Influence of a Magnetic Field on the Spin-Diffusion in a Gas*

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On the basis of the Waldmann equation for neutral particles with spin, the influence of a homogeneous magnetic field on spin-diffusion in a gas has been studied. The spin-diffusion constant for the components of the magnetic moment perpendicular to the external field is decreased. Furthermore a transverse spin-flux is found which leads to a shift of the resonance frequency if the magnetization is spatially inhomogeneous. Both effects vanish at high densities.

Spin-diffusion plays an important role in nuclear spin induction (spin-echo) experiments [1] and provides a method for the measurement of self-diffusion constants [2]. A phenomenological Bloch equation [3] with a spin-diffusion term has been proposed by Torrey [4] for spin-relaxation in a spatially inhomogeneous fluid. In this theory spin-diffusion is characterized by a single transport constant, namely the spin-diffusion constant D_{spin} which was assumed to equal the particle (self)-diffusion constant D (apart from spin exchange contributions). This Bloch-Torrey equation proved successful to explain the experiments. If boundary effects are important Torrey's formula [4] for the attenuation of a spin-echo signal by spin-diffusion, however, has to be modified [5].

Here we shall deal with spin-diffusion in an unbounded dilute gas from a kinetic point of view. The main results to be reported are linked with the influence of a constant magnetic field on spin-diffusion via the magnetic moments of the particles.

It has been observed experimentally that transport constants, in particular heat conductivity and viscosity of paramagnetic gases [6] and of diamagnetic gases [7] (Senftleben-Beenakker effect) depend on an external magnetic field. A similar effect might be expected to occur with spin-diffusion. A theoretical investigation indeed shows that the diffusion constant for the components of the spin perpendicular to an external magnetic field depends on this field. The influence of the magnetic field on the spin-diffusion constant, however, is different from the influence of the field on the particle-diffusion constant [8]. Hence, contrary to Torrey's assumption, the spin-diffusion constant differs from the self-diffusion constant even if spin exchange processes are absent. Furthermore there is a "transverse" spin flux leading to a shift of the resonance frequency. For a given magnetic field both "difference effects", i. e. the difference between spin- and self-diffusion constants and the frequency shift vanish at high densities. This explains why the effects predicted — to the author's knowledge — have not yet been observed experimentally.

A kinetic treatment of the spin-diffusion problem based on the correlation function (Kubo) method already has been given by Fuknada and Kubo [9]. Starting from a transport (Boltzmann) equation for the singlet distribution function, spin-diffusion in a gas first has been attacked by Emery [10]. A concise treatment of this problem based on the Waldmann-Snider equation [11] and using a Chapman-Enskog solution procedure has been given by McCourt and Snider [12]. In all these papers the magnetic field dependence of the spin-diffusion constant has not been considered. Recently, the magnetic field depen-

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dence of spin-diffusion of conduction electrons has been studied [13].

Starting point for the present investigations is the WALDMANN equation [14] for a gas consisting of neutral particles with spin. A moment method has been applied to this transport equation to obtain a set of coupled linear differential equations for certain mean values characterizing the non-equilibrium state of the gas [15]. The transport relaxation equations needed for the discussion of the spin-diffusion problem are already contained in ref. [15].

Relaxation Equation for the Magnetization

Now let us write down the relaxation equation for the local magnetization per unit volume $\boldsymbol{m}$

$$\frac{\partial \boldsymbol{m}}{\partial t} + \nabla \cdot \mathbf{J} + \omega_{\mathrm{H}}\, \boldsymbol{h} \times \boldsymbol{m} + \text{relaxation term} = 0 . \tag{1}$$

Here the second rank (pseudo) tensor $\mathbf{J}$ denotes the flux of the magnetic moment per unit volume, ∇ is the gradient (Nabla) operator, $\omega_H = \gamma H$ is the precession frequency of a particle with the gyromagnetic ratio γ in a magnetic field with magnitude H; $\boldsymbol{h}$ is a unit vector parallel to the external magnetic field. The magnetic moment (with magnitude μ) of a particle is assumed to be parallel to the spin $\hbar\, \boldsymbol{s}$ of a particle. Then $\boldsymbol{m}$ and $\mathbf{J}$ are related to local averages (denoted by the bracket $\langle\ \rangle$) in the following way:

$$\boldsymbol{m} = n\, \mu\, \hbar \langle \boldsymbol{s} \rangle , \quad \mathbf{J} = n\, \mu\, \hbar \langle \boldsymbol{v}\, \boldsymbol{s} \rangle , \tag{2}$$

where n is the number density and $\boldsymbol{v}$ is the velocity of a particle. The magnetization density $\boldsymbol{m}$; the Cartesian trace of $\mathbf{J}$, the vector linked with the antisymmetric part and the symmetric irreducible (traceless) part of $\mathbf{J}$ are proportional to $\boldsymbol{b}^{(1)}$; $b^{(1)}$, $\boldsymbol{a}^{(2)}$ and $\mathbf{b}^{(1)}$ respectively which occur in ref. [15]. So, Eq. (1) corresponds to the first of the Eqs. (11.4) of ref. [15].

