Influence of magnetic fields on the spectra of depolarized scattering of light in paramagnetic liquids

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Methods of controlled action on rotational and shear perturbations in paramagnetic liquids and on anisotropic perturbations in diamagnetic liquids are proposed for the purpose of identification of the characteristics of the spectra of depolarized molecular scattering of light and types of molecular motion. Rotational and shear modes are studied on the basis of hydrodynamics with a symmetric stress tensor. An analysis is made of the characteristic changes in the spectra of symmetric-symmetric and antisymmetric-antisymmetric scattering spectra in magnetic fields. A method is suggested for investigating molecular motion in diamagnetic liquids by the scattering of light in strongly concentrated solutions of paramagnetic radicals similar to these liquids.

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1. INTRODUCTION

Discovery of complex structures in the spectra of depolarized scattering of light in organic liquids (doublet structure,[1,2] contributions characterized by different widths but comparable intensities to line profiles[3]) has made it highly desirable to study the problem of explicit identification of the contributions of various mechanisms to the scattering cross section and of the observed spectral features and types of molecular motion.[4-7]

We shall propose that these problems be tackled by the method of controlled action of magnetic fields on the dynamics of paramagnetic liquids and we shall investigate the changes in the molecular scattering spectra caused by such fields. Magnetic fields affect particularly strongly the rotational, shear, and anisotropic modes of paramagnetic liquids and concentrated solutions of paramagnetic stable radicals in diamagnetic liquids. The present paper is concerned with the characteristic changes in the spectral composition of depolarized scattering of light in magnetic fields.

In § 2 we shall discuss the influence of magnetic fields on the angular and polarization characteristics of the differential (in respect of the angle and frequency) scattering cross section. The proposed approach is suitable for paramagnetic and diamagnetic liquids. We shall allow for the effects of fluctuation gyrotropy of a medium.

We shall study the low-frequency parts of the scattering spectra using the hydrodynamic approach. In § 3 we shall develop hydrodynamics of paramagnetic liquids with a symmetric stress tensor in a magnetic field. We shall study the influence of magnetic fields on the rotational and shear perturbations in liquids and the corresponding changes in the spectral line profiles (§§ 4 and 5). We shall deal with the fluctuation optical activity in § 6. We shall also discuss the scattering of light in concentrated solutions of stable radicals (§ 6). We shall consider the possibility of investigating the mechanisms responsible for the doublet structure in the *VH* scattering spectra.

2. STRUCTURE OF THE SCATTERING TENSOR IN MAGNETIC FIELDS

It is known[8,9] that the differential scattering cross section is given by the expression

$$\frac{d^2I}{d\Omega\, d\omega}=\left(\frac{\omega}{c}\right)^4\frac{1}{(4\pi)^2}T_{iklm}(\Delta\omega,\mathbf{q})e_{2i}e_{ik}^{*}e_{2l}^{*}e_{1m}, \tag{1}$$

where $\Delta\omega=\omega_1-\omega_2$ and $\mathbf{q}=\mathbf{k}_1-\mathbf{k}_2$ are the changes in the frequency and wave vector in the course of the scattering; $\mathbf{e}_1$ and $\mathbf{e}_2$ are unit polarization vectors of the incident and scattered radiation; $T_{iklm}=\langle\delta\varepsilon_{ik}(\mathbf{r},t)\delta\varepsilon_{lm}(0,0)\rangle_{\omega q}$ is the scattering vector.

We shall consider a fluctuation-gyrotropic nonabsorbing medium with fluctuations of the permittivity $\delta\varepsilon_{ik}$ satisfying the condition

$$\delta\varepsilon_{ik}(\mathbf{r},t)=\delta\varepsilon_{ki}(\mathbf{r},t), \tag{2}$$

or

$$\begin{aligned}\delta\hat{\varepsilon}_{ik}&=\delta\hat{\varepsilon}_{ik}^{s}+i\delta\hat{\varepsilon}_{ik}^{a},\\ \delta\hat{\varepsilon}_{ik}^{s}&=\delta\hat{\varepsilon}_{ki}^{s},\\ \delta\hat{\varepsilon}_{ik}^{a}&=-\delta\hat{\varepsilon}_{ki}^{a}.\end{aligned} \tag{3}$$

