. Hartland and M. Lipsicas, following paper, *Phys. Rev.* **133**, A665 (1963).

<sup>3</sup> K. Luszczynski, R. E. Norberg, and J. E. Opfer, *Phys. Rev.* **128**, 186 (1962).

<sup>4</sup> J. O. Hirschfelder, C. F. Curtiss, and R. Byron Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

<sup>5</sup> E. G. D. Cohen, M. J. Offerhaus, J. M. J. Van Leeuwen, B. W. Roos, and J. deBoer, *Physica* **22**, 791 (1956).

<sup>6</sup> E. G. D. Cohen, M. J. Offerhaus, and J. deBoer, *Physica* **20**, 501 (1954).

TABLE I. The spin diffusion coefficient in gaseous He<sup>3</sup>.

$T$ (°K)	$D_{mn}(10^{-6} \text{ g cm}^{-1} \text{ sec}^{-1})$	
	Theory	Experiment
2	10	10
3	13	13.8
4	16	17

been obtained by using<sup>5</sup>

$$\Omega_{12}^{(1,1)} = (5/9)\Omega_s^{(1,1)} + (4/9)\Omega_a^{(1,1)}, \quad (4)$$

where  $\Omega_s^{(1,1)}$  and  $\Omega_a^{(1,1)}$  come from scattering in even and odd states, respectively. If this form of  $\Omega_{12}^{(1,1)}$  is substituted into Eq. (1), it fails to reproduce the measured values of  $D$  in hydrogen.<sup>1,2</sup>

Hartland and Lipsicas<sup>1</sup> pointed out that it is possible to fit their experiments on hydrogen by calculating cross sections as if particles with different values of  $m_I$  or  $m_J$  were distinguishable so that

$$\Omega_{12}^{(1,1)} = (1/9)\Omega_s^{(1,1)} + (8/9)\Omega_{ns}^{(1,1)}, \quad (5)$$

where  $\Omega_{ns}^{(1,1)}$  refers to distinguishable particle scattering and is obtained from

$$Q_{ns}^{(1)}(\gamma) = \frac{4\pi\hbar^2}{mkT} \frac{1}{\gamma^2} \sum_{l=0,1,2}^{\infty} (l+1) \sin^2(\eta_{l+1} - \eta_l), \quad (6)$$

where  $\eta_l$  are the phase shifts for scattering at relative kinetic energy  $\gamma^2 kT$ .

However, this expression is still not quite correct. It is always possible to argue that the differential cross sections may be calculated as if particles with different values of  $m_I$  or  $m_J$  were distinguishable. If then the transport process treats all particles in the same way, whatever their spin, the end result will be the same as if the indistinguishable particle cross section was used. Thus, for example, the viscosity and thermal conductivity coefficients<sup>4</sup> involve  $Q^{(2)}(\gamma)$  and since  $(1 - \cos^2 x)$  is an even function of  $\cos x$ , the interference terms between odd and even angular momentum states which are odd functions of  $\cos x$  vanish on integration over  $x$ , and the expressions corresponding to Eqs. (4) and (5) give the same result.

In a diffusion process, this statement is no longer true since  $(1 - \cos x)$  is neither an odd function nor an even function of  $\cos x$ , and it is necessary to go back to a much earlier stage in the calculation. Now, collisions between particles of the same component do not inhibit diffusion directly since as a result of momentum conservation they do not change the flux of one component relative to the other. They may modify diffusion indirectly (see Sec. II) but usually this effect is small and it has been neglected in the derivation of Eq. (1). In the same approximation, spin-diffusion is not affected by collision between particles in the same spin

state and so nonsymmetrized cross sections

$$\Omega_{12}^{(1,1)} = \Omega_{ns}^{(1,1)}, \quad (7)$$

may be used to calculate  $D$  from Eq. (1).

Physically there must be something (in this case the spin wave functions) to distinguish a set of particles from the (otherwise) identical particles through which they are diffusing. If not, the diffusion could not be observed. Thus,  $D_0$  as given by Eqs. (1) and (4) can never be measured, and quantum symmetry effects would show up in a diffusion process only if corrections to Eq. (1) were important.

Equations (1), (7), (2), and (6) also give the spin-diffusion coefficient in a mixture of orthohydrogen and parahydrogen, provided  $n$  is the total number density. Thus,  $D$  is independent of the relative ortho-para concentrations. This result is consistent with the measurements of Hartland and Lipsicas,<sup>1,2</sup> and so also are the calculated absolute values of  $D$ . [There is little numerical difference between the results given by Eqs. (5) and (7).]