For the well known relaxation term of the BLOCH equation e. g. see ref. [3] or [4]. Of course, it also can be derived from a generalized Boltzmann equation [16]. By the way, to obtain the corect equilibrium polarization, the influence of the external magnetic field on the collision term has to be taken into account [17]; for the discussion of transport properties this effect is unimportant and has been neglected in ref. [15].

Transport Equation for the Spin-Flux

If spin-diffusion is the only transport process going on in a gas and if higher moments of the distribution function are neglected one readily infers from Eq. (11.2), (11.3) and (11.6) of ref. [15] that in steady state and if no magnetic field is applied, the Cartesian trace, the vector pertaining to the antisymmetric part and the symmetric irreducible part of $\mathbf{J}$ are proporional to div $\boldsymbol{m}$, rot $\boldsymbol{m}$ and the symmetric irreducible part of the tensor $\nabla \boldsymbol{m}$. The three transport constants involved are inversely proportional to the relaxation coefficients $\omega_{-0}^{(11)}$, $\omega_{-1}^{(22)}$, $\omega_{-2}^{(11)}$ as defined in ref. [15]. These relaxation coefficients become equal if the non-spherical part of the two-particle scattering amplitude operator is negligible compared with its spherical part [18]. This is fulfilled with NMR in a noble gas. Then spin-diffusion can be described by a single spin-diffusion constant. In the following, we confine our attention to this case and denote the common relaxation coefficient of the irreducible parts of $\mathbf{J}$ by ω_{sd}.

Now one transport relaxation equation can be written down for the second rank tensor $\mathbf{J}$. This equation is simpler in appearance if it is written for the (axial) vector $\boldsymbol{j} = \nabla \cdot \mathbf{J}$ which is needed in Eq. (1) anyway. In steady state this equation reads:

$$(k\,T/m)\; \Delta \boldsymbol{m} + \omega_H\, \boldsymbol{h} \times \boldsymbol{j} + \omega_{\mathrm{sd}}\, \boldsymbol{j} = 0 . \tag{3}$$

Here T is the temperature of the gas, k is Boltzmann's constant, m is the mass of a particle and Δ denotes the Laplacian. In general the equilibrium magnetization density $\boldsymbol{m}_0$ (which is parallel to $\boldsymbol{h}$) should be subtracted from $\boldsymbol{m}$ in the first term of Eq. (3). For simplicity we here assume $\Delta \boldsymbol{m}_0$ to vanish.

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Zero Field Spin-Diffusion Constant

Without a magnetic field ($\omega_H = 0$) Eq. (3) easily is solved for $\boldsymbol{j}$ to give:

$$\boldsymbol{j} = -D_{\text{spin}} \, \Delta \boldsymbol{m} \,, \tag{4}$$

where the spin-diffusion constant for zero magnetic field is

$$D_{\text{spin}} = (k\,T)/(m\,\omega_{\text{sd}}) \,. \tag{5}$$

If furthermore the spherical part of the scattering amplitude is independent of the spin, the spin-diffusion constant D_{spin} equals the particle (self)-diffusion constant D.

Plugging (4) into Eq. (1) one obtains the Bloch-Torrey equation [4].

Spin-Flux in the Presence of a Magnetic Field

In the presence of a magnetic field ($\omega_H \neq 0$) the spin-diffusion constant becomes a second rank tensor characterized by three scalar transport constants $D^{\parallel}_{\text{spin}}$, $D^{\perp}_{\text{spin}}$, and $D^{\text{trans}}_{\text{spin}}$. The solution of Eq. (3) now reads

$$\boldsymbol{j} = -D^{\parallel}_{\text{spin}} \, \boldsymbol{h}\,\boldsymbol{h}\cdot\Delta\boldsymbol{m} - D^{\perp}_{\text{spin}} \, (\Delta\boldsymbol{m} - \boldsymbol{h}\,\boldsymbol{h}\cdot\Delta\boldsymbol{m}) + D^{\text{trans}}_{\text{spin}} \, \boldsymbol{h}\times\Delta\boldsymbol{m} \,, \tag{6}$$

with

$$D^{\parallel}_{\text{spin}} = D_{\text{spin}} \,, \quad D^{\perp}_{\text{spin}} = (1+\varphi^2)^{-1} D_{\text{spin}} \,, \quad D^{\text{trans}}_{\text{spin}} = \varphi\,(1+\varphi^2)^{-1} D_{\text{spin}} \,, \tag{7}$$

where D_{spin} is the zero field spin-diffusion constant (5). The angle $\varphi = \omega_H/\omega_{\text{sd}}$ signifies the number of precessions which the magnetic moment of a particle undergoes during an effective time of free flight $\tau_{\text{sd}} = \omega_{\text{sd}}^{-1}$. Clearly the spin-diffusion constant $D^{\parallel}_{\text{spin}}$ for the component of the magnetization parallel to the external field is not influenced by this field. The spin-diffusion constant $D^{\perp}_{\text{spin}}$ for the components of $\boldsymbol{m}$ perpendicular to the field, on the other hand, is decreased by a factor $(1+\varphi^2)^{-1}$.