We shall investigate the properties of T_{iklm} in the case when the applied magnetic field is directed along the "recoil" vector $\mathbf{q}$ (the case closest to experimental situations). We shall assume that the wave vectors of the incident ($\mathbf{k}_1$) and scattered ($\mathbf{k}_2$) waves lie in the xz plane and that the z axis is directed along the external field $\mathbf{H}$ and also is the bisector of the angle formed by $\mathbf{k}_1$ and $\mathbf{k}_2$ (Fig. 1). We shall now formulate the general requirements which the scattering tensor must satisfy:

1) T_{iklm} should satisfy the condition of conjugacy

$$T_{iklm}=T_{lmik}^{*}, \tag{4}$$

2) T_{iklm} should be invariant under rotations through any angle about the z axis, and also under reflections in the xy plane.

According to Eq. (3), the scattering tensor can be divided into four contributions:

$$T_{iklm}=T_{iklm}^{ss}+T_{iklm}^{sa}+T_{iklm}^{as}+T_{iklm}^{aa}, \tag{5}$$

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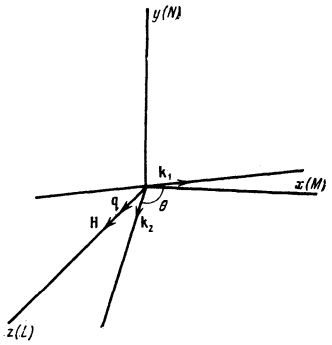

FIG. 1. Geometry of a typical light scattering experiment.

which are symmetric (s) or antisymmetric (a) under transpositions within pairs of indices. We shall represent the geometric structure of T_{iklm} in a transverse–longitudinal form, frequently employed in the theory of turbulence.[10] Combining the direct method for the transformation of tensors with the method of the theory of invariants, we obtain

$$T^{ss}_{iklm}=T_{MM,NN}\Delta_{ik}\Delta_{lm}+{}^1/_4(T_{MN,MN}+T_{MN,NM})\times(\Delta_{il}\Delta_{km}+\Delta_{im}\Delta_{kl})+{}^1/_4(T_{MM,MN}+T_{MM,NM}-T_{MN,MM}-T_{NM,MM})\{\Delta_{il}n_{km}\}^{ss}+{}^1/_4\{T_{LM,LM}\}^{ss}\{n_in_l\Delta_{km}\}^{ss}+{}^1/_2(T_{LL,MM}+T_{MM,LL})\times(n_in_k\Delta_{lm}+n_in_m\Delta_{ik})+{}^1/_2(T_{LL,MM}-T_{MM,LL})(n_in_k\Delta_{lm}-n_in_m\Delta_{ik})+{}^1/_4\{T_{LM,LN}\}^{ss}\{n_in_ln_{km}\}^{ss}+T_{LL,LL}n_in_kn_ln_m, \quad (6)$$

$$T^{sa}_{iklm}={}^1/_2(T_{MM,MN}-T_{MM,NM})\{\Delta_{il}n_{km}\}^{sa}+{}^1/_4\{T_{LM,LM}\}^{sa}\{n_in_l\Delta_{km}\}^{sa}+{}^1/_4\{T_{LM,LN}\}^{sa}\{n_in_ln_{km}\}^{sa}+T_{LL,MN}n_in_kn_{lm}, \quad (7)$$

$$T^{as}_{iklm}={}^1/_2(T_{NM,MM}-T_{MN,MM})\{\Delta_{il}n_{km}\}^{as}+{}^1/_4\{T_{LM,LM}\}^{as}\{n_in_l\Delta_{km}\}^{as}+{}^1/_4\{T_{LM,LN}\}^{as}\{n_in_ln_{km}\}^{as}+T_{MN,LL}n_{ik}n_ln_m, \quad (8)$$

$$T^{aa}_{iklm}={}^1/_4\{T_{MN,MN}\}^{aa}(\Delta_{il}\Delta_{km}-\Delta_{im}\Delta_{kl})+{}^1/_4\{T_{LM,LM}\}^{aa}\{n_in_l\Delta_{km}\}^{aa}+{}^1/_4\{T_{LM,LN}\}^{aa}\{n_in_ln_{km}\}^{aa}. \quad (9)$$

