

# Acoustic paramagnetic resonance line formation induced in a liquid by anisotropic spin-lattice interactions

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It is shown that in a liquid, there should exist electron and nuclear acoustic paramagnetic resonance (APRL) lines due to anisotropic spin-lattice interactions. The dispersion equations for sound excitations under APRL conditions are derived. Their dependence on the polarization and direction of propagation of the sound and on the spin-lattice interactions mechanisms is analyzed. The APRL selection rules are considered.

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## 1. INTRODUCTION

Acoustic paramagnetic resonance (APR) in a solid, which was predicted by Al'tshuler<sup>[1]</sup> and Kastler,<sup>[2]</sup> has been successfully studied at the present time in a number of laboratories. The situation of acoustic paramagnetic resonance in a liquid (APRL) is quite different. For a long time, attempts at observation of APRL ended unsuccessfully, which was apparently in agreement with the theoretical representations,<sup>[3]</sup> according to which the APRL lines should have a huge width:  $\sim\tau^{-1}$  ( $\tau^{-1} \sim 10^{10} - 10^{12} \text{ sec}^{-1}$  is the rotational relaxation rate of the molecules of the liquid). However, it has since been shown theoretically<sup>[4]</sup> that the APRL lines exist and have widths of the same order as the corresponding EPR lines or NMR lines in liquids.

In a previous work,<sup>[5]</sup> we reported the first observation of APRL, the lines of which are evidently due to the anisotropic spin-lattice interactions. The reasoning underlying the theoretical approach to the phenomenon was also given there. The gist of the reasoning is the following: in a liquid, the orientation of the molecules interacts with the shear deformations (in particular, this is the reason for the Maxwell effect<sup>[6,7]</sup>). In a magnetic field  $H$ , the fluctuation spectrum of the orientation of the molecules is deformed as a result of the anisotropic spin-lattice interactions; against a continuous background with width  $\sim\tau^{-1}$ , there is a small  $\delta$ -shaped component at the precession frequency of the spins  $\omega_0$ . Therefore, in the given case, the liquid exhibits "solid-like" properties when sound of frequency  $\omega \approx \omega_0$  propagates in it, whereas under ordinary conditions generation of frequencies  $\omega \gtrsim \tau$  is necessary for this purpose. The intensity of the APRL lines turns out to be several orders higher than predicted previously.<sup>[4]</sup> A theory of APRL based on these considerations is given below.

## 2. THE MODEL

Let us consider a liquid consisting of anisotropic, undeformed molecules, the orientation of which relaxes at a rate  $\tau^{-1}$  to the local-equilibrium distribution. Such a model has been studied by Leontovich<sup>[6]</sup> and Rytov<sup>[7]</sup> in researches on the depolarized scattering of light. In these papers, a very general description of a liquid in terms of a set of relaxing tensors of different rank is

used. However, it is somewhat unsuitable for application to the problem of APRL because of the difficulty of explicitly accounting for the symmetry of the spin Hamiltonian, which can be different for different spins in the same molecule. We therefore use here as the relaxing variable the small  $f(\alpha, \beta, \gamma, \mathbf{x})$  departure of the distribution function of the molecular orientation from the spherically symmetric distribution at the given point  $\mathbf{x}$  of the liquid. The Eulerian angles  $\alpha$ ,  $\beta$  and  $\gamma$  give the orientation of a set of coordinates, (MSC) attached to the molecule but moving relative to the laboratory system (LSC). The lattice contribution to the free energy density has the form

$$F_l = \frac{1}{2} \rho \dot{d}^2 + \frac{1}{2} K u_{ii}^2 + \mu_{\alpha\beta\gamma\delta} \tilde{u}_{\alpha\beta} \tilde{u}_{\gamma\delta} + a \int (\tilde{u} \cdot (D^{(2)} P)) f dg + \int f dg, \quad (1)$$

$$d g = \sin \beta d\alpha d\beta d\gamma,$$

$$u_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial d_\alpha}{\partial x_\beta} + \frac{\partial d_\beta}{\partial x_\alpha} \right), \quad \tilde{u}_{\alpha\beta} = u_{\alpha\beta} - \frac{1}{3} u_{ii} \delta_{\alpha\beta},$$

