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Stochastic Theory of Dynamic Spin Polarization in Viscous Liquids with Anisotropic Electron-Spin Relaxation

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A previously developed theory of dynamic nuclear polarization (DNP) in liquids is extended and applied to viscous liquids with anisotropic electron-spin relaxation ($T_{1e} \gg T_{2e}$). It is based on a Schrödinger equation for two spins, S and I, in which the influence of the "lattice" motion is incorporated by a randomly time-dependent field acting on the spin S and a random time dependence of the dipole interaction between S and I. The quantum-mechanical equations of motion in an applied rotating field near S-spin resonance are solved and the DNP of the I spin is expressed in terms of the stochastic parameters which characterize the liquid motion. Using values of these parameters as obtained from EPR and NMR experiments on two dilute organic radical solutions, one finds excellent agreement with our DNP measurements on these systems as reported in the preceding paper. It is characteristic of these solutions that the NMR requires a distribution of relaxation times. The analysis of DNP measurements confirms this; it gives a somewhat different distribution and permits a more specific correlation between it and the structure of the liquid. The range of applicability of the theory is discussed, and in an appendix a completely general set of equations for the two-spin relaxation in our model is derived. Using these, the only restrictions on the application of our theory would be that the S-S as well as the I-I interactions must be small and that the amplitude of the rotating field must be substantially smaller than the constant external field.

I. INTRODUCTION

In the preceding paper[1] we have presented data on the dynamic polarization of protons in two solutions of organic radicals at temperatures covering a wide range of viscosities. We will now show how this quantity can be calculated on the basis of known dynamical and stochastical properties of these systems. The theory to be used is an extension of one developed previously for this type of problem.[2]

The relevant properties of the two samples, viz., a 0.02-mole/liter solution of tanone in isopropanol and a 0.03-mole/liter solution of tetrachlorosemiquinone in tetraethyleneglycol, are described in Paper I and can be summarized as follows: (i) The electron spin of each radical ion has a dipolar interaction with the spins of protons in the molecules of its solvation layer. (ii) This interaction, modulated by a random rotation of this aggregate, can well account for the relaxation of the protons in the solvent, each of which spends a sufficient amount of time in a solvation layer. (iii) The electron spins relax through an anisotropic g factor modulated by a random rotation of the radical; neither the electron-proton nor the electron-electron spin dipole interaction contributes significantly. (iv) In the constant magnetic field H_0 of about 3300 G, in which all experiments were performed, the electron-spin relaxation as a function of the temperature θ is adequately described by a Markoffian model for the rotation of the radical, with correlation time τ_c. (v) One has $\tau_c \sim e^{\theta_0/\theta}$ and at all temperatures of interest to us τ_c satisfies the inequality $\tau_c\gamma_s H_0 \gg 1$. As a consequence, the electronic relaxation times obey the inequality $T_{1e} \gg T_{2e}$. (vi) The proton relaxation rates produced by the electron-proton spin dipole interaction cannot be obtained from a simple Markoffian model. We found an accurate expression for the proton relaxation times T_1 and T_2 by taking the standard relations based on a Markoffian model, replacing the distances r_i by some average $\langle r\rangle$ and averaging over a Gaussian distribution of $\ln\tau$. $\ln\tau^*$, which is the average of $\ln\tau$, and the width of the Gaussian are linear functions of $1/\theta$; τ^* is of the same order of magnitude as τ_c introduced above.[3] (vii) The two samples differ in that tanone has a hyperfine (hfs) splitting and tetrachlorosemiquinone has not and that the width of the distribution in the former is much more important than in the latter. The hyperfine interaction is anisotropic, thereby contributing to T_{1e} and T_{2e}, but we will neglect this feature in the following.

From these properties one can infer that the dynamic polarization must be calculable as an ensemble average of values obtained from suitably chosen two-spin Hamiltonians. These will contain a randomly time-dependent Zeeman-dipole interaction term, simulating the effects of the lattice degrees of freedom on the spin motion. The finiteness of the "lifetime" of a given electron-proton pair, due to the proton's departure from the solvation layer of the radical, can be completely ignored in the calculation. The reason for this is as follows: The dynamic polarization is produced quickly in each proton of the solvation layer individually by its interaction with the electron and takes a value given by the ratio of the rate of H_1-driven spin flips to the rate of electron-induced relaxation. After departing, the proton preserves the acquired polarization because relaxation in the solvent is negligibly slow. Thus each proton obtains a polarization as if it were permanently attached to a radical ion. In all this it is assumed that the reaction of the protons on the electron-spin motion is so small that it makes no difference that the protons are frequently replaced by others. This is valid because other forces on the electron dominate its motion. The existance of a hyperfine interaction need not be explicitly introduced. Although it is anisotropic and therefore contributes to T_{1e} and T_{2e}, the corresponding transitions between the hyperfine components are of no direct consequence for the dynamic polarization. It is therefore sufficient to calculate as if the hyperfine interaction were isotropic, i.e., to add the results obtained for each of the hyperfine states separately.