The following notation is used in Eqs. (6)–(9): $\Delta_{ik}=\delta_{ik}-n_in_k$ and $n_{ik}=e_{ikl}n_l$, where n_i are the components of a unit vector directed along the z axis; the letters M, N, and L denote, respectively, the x, y, and z components of the scattering tensor in a special coordinate system shown in Fig. 1; $\{n_in_l\Delta_{km}\}^{aa}$ is a combination which is antisymmetric in both pairs of indices (ik) and (lm):

$$\{n_in_l\Delta_{km}\}^{aa}=n_in_l\Delta_{km}-n_in_m\Delta_{kl}-n_kn_l\Delta_{im}+n_kn_m\Delta_{il}$$

and similarly in other cases, also with respect to $\{T_{LM,LM}\}^{aa}$, etc.

Zel'dovich[11] used a different method to obtain T^{ss}_{iklm}. The nineteen coefficient functions in Eqs. (6)–(9) represent all possible contributions to the scattering cross section. They are real because of the self-conjugacy condition (4) and this is true in spite of the fact that $\delta\varepsilon_{ik}$ and the polarization unit vectors are complex. The following two identities are obtained from the theory of invariants[10]

$$T_{MM,MM}=T_{MM,NN}+T_{MN,MN}+T_{MN,NM}, \quad (10)$$

$$T_{MM,MN}+T_{MM,NM}+T_{MN,MM}+T_{NM,MM}=0. \quad (11)$$

The first of them is a generalization of the well-known Millionshchikov identity. Some of the coefficient functions, for example $T_{MM,MN}$ differ from zero only in the presence of a field and are of different order of smallness with respect to the field.

3. HYDRODYNAMICS OF PARAMAGNETIC LIQUIDS WITH A SYMMETRIC STRESS TENSOR

We shall describe the low-frequency parts of the spectra of depolarized scattering of light in paramagnetic liquids subjected to magnetic fields by adopting the hydrodynamic approach. With this in mind, we shall study the characteristics of the hydrodynamic equations for paramagnetic liquids with a symmetric stress tensor in magnetic fields.[12]

The kinetic parts of the densities of the main hydrodynamic quantities will be obtained using explicit correspondence with the form of these densities in the microscopic model of noninteracting spin-1/2 particles (Pauli hydrodynamics). The densities of the momentum and of the kinetic part of the stress tensor ($\mathbf{p}$, $T_{\alpha\beta}$) are related to the mass density ρ, the field of velocities $\mathbf{v}$, and the spin density $\mathbf{s}$ by

$$\mathbf{p}(\mathbf{x})=\rho\mathbf{v}(\mathbf{x})+{}^1/_2\operatorname{rot}\mathbf{s}(\mathbf{x}), \quad (12)$$

$$T_{\alpha\beta}{}^{s}(\mathbf{x})=p_\alpha p_\beta/\rho+\dots . \quad (13)$$

If we include terms up to ~(curl $\mathbf{s}$)^2, the kinetic energy density is

$$\varepsilon^k(\mathbf{x})={}^1/_2\mathbf{p}^2/\rho-\mathbf{s}\Omega. \quad (14)$$

In this approach the main variables are the densities of the particle number, momentum, energy, entropy S, and magnetization $\mathbf{M}=\lambda\mathbf{s}$, where λ is the gyromagnetic ratio. We can check directly that the selection of the momentum density in the form of (12) automatically symmetrizes the Maxwellian stress tensor for an ideal paramagnetic liquid in a magnetic field. The magnetization-dependent part of the internal energy of a liquid and its differential are given by the expressions

$$u_M=\frac{1}{8\pi}\mathbf{B}^2+\frac{\mathbf{M}^2}{2\chi}-\mathbf{MB}',\quad \mathbf{B}'=\mathbf{B}+\frac{\Omega}{\lambda},\quad \Omega=\frac{1}{2}\operatorname{rot}\mathbf{v}, \quad (15)$$

$$\delta u_M=\frac{1}{4\pi}\mathbf{H}\delta\mathbf{B}+\left(\frac{\mathbf{M}}{\chi}-\mathbf{B}'\right)\delta\mathbf{M}. \quad (16)$$

The first term in Eq. (16) describes the change in the internal energy in the presence of an equilibrium coupling between $\mathbf{M}$ and $\mathbf{H}$ ($\mathbf{M}=\chi\mathbf{H}$), whereas the second term represents weak nonequilibrium effects.