$$(A \cdot B) = A_{\alpha\beta} B_{\beta\alpha}.$$

Here  $\rho$  is the density of the liquid,  $d$  is the displacement vector,  $K$  and  $\mu_{\alpha\beta\gamma\delta}$  are the hydrostatic compression modulus and the shear modulus tensor, measured at frequencies  $\omega \gtrsim \tau^{-1}$ ,  $a \sim (V_0 / 8\pi^2 T)^{1/2}$  is a normalization constant,  $V_0$  is the volume per molecule, and  $T$  is the temperature. A symmetrical tensor of second rank  $P$  ( $\text{Sp } P = 0$ ) describes the interaction (in the MSC) of the orientation of the molecule with the instantaneous shear. The transformation of the tensors in the transition from the MSC to the LSC is carried out with the help of the Wigner finite rotation matrices  $D_{\mu\nu}^{(2)}(\alpha, \beta, \gamma)$ .<sup>[8]</sup> The last term in (1) is connected with the change in the free energy upon departure of the state of the liquid from the equilibrium isotropic state.

For concreteness, we assume that each molecule contains one spin  $S > 1/2$  with quadrupole moment  $Q > 0$ , and we shall take into account the isotropic and anisotropic Zeeman interactions and the interaction of  $Q$  with the gradient  $V_{\alpha\beta}$  of the intramolecular electric field. The total density of the free energy is of the form

$$F = F_l + F_s,$$

$$F_s = a\beta \int (\mathbf{H} \cdot (D^{(2)} g^e) \cdot \mathbf{s}) f dg + a \int (q \cdot (D^{(2)} V)) f dg - g\beta \mathbf{H} \cdot \mathbf{s}, \quad (2)$$

$$(A \cdot B \cdot C) = A_{\alpha\beta} B_{\beta\gamma} C_{\gamma\alpha}.$$

Here  $\beta$  is the electronic or nuclear magneton,  $g$  is the isotropic part of the  $g$  tensor,  $g^e$  is the anisotropic part

of the  $g$  tensor,  $s$  and  $q$  are the densities of the spin and quadrupole moments:

$$s(x) = \sum_i S_i \delta(x-x_i), \quad s_\alpha s_\beta = \sum_i S_{i,\alpha} S_{i,\beta} \delta(x-x_i),$$

$$q_{\alpha\beta} = \frac{3Q}{2S(2S-1)} \sum_i (S_{i,\alpha} S_{i,\beta} + S_{i,\beta} S_{i,\alpha} - \frac{2}{3} S(S+1) \delta_{\alpha\beta}) \delta(x-x_i);$$

$S_i$  is the spin operator of the  $i$ -th particle located at the point  $x_i$ .

From (1) and (2) we obtain the linear equations of motion for displacements in the liquid:

$$\rho d_\alpha = K \frac{\partial}{\partial x_\alpha} \left( \frac{\partial d_\alpha}{\partial x_\alpha} \right) + 2\mu_{\alpha\beta} \frac{\partial}{\partial x_\beta} \tilde{u}_{\alpha\beta} + a \frac{\partial}{\partial x_\beta} R_{\alpha\beta},$$

$$R_{\alpha\beta} = \int (D^{(2)}P)_{\alpha\beta} f dg \quad (3)$$

and, limiting ourselves for simplicity to the approximation of a single relaxation time  $\tau$ , we obtain for the distribution function:

$$\tau j = -f - a \beta (H \cdot (D^{(2)}g^\alpha) \cdot s) - a (\tilde{u} \cdot (D^{(2)}P)) - a (q \cdot (D^{(2)}V)). \quad (4)$$

The motion of the spin operators  $s_\pm, \{s_x, s_z\}$  and  $s_z^2$ , which relax with different rates  $T_{2g}^{-1}, T_{2d}^{-1}$  and  $T_{2q}^{-1}$  in the general case, is described by the Bloch-Bloembergen equations (see, for example, Ref. 9). For high temperatures ( $T \gg \omega_0$ ) and at  $H_x = H_y = 0$  and  $H_z = H$ , they have the form

$$i \frac{d}{dt} \langle s_x \rangle = \mp g \beta H s_z + a \beta \langle s_z \rangle H \int (D^{(2)}g^\alpha)_{\pm} f dg$$

$$- \frac{1}{T_{2g}} \left[ \langle s_x \rangle + \frac{a \beta H S(S+1)}{3TV_0} \int (D^{(2)}g^\alpha)_{\pm} f dg \right], \quad (5)$$