DeBoer *et al.*<sup>6</sup> did not calculate  $\Omega_{ns}^{(1,1)}$  for gaseous He<sup>3</sup>, but it may be determined from the tabulated scattering phase shifts.<sup>7</sup> The results are shown in Table I. It can be seen that they agree with the experimental values within the maximum experimental error of 6%.

In the next section, these remarks will be amplified into a detailed derivation of Eqs. (1), (2), (6), and (7) for gaseous He<sup>3</sup>, and the way in which the calculation may be carried out for hydrogen will be indicated. The Bloch-Torrey equation<sup>8</sup> for the decay of magnetization by spin diffusion will be derived from a Boltzmann equation. The discussion avoids several of the assumptions made by Hone<sup>9</sup> in his calculation of the spin-diffusion coefficient in a Fermi liquid.

## II. CALCULATION OF THE SPIN-DIFFUSION

### 1. Gaseous He<sup>3</sup>

In a spin-echo experiment, the system is given an initial magnetization  $\mathbf{M}_0$  by means of a magnetic field  $\mathbf{H}$  and then a pulsed rf field is used to turn  $\mathbf{M}_0$  so that it makes an angle  $\alpha$  with  $\mathbf{H}$ . For times which are short compared to the spin relaxation time, the subsequent motion of the magnetization  $\mathbf{M}$  is given by the Bloch-Torrey equation<sup>8</sup>

$$\partial \mathbf{M} / \partial t = (\mu / \hbar I) (\mathbf{M} \times \mathbf{H}) + \nabla \cdot D \nabla (\mathbf{M} - \mathbf{M}_0), \quad (8)$$

where  $\mu$  and  $I$  are, respectively, the magnetic moment and spin of the nucleus. Experimentally,<sup>1-3</sup> the decay of  $M$  according to Eq. (8) is observed by applying further rf pulses to produce echoes, but the problem

<sup>7</sup> J. deBoer, J. Van Kranendonk, and D. Compaan, *Physica* **16**, 545 (1950).

<sup>8</sup> H. C. Torrey, *Phys. Rev.* **104**, 563 (1956).

<sup>9</sup> D. Hone, *Phys. Rev.* **121**, 669 (1961).

here is to derive the equation together with an expression for  $D$ .

In the presence of the magnetic fields, the particles are not in eigenstates of spin, and for  $\text{He}^3$ , whose nuclear spin is  $\frac{1}{2}$ , it is necessary to use a Boltzmann equation for a  $(2 \times 2)$  matrix  $\rho(\mathbf{v}, \mathbf{r}, t)$  which represents the distribution of spin of a particle with velocity  $\mathbf{v}$  and position  $\mathbf{r}$  at time  $t$ . This equation may be derived from the equations of motion for the one-particle Green function<sup>10</sup> of the system in the long-wavelength limit and it is a plausible generalization

$$\frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \frac{\partial \rho}{\partial \mathbf{r}} - \frac{1}{2n} \left[ \frac{\partial \epsilon}{\partial \mathbf{r}}, \frac{\partial \rho}{\partial \mathbf{v}} \right] + \frac{i}{\hbar} [\epsilon, \rho]_- = I(\rho) \quad (9)$$

of the usual Boltzmann equation. Here,  $[a, b]_+$  and  $[a, b]_-$  are, respectively, the anticommutator and the commutator of  $(2 \times 2)$  matrices  $a$  and  $b$ , and  $\epsilon$  is the single-particle energy

$$\epsilon = \frac{1}{2} m v^2 - \mu (\boldsymbol{\sigma} \cdot \mathbf{H}), \quad (10)$$

where  $\boldsymbol{\sigma}$  is the spin vector.  $I(\rho)$  is the collision term. The first three terms on the left-hand side of Eq. (9) are the usual streaming terms in which matrix products have been symmetrized. The remaining term on the left-hand side represents the couple which  $\mathbf{H}$  exerts on the spins.

At the temperature of interest, it is possible<sup>4</sup> to neglect the final-state statistical factors in the collision term and

$$I(\rho(1)) = 2\pi \int d\mathbf{v}_2 \int_0^\pi dx \sin x \{ \alpha_a(x, \gamma) [\rho(3)\rho(4) - \rho(1)\rho(2)] + \alpha_{ns}(x, \gamma) [\rho(3)(\text{Tr}\rho(4) - \rho(4)) - \rho(1)(\text{Tr}\rho(2) - \rho(2))] \}, \quad (11)$$

where  $\rho(i)$  is  $\rho(\mathbf{v}_i, \mathbf{r}, t)$ ;  $\mathbf{v}_1$  and  $\mathbf{v}_2$  are initial velocities, and the final velocities  $\mathbf{v}_3$  and  $\mathbf{v}_4$  must satisfy momentum conservation and correspond to the scattering angle  $x$ . The quantities  $\alpha_a(x, \gamma)$  and  $\alpha_{ns}(x, \gamma)$  are proportional to the differential cross sections which lead to  $\Omega_a^{(1,1)}$  and  $\Omega_{ns}^{(1,1)}$  defined in Sec. I. It is easy to verify that, when  $\rho$  is a diagonal matrix,  $I(\rho(1))$  reduces to the usual collision integral for a two-component system.