The entropy production $T\sigma$ is defined in the usual way.[13] Let $\sigma^{(0)}_{\alpha\beta}$ and $g^{(0)}_{\alpha\beta}$ be the trace-free parts of the tensors of viscous stresses and magnetization flux; g_α and q_α be the vector parts of the magnetization and heat fluxes; l_α be the dissipative source in the equation for the magnetization:

$$\frac{\partial M_\alpha}{\partial t}+\frac{\partial g_{\alpha\beta}}{\partial x_\beta}=l_\alpha,\quad g_{\alpha\beta}=g^{(0)}_{\alpha\beta}+e_{\alpha\beta\gamma}g_\gamma+g\delta_{\alpha\beta}. \quad (17)$$

Then,

$$T\sigma=\mathbf{q}(-\nabla\ln T)-\sigma^{(0)}_{\alpha\beta}G^{(0)}_{\alpha\beta}-g^{(0)}_{\alpha\beta}\Gamma^{(0)}_{\alpha\beta}-g\operatorname{rot}\mathbf{A}-l\mathbf{A}-\sigma\operatorname{div}(\mathbf{p}/\rho)-g\operatorname{div}\mathbf{M}, \quad (18)$$

$$\mathbf{A}=\mathbf{M}-\chi\mathbf{B}' \quad (19)$$

$$G^{(0)}_{\alpha\beta}=\frac{1}{2}\left(\frac{\partial}{\partial x_\beta}\frac{p_\alpha}{\rho}+\frac{\partial}{\partial x_\alpha}\frac{p_\beta}{\rho}\right)-\frac{1}{3}\delta_{\alpha\beta}\operatorname{div}\frac{\mathbf{p}}{\rho}, \quad (20)$$

$$\Gamma^{(0)}_{\alpha\beta}=\frac{1}{2}\left(\frac{\partial}{\partial x_\beta}A_\alpha+\frac{\partial}{\partial x_\alpha}A_\beta\right)-\frac{1}{3}\delta_{\alpha\beta}\operatorname{div}\mathbf{M}. \quad (21)$$

The kinetic coefficients for a system in a magnetic field are tensors of the appropriate rank and they are

responsible for the cross effects allowed by the symmetry rules. In particular, the viscosity coefficient $\eta_{\alpha\beta\gamma\delta}$ is a fourth-rank tensor symmetric in respect of the transpositions of index pairs and it contains seven independent functions. Two of these functions do not depend strongly on the field, one is a linear function of the field, and others are of higher orders of smallness. From the effects linear in the field we can distinguish the magnetization precession

$$I_\alpha^{(1)}=\lambda[\mathbf{M}\times\mathbf{B}]_\alpha \tag{22}$$

and the additional nonequilibrium contribution to the magnetic stress tensor

$$\Delta T_{\alpha\beta}^{M}=\theta\{B_\alpha A_\beta+B_\beta A_\alpha-{}^2/_3\delta_{\alpha\beta}\mathbf{BA}\}. \tag{23}$$

Thus, the momentum flux tensor

$$T_{\alpha\beta}=p\delta_{\alpha\beta}+\sigma_{\alpha\beta}^{(0)}+T_{\alpha\beta}^{M}+\Delta T_{\alpha\beta}^{M},\quad \sigma_{\alpha\beta}^{(0)}=\eta_{\alpha\beta\gamma\delta}G_{\gamma\delta}^{(0)}, \tag{24}$$

where p is the pressure and $T_{\alpha\beta}^{M}$ is the Maxwellian stress tensor

$$T_{\alpha\beta}^{M}=-\frac{1}{8\pi}\{B_\alpha H_\beta+B_\beta H_\alpha-\delta_{\alpha\beta}(2\mathbf{BH}-\mathbf{B}^2)\}, \tag{25}$$

is explicitly symmetric.