$$i \frac{d}{dt} \langle s_z \rangle = \mp g \beta H \langle s_z \rangle + \mp \frac{3a \beta g \zeta Q H}{2TS(2S-1)V_0} \int (D^{(2)}V)_{\pm} f dg$$

$$- i \frac{1}{T_{2d}} \left[ \langle s_z \rangle + \frac{3a \zeta Q}{2TS(2S-1)} \int (D^{(2)}V)_{\pm} f dg \right], \quad (6)$$

$$i \frac{d}{dt} \langle s_z^2 \rangle = \mp 2g \beta H s_z^2$$

$$\mp \frac{3a g \beta H Q}{2TV_0 S(2S-1)} \int [(D^{(2)}V)_{xx} - (D^{(2)}V)_{yy} \pm 2i(D^{(2)}V)_{xy}] f dg$$

$$- i \frac{1}{T_{2q}} \left\{ \langle s_z^2 \rangle + \frac{3a \zeta Q}{4TV_0 S(2S-1)} \right.$$

$$\times \left. \int [(D^{(2)}V)_{xx} - (D^{(2)}V)_{yy} \pm 2i(D^{(2)}V)_{xy}] f dg \right\}, \quad (7)$$

$$\langle s_z \rangle \approx g \beta H S(S+1)/3TV_0,$$

$$(D^{(2)}g^\alpha)_{\pm} = (D^{(2)}g^\alpha)_{zx} \pm i(D^{(2)}g^\alpha)_{zy},$$

$$(D^{(2)}V)_{\pm} = (D^{(2)}V)_{zx} \pm i(D^{(2)}V)_{zy},$$

$$\zeta = (2S+1)^{-1} \sum_{M=-S}^S (2M-1)^2 (S+M)(S-M+1).$$

Equations (3)–(7) give a closed set of equations describing the dynamics of the coupled spin-lattice excitations. By requiring in accord with Ref. 6, that shear strains be absent from the liquid at  $\omega=0$ , we get from (3)

$$2\mu_{\alpha\beta} \tilde{u}_{\alpha\beta} = -a R_{\alpha\beta} \quad (\omega=0). \quad (8)$$

Using (4) and the symmetry properties of the problem ( $H \neq 0$ ), with the help of which the number (equal to three) of independent components of the tensor  $\mu_{\alpha\beta\gamma\delta}$  can be established, we can verify that the conditions (8) are consistent. This fact is a consequence of the correct description of the relaxation of the spin variables

as  $\omega \rightarrow 0$  in the Bloch-Bloembergen approximation. We can then represent (3) in the form

$$\rho \omega^2 d_\alpha = K \frac{\partial}{\partial x_\alpha} \left( \frac{\partial d_\alpha}{\partial x_\alpha} \right) + a \frac{\partial}{\partial x_\beta} (R_{\alpha\beta}(\omega) - R_{\alpha\beta}(0)),$$

$$d_\alpha(x, t) = d_\alpha(x) e^{-i\omega t}, \quad (9)$$

which is suitable for calculations of excitations with frequency  $\omega \neq 0$ .

The components of the tensor  $R_{\alpha\beta}$  are determined from (3)–(7), if we expand  $f(\alpha, \beta, \gamma, x)$  in generalized spherical harmonics and use the properties of orthogonality of the latter. This calculation is carried out exactly but the answer obtained in such a way is too complicated to write out here. Since the spin-lattice interactions have a weak effect on the sound propagation in the liquid, it suffices to limit ourselves to the linear terms in the expansion of  $R_{\alpha\beta}$  in terms of the small parameters  $\Phi_x^e, \Phi_y^e$  and  $\Phi_z^e$  defined below. After complicated calculations, we obtain

$$R_{\alpha\beta} = R_{\alpha\beta}^0 + R_{\alpha\beta}^e + R_{\alpha\beta}^q,$$

where

$$R_{\alpha\beta}^0 = \frac{8\pi^2 a}{5(1-i\omega\tau)} (P \cdot P) \tilde{u}_{\alpha\beta},$$

$$R_{\alpha\beta}^e = 0, \quad \alpha\beta = XX, YY, ZZ, YZ,$$

$$R_{xz}^e \approx \left[ \frac{2\pi^2 a}{5(1-i\omega\tau)} \right]^2 \{ [(P \cdot g^\alpha)^2 \Psi_-^e + (P \cdot V)^2 \Psi_-^e] (\tilde{u}_{xz} - i\tilde{u}_{yz})$$