In the absence of a magnetic field,  $\rho$  is simply  $(f_0 I_2)$ , where  $I_2$  is the  $(2 \times 2)$  unit matrix and  $f_0$  is a Maxwell distribution function. When  $\mathbf{H}$  is switched on,  $\rho$  becomes

$$\rho_E = f_0 [I_2 + (\boldsymbol{\sigma} \cdot \mathbf{M}_0) / \mu n] \quad (12)$$

to first order in  $\mathbf{H}$  since the susceptibility follows Curie's law. Immediately after the first rf pulse,  $\mathbf{M}$  is no longer parallel to  $\mathbf{H}$  and  $\rho$  is then

$$\rho_0 = f_0 [I_2 + (\boldsymbol{\sigma} \cdot \mathbf{M}) / \mu n]. \quad (13)$$

<sup>10</sup> L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

The system will relax from this initial distribution function.

Enskog's method<sup>4</sup> of solving the Boltzmann equation is to construct a solution to first order in the collision rate.

Suppose

$$\rho = \rho_0 + \rho_1. \quad (14)$$

Then to first order in  $\rho_1$ , Eq. (9) becomes

$$\frac{\partial \rho_0}{\partial t} + \mathbf{v} \cdot \frac{\partial \rho_0}{\partial \mathbf{r}} - \frac{1}{2m} \left[ \frac{\partial \epsilon}{\partial \mathbf{r}}, \frac{\partial \rho_0}{\partial \mathbf{v}} \right] + \frac{i}{\hbar} [\epsilon, \rho_0]_- = I_1(\rho). \quad (15)$$

$I_1(\rho)$  is calculated from Eq. (11) to first order in  $\rho_1$ .  $I(\rho_0)$  vanishes and  $\rho_0$  may be replaced by  $(f_0 I_2)$  to the lowest order in  $H$ . Then if

$$\rho_1 = f_0 \varphi, \quad (16)$$

$I_1(\rho(1))$  is given by

$$I_1(\rho(1)) = 2\pi \int d\mathbf{v}_2 \int_0^\pi \sin x dx f_0(1) f_0(2) \times \{ \alpha_a(x, \gamma) [\varphi(3) - \varphi(1) + \varphi(4) - \varphi(2)] + \alpha_{ns}(x, \gamma) [\varphi(3) - \varphi(1) + \varphi(2) - \varphi(4)] + \text{Tr}(\varphi(4) - \varphi(2)) I_2 \}. \quad (17)$$

Now, using Eq. (13), Eq. (15) becomes

$$\frac{f_0}{\mu n} \left[ \boldsymbol{\sigma} \cdot \frac{\partial \mathbf{M}}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} \boldsymbol{\sigma} \cdot (\mathbf{M} - \mathbf{M}_0) - \frac{\mu}{\hbar I} (\mathbf{M} \times \mathbf{H}) \right] = I_1(\rho). \quad (18)$$

$\partial \mathbf{M} / \partial t$  has to be found from the equation of change which is obtained by multiplying Eq. (9) by  $\mu \boldsymbol{\sigma}$ , taking the trace of both sides, and integrating over  $\mathbf{v}$ . The collision term gives no contribution and the result is

$$\frac{\partial \mathbf{M}}{\partial t} + \mu \text{Tr} \boldsymbol{\sigma} \text{div} \int \mathbf{v} \rho d\mathbf{v} - \frac{\mu}{\hbar I} (\mathbf{M} \times \mathbf{H}) = 0. \quad (19)$$

For use in Eq. (18),  $\partial \mathbf{M} / \partial t$  has to be evaluated in the lowest approximation  $\rho = \rho_0$ , and then it is simply  $(\mu / \hbar I) (\mathbf{M} \times \mathbf{H})$ . Thus Eq. (18) becomes

$$\left( \frac{f_0}{\mu n} \right) \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} \boldsymbol{\sigma} \cdot (\mathbf{M} - \mathbf{M}_0) = I_1(\rho). \quad (20)$$