The linearized equations of hydrodynamics considered in the approximation linear in the field have the following structure:

$$\frac{\partial p_\alpha}{\partial t}=\nu\Delta p_\alpha-\frac{\zeta+{}^4/_3\eta}{\rho}\frac{\partial}{\partial x_\alpha}\operatorname{div}\mathbf{p}-\frac{\partial p}{\partial x_\alpha}$$
$$-\theta B\begin{cases}\partial M_x/\partial z-{}^2/_3\partial M_z/\partial x, & \alpha=x\\ \partial M_y/\partial z-{}^2/_3\partial M_z/\partial y, & \alpha=y,\\ \operatorname{div}\mathbf{M}+{}^1/_3\partial M_z/\partial z, & \alpha=z\end{cases} \tag{26}$$

$$\frac{\partial M_\alpha}{\partial t}=\lambda[\mathbf{M}\times\mathbf{B}]_\alpha-\frac{1}{\tau}M_\alpha$$
$$+2\theta\chi B\begin{cases}\partial p_x/\partial z+\partial p_z/\partial x, & \alpha=x\\ \partial p_y/\partial z+\partial p_z/\partial y, & \alpha=y.\\ {}^2/_3\operatorname{div}\mathbf{p}-2\,\partial p_z/\partial z, & \alpha=z\end{cases} \tag{27}$$

In the above equations we have the usual terms describing the diffusion of momentum, propagation of sound, precession and relaxation of the magnetization, as well as the "linearized" Maxwellian stresses and the associated effect of the field of momenta on the motion of the magnetization.

4. DEPOLARIZED SYMMETRIC–SYMMETRIC SCATTERING IN PARAMAGNETIC LIQUIDS SUBJECTED TO MAGNETIC FIELDS

The change in the nature of the transverse–longitudinal diffusion and relaxation modes of a paramagnetic liquid magnetic field results in corresponding changes in the spectra of depolarized VH scattering of light. We shall consider paramagnetic liquids such as NO or O_2, which are almost isotropic in the optical sense. This allows us to assume that fluctuations of the permittivity tensor are entirely due to stresses and local internal rotations of the liquid. Following Eq. (18), we shall take $\delta\varepsilon_{ik}^{s}$ in the form

$$\delta\varepsilon_{ik}^{s}=c_1G_{ik}^{(0)}+c_2\Gamma_{ik}^{(0)}, \tag{28}$$

where $G_{ik}^{(0)}$ and $\Gamma_{ik}^{(0)}$ are given by Eqs. (20) and (21), and the isotropic parts are dropped. It follows from Eqs. (1) and (28) that the symmetric–symmetric (ss) scattering cross section with the vertical polarization of the incident light and the horizontal polarization of the scattered light is

$$M_{VH}^{ss}=\frac{1+\beta}{2}\{c_1^2\langle G_{xz}^{(0)}G_{xz}^{(0)}\rangle_{\omega q}+c_2^2\langle\Gamma_{xz}^{(0)}\Gamma_{xz}^{(0)}\rangle_{\omega q}+c_1c_2\langle G_{xz}^{(0)}\Gamma_{xz}^{(0)}\rangle_{\omega q}\}, \tag{29}$$

where $\beta=\cos\theta$ (see Fig. 1).

It follows from Eqs. (26) and (27) that in a magnetic field the contribution due to $\langle\Gamma_{xz}^{(0)}\Gamma_{xz}^{(0)}\rangle_{\omega q}$ splits because of the spin precession:

$$\langle\Gamma_{xz}^{(0)}\Gamma_{xz}^{(0)}\rangle_{\omega q}\sim\left\{\frac{1/\tau}{(\omega-\lambda B)^2+1/\tau^2}+\frac{1/\tau}{(\omega+\lambda B)^2+1/\tau^2}\right\}. \tag{30}$$

For $\lambda\sim10^6$–10^7 and $B\sim10^4$–10^5 G the precession shift reaches 10^{10}–10^{12} Hz and it can be greater than the linewidth $1/\tau$.