$$+ [(P \cdot g^\alpha)^2 \Psi_+^e + (P \cdot V)^2 \Psi_+^e] (\tilde{u}_{xz} + i\tilde{u}_{yz}) \},$$

$$R_{yz}^e \approx i \left[ \frac{2\pi^2 a}{5(1-i\omega\tau)} \right]^2 \{ [(P \cdot g^\alpha)^2 \Psi_-^e + (P \cdot V)^2 \Psi_-^e] (\tilde{u}_{xz} - i\tilde{u}_{yz})$$

$$- [(P \cdot g^\alpha)^2 \Psi_+^e + (P \cdot V)^2 \Psi_+^e] (\tilde{u}_{xz} + i\tilde{u}_{yz}) \};$$

$$R_{\alpha\beta}^q = 0, \quad \alpha\beta = XZ, YZ, ZZ,$$

$$R_{xx}^q = -R_{yy}^q \approx \left[ \frac{\pi^2 a}{10(1-i\omega\tau)} \right]^2 (P \cdot V)^2 \{ (\tilde{u}_{xx} - \tilde{u}_{yy} + 2i\tilde{u}_{xy}) \Psi_+^e$$

$$+ (\tilde{u}_{xx} - \tilde{u}_{yy} - 2i\tilde{u}_{xy}) \Psi_-^e \},$$

$$R_{xy}^q \approx i \left[ \frac{\pi^2 a}{10(1-i\omega\tau)} \right]^2 (P \cdot V)^2 \{ (\tilde{u}_{xx} - \tilde{u}_{yy} - 2i\tilde{u}_{xy}) \Psi_-^e$$

$$- (\tilde{u}_{xx} - \tilde{u}_{yy} + 2i\tilde{u}_{xy}) \Psi_+^e \};$$

here

$$\Psi_{\pm}^e = \frac{a \beta^2 H^2 S(S+1)}{6TV_0} \frac{\mp g \beta H - iT_{2g}^{-1}}{\omega \pm g \beta H + iT_{2g}^{-1}}$$

$$\Psi_{\pm}^e = \frac{a \zeta}{TV_0} \left( \frac{3Q}{2S(2S-1)} \right)^2 \frac{\mp g \beta H - iT_{2d}^{-1}}{\omega \pm g \beta H + iT_{2d}^{-1}}$$

$$\Psi_{\pm}^e = \frac{a \zeta}{TV_0} \left( \frac{3Q}{2S(2S-1)} \right)^2 \frac{\mp 2g \beta H - iT_{2q}^{-1}}{\omega \pm 2g \beta H + iT_{2q}^{-1}}$$

$$\tilde{u}_{\alpha\beta}(x, t) = \tilde{u}_{\alpha\beta}(x) e^{-i\omega t}.$$

$R_{\alpha\beta}^0, R_{\alpha\beta}^e$  and  $R_{\alpha\beta}^q$  describe the effective shear elasticity of the liquid, which is due respectively to the displacement-orientation, anisotropic Zeeman and quadrupole interactions.

### 3. DISPERSION EQUATIONS

For the determination of the elastic properties of a liquid, with account of the effect of the spins, we have used the set of coordinates  $O$  whose  $Z$  axis is directed along  $H$ . On the other hand, the process of sound propagation is more conveniently considered directly, by choosing the set of coordinates  $O'$  such that one of its axes is directed along the wave vector  $k(\mathbf{d}(x, t) = d \exp \times (ik \cdot x - i\omega t))$ . With such a choice, the longitudinal and

transverse sound modes are coupled only through the weak spin-lattice interaction. Without limitation of generality, we assume that the vector  $\mathbf{k}$  lies in the  $XZ$  plane of the system  $O$  and therefore transformation to the system  $O'$  is made by rotation around the  $Y$  axis by an angle  $\vartheta$  such that  $k_y = k_{y'} = k$ . Choosing the components of the tensor  $R_{\alpha\beta}$  in the set of coordinates  $O'$  it is easy to get the dispersion equations from (9). When the frequency of the sound is close to one of the resonances and, consequently,  $|\Psi_{\pm}^{\alpha, \beta, \gamma}| \ll |\Psi_{\pm}^{\alpha, \beta, \gamma}| \ll 1$ , they have the following form (interaction between the longitudinal and transverse modes can be neglected):

a) The region  $\omega \approx g\beta H$ ; the longitudinal wave ( $d_{y', z'} = 0$ ):