The solution of this equation has the form

$$\varphi = g(v) \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} \boldsymbol{\sigma} \cdot (\mathbf{M} - \mathbf{M}_0), \quad (21)$$

where, from Eqs. (17) and (20)

$$\left(\frac{f_0}{\mu n}\right)_{\mathbf{v}} = 2\pi \int d\mathbf{p}_2 \int_0^\pi dx \sin x f_0(1) f_0(2) \\ \times \{ \alpha_a(x, \gamma) [\mathbf{v}_3 g(v_3) - \mathbf{v}_1 g(v_1) + \mathbf{v}_4 g(v_4) - \mathbf{v}_2 g(v_2)] \\ + \alpha_{ns}(x, \gamma) [x_3 g(v_3) - x_1 g(v_1) - x_4 g(v_4) + x_2 g(v_2)] \}. \quad (22)$$

This equation is independent of the direction of  $\mathbf{M}$  although, in general, this would not be so. The diffusion is limited by scattering of particles from neighboring regions of space in which the spins, on average, point in different directions. The forces are spin-independent but the scattering is not, since the relative wave functions must be antisymmetrized. In deriving Eq. (22) only the lowest order in  $\mathbf{M}$  has been retained. In this approximation, particles from a region in space in which the spins are, on average, parallel to  $\mathbf{M}$ , scatter from particles in a region of space in which the average spin is zero, so that the result is independent of the direction of  $\mathbf{M}$ .

Equation (22) may be solved by expanding  $g(v)$  in a series of Sonine polynomials.<sup>4</sup> In practice<sup>6</sup> it is sufficient to use the first term of the series and to set  $g(v)$  equal to a constant  $g_0$ . Then, by conservation of momentum, the term involving  $x_a$  vanishes, and

$$g_0 = -\frac{3}{8} [\mu n^2 \Omega_{ns}^{(1,1)}]^{-1}, \quad (23)$$

so that

$$\rho = f_0 \left[ I_2 + \frac{(\boldsymbol{\sigma} \cdot \mathbf{M})}{\mu n} - \frac{3}{8} \frac{1}{\mu n^2 \Omega_{ns}^{(1,1)}} \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} \boldsymbol{\sigma} \cdot (\mathbf{M} - \mathbf{M}_0) \right]. \quad (24)$$

If this expression is substituted into the equation of change [Eq. (19)] then the Bloch-Torrey equation [Eq. (8)] is obtained with  $D$  given by

$$D = \frac{3}{8} [kT / mn \Omega_{ns}^{(1,1)}]. \quad (25)$$

In the higher approximations to  $g(v)$ ,  $\alpha_a$  will appear and, in principle, it could produce a non-negligible effect (a similar effect is essential for superconductivity in

metals.<sup>11</sup>) In practice<sup>5,6</sup> the corrections are not large for hydrogen or for gaseous He<sup>3</sup>. For liquid helium three in the Fermi liquid region, they have not been estimated.<sup>9</sup>

## 2. Spin Diffusion in Hydrogen Gas

Orthohydrogen molecules have nuclear spin  $I=1$ , and rotational angular momentum  $J=1$ . The discussion of He<sup>3</sup> showed that the spin diffusion is isotropic so that  $D$  may be calculated by considering only the diagonal elements of Eq. (9) or, more simply, by discussing the initial diffusion of  $\mathbf{M}$  when  $\mathbf{H}$  is switched off suddenly and no pulsed rf fields are applied.

Since the magnetic effects and the two-particle forces are taken to be independent of  $J$ , it is necessary to consider four simultaneous scalar Boltzmann equations, one for each value of  $m_I$  and one for the parahydrogen. Once again, in the first approximation, collisions between particles with the same values of both  $I$  and  $J$  do not contribute. All other collisions involve nonsymmetrized cross sections and since the ortho-ortho and ortho-para potentials are assumed to be identical, only one cross section  $\Omega_{ns}^{(1,1)}$  enters.

If  $n_o$  and  $n_p$  are, respectively, the number densities of the ortho and para forms of hydrogen the result is

$$D = -\frac{3}{8} \frac{kT}{m(n_o + n_p) \Omega_{ns}^{(1,1)}}, \quad (26)$$

in agreement with Eqs. (1) and (7).

## ACKNOWLEDGMENTS

The author is indebted to Dr. Max Lipsicas for drawing his attention to the theoretical problem posed by his experimental results and for many discussions of spin-echo experiments. He would also like to thank Dr. R. L. Mills for his critical discussion of some aspects of the work, and to acknowledge the hospitality of the Department of Physics at Brookhaven National Laboratory.

<sup>11</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).