The correlation function $\langle G_{xz}^{(0)}G_{xz}^{(0)}\rangle_{\omega q}$ is also affected by the applied magnetic field but its form depends more strongly on the nature of relaxation of the shear viscosity. In the diffusion case

$$\langle G_{xz}^{(0)}G_{xz}^{(0)}\rangle_{\omega q}\sim\tilde{\nu}q^4\left\{\frac{1}{(\omega+\tilde{\mu}q^2B)^2+(\tilde{\nu}q^2)^2}+\frac{1}{(\omega-\tilde{\mu}q^2B)^2+(\tilde{\nu}q^2)^2}\right\}, \tag{31}$$

the applied magnetic field broadens the Lorentzian

$$\frac{1}{\omega^2+(\nu q^2)^2},\quad \tilde{\mu}=\frac{\theta}{2\rho\lambda}+\frac{\lambda\tau}{1+(\lambda\tau B)^2}\chi\theta^2\tau B^2,\quad \tilde{\nu}=\nu+\frac{\chi B^2\theta^2\tau}{1+(\lambda\tau B)^2}.$$

In sufficiently strong fields (~10^5 G) this broadening can reach 10%. If the shear viscosity relaxes in accordance with the law $\nu(\omega)=\nu(0)/(1-i\omega\tau_\mu)$, the line profile becomes more complex but the qualitative nature of the influence of the magnetic field is still the same. Figure 2 shows schematically the nature of the changes in the line profile caused by the application of a magnetic field in two different cases $c_1\gtrless c_2$.

The ss scattering described by Eq. (30) is due to local internal rotations in the liquid. The shift by the precession frequency ($\pm\lambda B$) is independent of the degree of "zeroth" ordering of magnetic moments in the external field. The fluctuation field of velocities is renormalized significantly only by Maxwellian stresses. The influence of new viscosity coefficients and other field-induced kinetic coefficients is negligible.[14] It follows from Eqs. (29)–(31) that the applied magnetic field alters the spectral composition of the scattered radiation but not its integrated intensity.

However, it is not clear whether the application of a

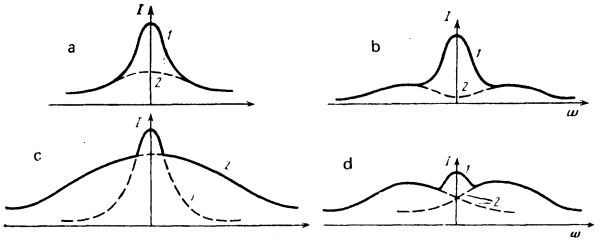

FIG. 2. Frequency dependences of the intensity of depolarized ss-type scattering: a) $c_1>c_2$, $H=0$; b) $c_1>c_2$, $H\neq0$; c) $c_1<c_2$, $H=0$; d) $c_1<c_2$, $H\neq0$. The numbers 1 and 2 denote the contributions of, respectively, the velocity field and the magnetization field to the spectral intensities.

magnetic field influences purely transverse modes of paramagnetic liquids and the corresponding contributions to the scattering cross section. In the hydrodynamic model adopted above there are no tensor variables of the t_{MM} and t_{MN} type (in the q representation).

5. FLUCTUATION-INDUCED OPTICAL ACTIVITY

It is known that the antisymmetric part of the permittivity tensor satisfying the condition (2) results in optical activity.[15] If a medium has fluctuation-induced gyrotropic parameters, the scattering of light may be accompanied by rotation of the plane of polarization. According to Eq. (18), such a parameter can be the internal rotation moment

$$\delta\varepsilon_{ik}^{a}=D_1 e_{ikl}A_l+D_2 e_{ikl}(\mathrm{rot}\,\mathbf{A})_l. \tag{32}$$

The optical activity in transmitted light is usually attributed to the spatial dispersion of ε_{ik} in regions of molecular dimensions. However, in dense media a certain role is played by many-body irreducible effects and, therefore, one can speak of spatial dispersion $\delta\varepsilon_{ik}$ with an inhomogeneity scale of the order of several molecular dimensions. In this case the fluctuation optical activity should be observed even in substances with symmetric molecules.

We may assume that the size of a spatial region in which the molecular spins are correlated is of the order of the radius of a Lagrangian particle.[16] The size of such a particle is related to the kinematic viscosity ν and to the Maxwellian relaxation time τ_μ by $r_L\propto(\nu\tau_\mu)^{1/2}$ (Ref. 16) and its order of magnitude is 10^{-7}–10^{-6} cm. Thus, the characteristic ratio $(r_L/\lambda)^2$ governing the intensity of the fluctuation optical activity is proportional to 10^{-4}–10^{-2} (it is the ratio to the intensity of the ss scattering).