$$\frac{\rho\omega^2}{k^2} \approx K - \frac{16}{15}\pi^2 a^2 (P \cdot P) \frac{i\omega\tau}{1 - i\omega\tau} + \frac{a}{6} B \sin^2 \vartheta; \quad (10)$$

transverse wave with the polarizations  $d_{y'} \cos 2\vartheta - id_{z'} \times \sin \vartheta = 0$ :

$$\frac{\rho\omega^2}{k^2} \approx -\frac{4}{5}\pi^2 a^2 (P \cdot P) \frac{i\omega\tau}{1 - i\omega\tau} + \frac{a}{4} B (\cos^2 2\vartheta + \sin^2 \vartheta); \quad (11)$$

transverse wave with polarization  $d_{y'} \sin \vartheta + id_{z'} \cos 2\vartheta = 0$ :

$$\frac{\rho\omega^2}{k^2} \approx -\frac{4}{5}\pi^2 a^2 (P \cdot P) \frac{i\omega\tau}{1 - i\omega\tau}, \quad (12)$$

$$B = \left(\frac{8\pi^2 a^2}{5}\right)^2 [(P \cdot g)^2 \Psi_{-}^{\alpha} + (P \cdot V)^2 \Psi_{-}^{\beta}].$$

b) The region  $\omega \approx 2g\beta H$ ; the longitudinal wave ( $d_{y', z'} = 0$ ):

$$\frac{\rho\omega^2}{k^2} \approx K - \frac{16}{15}\pi^2 a^2 (P \cdot P) \frac{i\omega\tau}{1 - i\omega\tau} + \frac{a}{6} C \cos^4 \vartheta; \quad (13)$$

transverse wave with polarization  $d_{y'} \cos \vartheta - id_{z'} = 0$ :

$$\frac{\rho\omega^2}{k^2} \approx -\frac{4}{5}\pi^2 a^2 (P \cdot P) \frac{i\omega\tau}{1 - i\omega\tau} - \frac{a}{4} C \cos^2 \vartheta (1 + \sin^2 \vartheta); \quad (14)$$

transverse wave with polarization  $d_{y'} + id_{z'} \sin \vartheta = 0$ :

$$\frac{\rho\omega^2}{k^2} \approx -\frac{4}{5}\pi^2 a^2 (P \cdot P) \frac{i\omega\tau}{1 - i\omega\tau}, \quad (15)$$

$$C = \left(\frac{32\pi^2 a^2}{5}\right)^2 (P \cdot V)^2 \Psi_{-}^{\alpha}.$$

At  $\omega \ll g\beta H$  and  $\omega \gg 2g\beta H$ ,  $R_{\alpha\beta}^g$  and  $R_{\alpha\beta}^a$  give small anisotropic contributions to the shear elasticity of the liquid. In the first case, the contribution is proportional to  $\omega$  and in the second, it does not depend on  $\omega$ .

#### 4. DISCUSSION OF THE RESULTS

It was shown above that at frequencies  $\omega \approx \omega_0$  and  $\omega \approx 2\omega_0$ . APRL lines should exist whose width corresponds in order of magnitude with the EPR or NMR lines in the liquid (10)–(15). As in APR in a solid, the matrix element of the resonance transition is proportional to  $\bar{u}_{\alpha\beta}$ . The physical explanation of this is contained in the character of the relaxation of the distribution function of the orientations of the molecules: in a magnetic field, the function  $f(\alpha, \beta, \gamma, \mathbf{x})$  relaxes at the rate  $\tau^{-1}$  to a non-isotropic quasi-equilibrium distribution, which is deter-

mined by the instantaneous orientation of the spins. As a result, singularities appear in the spectrum of the fluctuation of the orientation of the molecules at frequencies  $\omega \approx \omega_0$ ,  $\omega \approx 2\omega_0$ . The fact that at  $\omega \gg \tau^{-1}$  the liquid reveals solid properties, has long been known.<sup>[6]</sup>

In our problem, the transition to the "solid" regime takes place at  $\omega_0$ ,  $2\omega_0$ , and  $\omega_0\tau \ll 1$ . Although the "shear elasticity" of the liquid, which is produced by the spin-lattice interactions, is numerically small, it is sufficient for the formation of the APRL lines. Some similarity with the APR in a solid appears also in that transitions  $\Delta S_z = \pm 2$  are excited in APRL because of the quadrupole interaction, with a probability of transitions  $\Delta S_z = \pm 1$ . It should be recalled that the transitions  $\Delta S_z = \pm 2$  are forbidden as resonance transitions in EPR and NMR in liquids if  $\omega\tau \ll 1$ .