A comparison with the Senftleben effect for particle diffusion [8] shows that in the presence of a magnetic field the spin-diffusion constants $D^{\parallel,\perp,\text{trans}}_{\text{spin}}$ are not equal to the particle-diffusion constants $D^{\parallel,\perp,\text{trans}}$ even if D_{spin} equals D for zero magnetic field.

It is of importance to note that the influence of the magnetic field on spin-diffusion is a 1st order effect whereas the magnetic field dependence of the classical transport properties is a 2nd order effect [18a]. Here the non-spherical part of the scattering amplitude may be ignored. This is contrary to the Senftleben-Beenakker effect where the maximal change of classical transport properties in a magnetic field is determined by relaxation coefficients which are nonzero only if the non-sphericity of the scattering amplitude is taken into account [8].

Generalized Bloch-Torrey Equation

Substituting (6) into Eq. (1) one obtains a generalized Bloch-Torrey equation where the influence of the magnetic field on spin-diffusion has been taken into account:

$$\frac{\partial \boldsymbol{m}}{\partial t} + \left(\omega_H + \frac{\varphi}{1+\varphi^2} D_{\text{spin}} \Delta\right) \boldsymbol{h}\times\boldsymbol{m} + (\omega_{\parallel} - D_{\text{spin}}\Delta)\,\boldsymbol{h}\,\boldsymbol{h}\cdot(\boldsymbol{m}-\boldsymbol{m}_0) + \left(\omega_{\perp} - \frac{1}{1+\varphi^2} D_{\text{spin}} \Delta\right)(\boldsymbol{m} - \boldsymbol{h}\,\boldsymbol{h}\cdot\boldsymbol{m}) = 0 \,. \tag{8}$$

Here $\omega_{\parallel}$ and $\omega_{\perp}$ respectively are the relaxation constants for the components of the magnetization parallel and perpendicular to the external field. For a gas the difference $\omega_{\parallel} - \omega_{\perp}$ is negligible. Again the unit vector $\boldsymbol{h}$ has been assumed to be space independent. Clearly for a spatially homogeneous magnetization Eq. (8) reduces to the Bloch equation.

[18a] This difference stems from the fact that the spin-flux tensor — unlike the diffusion flow, the heat flow, and the friction pressure tensor — is a mean value of a quantity which explicitly depends on the spin.

Resolving the space dependence of an inhomogeneous magnetization into Fourier components one infers from (8) that the effective relaxation constants for the various Fourier components depend on their wave numbers and that there is a shift of the resonance frequency which is proportional to $\varphi(1+\varphi^2)^{-1} D_{\text{spin}}$.

It is of importance to note that

$$D^{\perp}_{\text{spin}} = (1+\varphi^2)^{-1} D_{\text{spin}}$$

instead of D_{spin} or D should appear in Torrey's formula [4] for the attenuation (of a spin-echo signal) by spin-diffusion.

Density Dependence of the Difference Effects

Finally, in order to estimate the importance of the difference $D_{\text{spin}}^{\perp} - D_{\text{spin}} = \varphi^2 (1+\varphi^2)^{-1} D_{\text{spin}}$ and of the frequency shift which is proportional to $D_{\text{spin}}^{\text{trans}} = \varphi (1+\varphi^2)^{-1} D_{\text{spin}}$ we consider the density dependence of these quantities. Replacing ω_{sd} by an effective cross section σ_{sd} according to

$$\omega_{\text{sd}} = n\, c\, \sigma_{\text{sd}}\,, \tag{9}$$

where c is a thermal velocity, one immediately sees that $\varphi = \omega_H / \omega_{\text{sd}}$ decreases with increasing density n for a fixed magnetic field. Hence both difference effects vanish at "high" densities.

To get an idea of the density or pressure range where the difference between $D_{\text{spin}}^{\perp}$ and D_{spin} should be noticeable we consider particles with a magnetic moment of one nuclear magneton in a magnetic field of 10 kOe at room temperature ($\omega_H \approx 10^8\ \text{s}^{-1}$, $c \approx 10^5\ \text{cm s}^{-1}$, $\sigma_{\text{sd}} \approx 4 \cdot 10^{-16}\ \text{cm}^2$).

Then φ will be close to 1 (i. e. $D_{\text{spin}}^{\perp} / D_{\text{spin}} \approx 1/2$) if the number density equals $0.25 \cdot 10^{19}\ \text{cm}^{-3}$. This density corresponds to a pressure of 100 Torr roughly. Clearly at lower values of the magnetic field lower densities are required to obtain the same value for φ.

Measurements of spin-diffusion [19] and NMR in gases [20] performed so far have been made at much higher densities. Hence the difference effects discussed in this paper could not be found. It should be possible, however, to measure the magnetic field and density dependence of the ratio $D_{\text{spin}}^{\perp} / D_{\text{spin}}$ in the pressure range around and below 100 Torr if the magnetization is produced by an optical technique rather than by the thermal polarization in an external magnetic field.

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