The above results hold also for organic liquids but the measure of gyrotropy should be defined differently.[17,18]

We shall now consider the possibility of recording the aa-type scattering. It follows from Eqs. (1), (9), and (32) that

$$M_{VH}^{aa}\sim D_1^2(\langle A_zA_z\rangle_{\omega q}{}^1/_2(1-\beta)+{}^1/_2(1+\beta)\langle A_yA_y\rangle_{\omega q}), \tag{33}$$

where the contributions proportional to $D_2^2q^2$ can be ignored. In the absence of a magnetic field the correlation functions in Eq. (33) are identical and the aa-type scattering is isotropic. In a strong magnetic field one of the correlation functions $\langle A_yA_y\rangle_{\omega q}$ splits and the scattering cross section becomes

$$M_{VH}^{aa}\sim D_1^2\left[\frac{1/\tau}{\omega^2+1/\tau^2}\frac{1-\beta}{2}+\frac{1+\beta}{2}\left(\frac{1/\tau}{(\omega+\lambda B)^2+1/\tau^2}+\frac{1/\tau}{(\omega-\lambda B)^2+1/\tau^2}\right)\right]. \tag{34}$$

We shall now compare the spin contributions of the ss and aa type described by Eqs. (30) and (34), respectively; we can see that one of them

$$\frac{1-\beta}{2}\frac{1/\tau}{\omega^2+1/\tau^2}$$

is not deformed by a magnetic field but has a different angular dependence.

A complete picture of the scattering in a magnetic field is more complex because of the additional sa contributions (which are absent if $H=0$). However, since these contributions are linear or quadratic with respect to B, we can control their relative importance. As in the case of the ss scattering, the total intensity of the contributions which are deformed is not affected.

6. DEPOLARIZED SCATTERING IN CONCENTRATED SOLUTIONS OF PARAMAGNETIC RADICALS

In this section we shall discuss the possibility of influencing the dynamics of diamagnetic liquids by the application of magnetic fields. It is assumed that a diamagnetic liquid acts as a solvent and that stable radicals (which are affected strongly by magnetic fields) are the solute.

Among the molecules with paramagnetic fragments which are most convenient for experimental studies are stable hydrocarbon and azoxy radicals (for example, benzyl, which is an analog of toluene, and Ph_2NO which is an analog of benzophenone). These radicals are stable and sufficiently inert in the chemical sense, and they dissolve readily in organic liquids.[19] We shall study the influence of magnetic fields on the doublet structure of the spectrum of VH scattering in organic liquids.

A fairly simple mechanism for the appearance of a doublet is proposed by Keyes and Kivelson.[6] The linear relationship between the velocity field and the field of reorientations produces the following pattern of depolarized scattering at $\theta=90°$:

$$I_{VH}\sim\frac{1/\tau}{\omega^2+1/\tau^2}-\nu_1k^2\tau\frac{(\nu+\nu_1)k^2}{(\omega^2+(\nu_1+\nu)^2k^4)}, \tag{35}$$

where τ is the reorientation relaxation time, ν is the "unrenormalized" shear viscosity, and ν_1 is the contribution to the shear viscosity made at zero frequency by reorientations. However, we shall not consider an independent method for estimating ν_1 and use Eq. (35) to define ν_1.

We shall consider the influence of a magnetic field on the proposed doublet mechanism. Application of a magnetic field to a concentrated solution of a stable radical, of nature similar to the investigated liquid, results in a characteristic change in the kinetics of fluctuations and, therefore, in a certain change in the molecular scattering spectra.