The quantity which determines the probability of observation of APRL directly is the ratio  $\Delta\alpha/\alpha$  of the coefficients of resonant and viscous absorption of the sound. The quantity  $\Delta\alpha/\alpha$  depends on the angle  $\vartheta$  between the wave vector and  $H$  (like  $\sin^2 2\vartheta$  for the transitions  $\Delta S_z = \pm 1$  and like  $\cos^4 \vartheta$  for the transitions  $\Delta S_z = \pm 2$ ). We shall give some numerical estimates.

The APRL lines have widths of the order of  $T_2^{-1} \sim \max\{(g^2\beta H)^2\tau, (QV)^2\tau\}$  so that  $\Delta\alpha/\alpha \sim 10^{-5} - 10^{-6}$  for  $T = 300$  K,  $H = 10^3$  Oe,  $\tau \sim 10^{-11}$  sec. The effect observed in nuclear APR in a solid is of the same order,<sup>[10]</sup> i.e., we can hope that the APRL can also be observed directly.

A flux of acoustic energy

$$W \geq \left(\frac{K}{\rho}\right)^{1/2} \frac{KT}{\mu V_0} \max\{(g^2\beta H\tau)^2, (QV\tau)^2\}$$

is necessary for saturation of the APRL lines. At  $g^2\beta H \sim QV \sim 2\pi \cdot 10^7$  sec<sup>-1</sup>,  $\tau \sim 10^{-11}$  sec,  $(K/\rho)^{1/2} \sim 10^5$  cm/sec,  $K \sim \mu$ ,  $T = 300$  K,  $V_0 \sim 10^{-22}$  cm<sup>3</sup>, we obtain  $W \sim 1$  W/cm<sup>2</sup> — a rather large value, which is in qualitative agreement with the experimental result of Ref. 5. The estimate of  $W$  is applicable to solutions of free radicals, which have narrow EPR lines.<sup>[11]</sup> In view of this, generation of sound of comparatively low frequency ( $\sim 10$  MHz) is necessary for detection of APRL,<sup>[5]</sup> which makes the free radicals promising objects for experiment.

For APR investigations of solids, low temperatures are customarily used to increase  $\Delta\alpha/\alpha$ .<sup>[12]</sup> On the other hand, upon cooling the liquid, the viscosity and the width of the resonance lines increase, so that  $\Delta\alpha/\alpha$  decreases. Therefore, it is better to investigate low-viscosity liquids by the method of APRL.

We note that in the search for the narrow lines of nuclear APRL it is necessary to take into account the specific mechanism of their broadening. Thus, diffusion or self-diffusion of molecules between nodes and antinodes of sound waves broadens the line by an amount  $\Delta\omega_D \sim Dk^2$  ( $D$  is the diffusion coefficient or the self-diffusion coefficient). A flow of liquid that is inhomogeneous in space, with velocity  $\mathbf{v}$ , shifts the line and broadens it by  $\Delta\omega \sim \mathbf{k} \times \mathbf{v}$ .<sup>[13]</sup>

In conclusion, we discuss the approximations allowed

in the calculation. First, in Eq. (4), we used only a single relaxation time  $\tau$ , which is clearly insufficient for the description, for example, of depolarized light scattering in a liquid.<sup>[7]</sup> However, this is valid in the APRL problem. Actually, in the model of continuous rotational diffusion<sup>[14]</sup> for APRL, solutions exist corresponding only to a single quantum number  $l=2$  and, because of this, to only a single relaxation time. Moreover, in the important practical case  $\omega\tau \ll 1$ , the orientation of the molecules follows that of the spins; therefore, the matrix element of the transition (but not the width of the APRL line) does not generally depend on  $\tau$  and on any details of the relaxation process. Finally, at  $\omega\tau \geq 1$ , the latter can also affect the matrix element of the APRL.