We shall assume that the change in the reorientation tensor $\zeta_{\alpha\beta}$ (moment-of-inertia tensor) is mainly due to: 1) relaxation; 2) ordering influence of the stress field; 3) ordering influence of the magnetic field. The magnetic field acts directly on the magnetic moments of the fragments and these produce an ordered distribution of the cores of the molecules. This effect should manifest itself phenomenologically by zero anisotropy $\zeta_{\alpha\beta}$ and by a difference between the relaxation times τ_i of the longitudinal, longitudinal–transverse, and transverse (relative to the field) components of the reorientation tensor. The hydrodynamic equations linearized with respect to fluctuations have the following form:

$$\frac{\partial p_\alpha}{\partial t} = -\frac{\partial}{\partial x_\beta}(T_{\alpha\beta} - \mu_i \zeta_{\alpha\beta}{}^i), \quad i = 1.2, \tag{36}$$

$$\frac{\partial \zeta_{\alpha\beta}{}^i}{\partial t} = -\frac{1}{\tau_i}(\zeta_{\alpha\beta}{}^i - \mu_i \tau_i T_{\alpha\beta}), \tag{37}$$

where the index i labels the transverse and longitudinal components, $T_{\alpha\beta}$ is the usual viscous stress tensor, and $\tau_i \sim 10^{-11}$ sec. In the case of anisotropic liquids the values of τ_1 and τ_2 may differ severalfold.

We shall consider three typical experimental situations: a) the magnetic induction vector is in the scattering plane (xz) (see Fig. 1) and directed along the recoil vector; b) the magnetic field is perpendicular to the recoil vector (along x); c) the magnetic field is perpendicular to the scattering plane. According to Eq. (6), the intensity of depolarized scattering is

$$I_{VH} = \langle \zeta_{xy}\zeta_{xy} \rangle_{\omega q} \sin^2 \frac{\theta}{2} + \langle \zeta_{xz}\zeta_{xz} \rangle_{\omega q} \cos^2 \frac{\theta}{2}. \tag{38}$$

In the three situations listed above, we have

$$I_{VH}^{(a)} \sim \frac{1/\tau_\perp}{\omega^2 + 1/\tau_\perp{}^2} \sin^2 \frac{\theta}{2} + \left(\frac{1/\tau_\parallel}{\omega^2 + 1/\tau_\parallel{}^2} - \nu_\parallel \tau_\parallel k^2 \frac{\nu k^2}{\omega^2 + (\nu k^2)^2} \right) \cos^2 \frac{\theta}{2}, \tag{39}$$

$$I_{VH}^{(b)} \sim \frac{1/\tau_\parallel}{\omega^2 + 1/\tau_\parallel{}^2} \sin^2 \frac{\theta}{2} + \left(\frac{1/\tau_\parallel}{\omega^2 + 1/\tau_\parallel{}^2} - \nu_\parallel \tau_\parallel k^2 \frac{\nu k^2}{\omega^2 + (\nu k^2)^2} \right) \cos^2 \frac{\theta}{2}, \tag{40}$$

$$I_{VH}^{(c)} \sim \frac{1/\tau_\parallel}{\omega^2 + 1/\tau_\parallel{}^2} \sin^2 \frac{\theta}{2} + \left(\frac{1/\tau_\perp}{\omega^2 + 1/\tau_\perp{}^2} - \nu_\perp \tau_\perp k^2 \frac{\nu k^2}{\omega^2 + (\nu k^2)^2} \right) \cos^2 \frac{\theta}{2}, \tag{41}$$

where the following notation is used: $\tau_\parallel$ and $\tau_\perp$ are the longitudinal and transverse relaxation times; $\nu_\parallel = \mu_\parallel \tau_\parallel$ and $\nu_\perp = \mu_\perp \tau_\perp$ are the magnetic-field-dependent reorientation contributions to the viscosity; $\nu = \nu_0 + \nu_\parallel(\nu_\perp)$ is the total kinematic viscosity. Equations (39)–(41) are derived ignoring the splitting of the kinetic coefficients and the numerous cross effects, and also ignoring the scattering by spin inhomogeneities. It follows from Eqs. (39)–(41) that both the splitting and the depth of the dip, as well as the width of the line of depolarized scattering are sensitive to the magnetic field intensity and direction. The viscosities $\nu_\parallel$ and $\nu_\perp$ can be determined in independent experiments.

Thus, if $\nu_0 \tau k^2 < 1$ and the ideas[6] on the viscosity of the system are valid, the addition of a paramagnetic fragment and the application of a magnetic field may provide sufficiently effective means for refining these ideas and establishing additional qualitative and quantitative relationships.

The present authors hope that this work will stimulate new experiments.

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