Second, the mechanisms of APRL considered above in liquids consisting of rigid, undeformed molecules, in which the form of the spin Hamiltonian (2) is determined by the orientation of the molecules. These mechanisms naturally do not take into account the excited electron states in the intra- and intermolecular electric fields, which is valid at least for many free radicals by virtue of the large excitation energy  $\Delta E$  of such states.<sup>[11]</sup> On the other hand, there are liquids in which the surrounding of the spin forms a sufficiently symmetric complex.<sup>[12]</sup> The quantity  $\Delta E$  is then smaller and in the APRL problem it is necessary to take into account the spin-orbit interaction, the deformability and the rotational motion of the complex. These features, and also other possible mechanisms of APRL (anisotropic hyperfine, dipole-dipole, and other interactions) are easily taken into account by the method outlined above. As in APR in solids, this can lead to a significant increase in the effect.

Finally, relaxation processes not considered above can exist in liquids, with such small  $\tau$  that their contribution to  $T_2$  would be negligibly small, but sig-

nificant in the matrix element of the APRL. Such processes also lead to an increase in  $\Delta\alpha/\alpha$ .

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- <sup>1</sup>S. A. Al'tshuler, Dokl. Akad. Nauk SSSR **85**, 1235 (1952); Zh. Eksp. Teor. Fiz. **28**, 38, 49 (1955) [Sov. Phys.-JETP **1**, **29**, 37 (1955)].
- <sup>2</sup>A. Kastler, *Experimentia* **8**, 1 (1952).
- <sup>3</sup>A. R. Kessel', Yadernyi akusticheski rezonans (Nuclear acoustic resonance) Nauka, 1969.
- <sup>4</sup>E. M. Iolin, Dokl. Akad. Nauk SSSR **211**, 809 (1973) [Sov. Phys.-Doklady **18**, 527 (1974)]. Magnetic resonance and related phenomena, Proc. XVII Congress AMPERE Turku, 1972. North Holland Publ. Co. 1973, p. 492; J. Phys. C: Sol. St. Phys. **6**, 3469 (1973).
- <sup>5</sup>G. L. Antokol'skiĭ, V. S. Baranov and E. M. Iolin, ZheTF Pis. Red. **23**, 685 (1976) [JETP Lett. **23**, 629 (1976)].
- <sup>6</sup>M. A. Leontovich, J. Phys. (USSR) **4**, 499 (1941).
- <sup>7</sup>S. M. Rytov, Zh. Eksp. Teor. Fiz. **58**, 2154 (1970); **59**, 2130 (1970) [Sov. Phys.-JETP **31**, 1163 (1970): **32**, 1153 (1971)].
- <sup>8</sup>A. R. Edmonds, Angular Momentum in Quantum Mechanics, Princeton Univ. Press, 1957.
- <sup>9</sup>A. Abragam, The Principals of Nuclear Magnetism, Clarendon Press, Oxford, 1961.
- <sup>10</sup>D. I. Bolef, in: Phys. Acoustics, (W. P. Mason, ed.), vol. 4, part A, Academic Press, New York, 1966.
- <sup>11</sup>A. L. Buchachenko and A. M. Vasserman, Stabil'nye radikaly (Stable radicals) Khimiya, Moscow, 1973.
- <sup>12</sup>S. A. Al'tshuler and B. M. Kozyrev, Elektronnyi paramagnitnye rezonans elementov promezhutochnykh grupp (Electron paramagnetic resonance of intermediate group element compounds). Nauka, 1972.
- <sup>13</sup>E. M. Iolin, VIII All-union conference on quantum acoustics and acousto-electronics. Abstracts of papers, Kazan', 1974, p. 73.
- <sup>14</sup>K. A. Valiev and E. N. Ivanov, Usp. Fiz. Nauk **109**, 31 (1973) [Sov. Phys.-Uspekhi **16**, 1 (1973)].

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## Slow thermal wave in a helium flow

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The motion of the He I-He II interphase boundary is considered in a narrow capillary tube for a specified flow rate. A temperature difference between the capillary and the thermostat (the temperature  $T_0$  of which is below  $T_c$ ) is maintained by the heat produced by the friction between the flow and the capillary walls. The flow regime with a constant velocity of the boundary and of the thermal wave due to the motion is investigated. The wave velocity, the temperature distribution  $T(x)$  along the capillary tube, and the distribution of the normal and superfluid velocities in the region  $T(x) < T_c$  are found. In some respects the solution is similar to that for a combustion regime, that is, to ignition and extinction waves.

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### INTRODUCTION

Steady flow of He I will take place along a capillary placed in a medium with a temperature below  $T_c$  if the

heat produced by friction against the walls is sufficient to maintain the temperature of the liquid in the capillary above  $T_c$ . The temperature difference between the capillary and the thermostat,  $T_1 - T_0$ , is proportional to the