II. HAMILTONIAN

From the above properties we distill a model Hamiltonian of the following form:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_L(t) + \mathcal{H}_d(t) + \mathcal{H}_1(t) \ . \qquad (1)$$

$\mathcal{H}_0$ is the Zeeman energy of the electron averaged over all orientations of the radical ion plus the Zeeman energy of the proton in the external field H_0:

$$\mathcal{H}_0 = \gamma_S H_0 S_z + \gamma_I H_0 I_z \ . \qquad (2)$$

$\mathcal{H}_L(t)$ is the orientation-dependent part of the electronic Zeeman energy. Instead of giving the g-tensor components and then specifying the random rotation of the radical, we introduce the equivalent local field[4] $\vec{\mathrm{H}}_L(t)$ through

$$\mathcal{H}_L(t) = \gamma_S \vec{\mathrm{H}}_L(t)\cdot\vec{\mathrm{S}} \ . \qquad (3)$$

Since in our samples the electron relaxation comes almost wholly from this term, we will determine $\vec{\mathrm{H}}_L(t)$ as a Markoffian random variable (for any temperature) in such a way that the observed electron relaxation times T_{1e} and T_{2e} are obtained. The random transitions due to the hyperfine interaction are thus automatically included. $\mathcal{H}_d$ is the dipole interaction, to be written as

$$\mathcal{H}_d = \gamma_I \gamma_S \vec{\mathrm{I}}\cdot\overleftrightarrow{\Phi}(t)\cdot\vec{\mathrm{S}} \ . \qquad (4)$$

The statistical properties of $\overleftrightarrow{\Phi}(t)$ will be chosen similar to but not identical with those that produce the observed proton relaxation. $\mathcal{H}_1(t)$ is the energy of the electron spin in a "pumping" field $\vec{\mathrm{H}}_1(t)$:

$$\mathcal{H}_1(t) = \gamma_S \vec{\mathrm{H}}_1(t)\cdot\vec{\mathrm{S}} \ , \qquad (5)$$

of which the frequency Ω is near resonance, $\Omega \approx \gamma_s H_0$. It is rotating in the xy plane; in theory its amplitude can have any value, but in our experiments it was sufficiently large to saturate the electron-spin system. The effect of the anisotropy of g in this term and the direct influence of $\vec{\mathrm{H}}_1(t)$ on the proton spins are neglected.

III. DEVIATIONS FROM THERMODYNAMIC EQUILIBRIUM

It has been shown[2,5,6] that a model Hamiltonian of the form (1) allows the calculation of the deviation of any observable Q from its thermal-equilibrium value at temperature θ, as a function of time. To first order in $\beta = 1/k\theta$, one has, taking for convenience units with $\hbar = 1$,

$$\Delta Q(t) \equiv \langle Q\rangle_{\theta,t} - \langle Q\rangle_{\theta}^{\text{eq}} = \tfrac{1}{4}\,\mathrm{Tr}\,\{\mathcal{W}^{\dagger}(t)Q\mathcal{W}(t)\}_{\text{av}} , \tag{6}$$

$$i\frac{d\mathcal{W}(t)}{dt} = [\mathcal{H}_0 + \mathcal{H}_L(t) + \mathcal{H}_d(t) + \mathcal{H}_1(t + \tfrac{1}{2}i\beta)]\mathcal{W}(t) , \tag{7a}$$

$$\mathcal{W}(0) = 1 . \tag{7b}$$

The symbol $\{\cdots\}_{\text{av}}$ means averaging over an ensemble describing the stochastic motion. We are interested in the steady-state proton enhancement, i.e., in

$$\Delta I_z \equiv \langle I_z\rangle_{\theta,\infty} - \langle I_z\rangle_{\theta}^{\text{eq}} , \tag{8}$$

which quantity has been measured as a function of temperature.

IV. INTERACTION REPRESENTATION

Equation (7) will be brought into the interaction representation by means of two successive transformations. The first is a rotation around the z axis, of frequency Ω in the electron-spin space and of frequency $\omega = \gamma_I H_0$ in the proton-spin space. The transformed Hamiltonian is, to first order in β,

$$\mathcal{H}^r = \Delta\omega S_z + \omega_1 S_x + \tfrac{1}{2}i\beta\omega_1\Omega S_y + \gamma_s \vec{\mathrm{H}}_L^r(t)\cdot\vec{\mathrm{S}} + \gamma_I\gamma_s\vec{\mathrm{I}}\cdot\overleftrightarrow{\Phi}^r(t)\cdot\vec{\mathrm{S}} , \tag{9}$$

where $\Delta\omega = \gamma_s H_0 - \Omega$, $\omega_1 = \gamma_s H_1$, and $\vec{\mathrm{H}}_L^R$ and $\overleftrightarrow{\Phi}^R$ are the $\vec{\mathrm{H}}_L$ and $\overleftrightarrow{\Phi}$ seen in the rotating frame. The second transformation is in electron-spin space only and is made to remove all but the last term from the Hamiltonian. It is nonunitary (on account of the imaginary term in $\mathcal{H}$) and stochastic in nature and has been described in Ref. 6, where it was used to derive the modified Bloch equations. It can be construed as a (complex) random rotation of the reference frame of the electron spin which follows the precession due to the fields contained in the first four terms of Eq. (9). The transformed spin operators are given by the equation

$$\vec{\mathrm{S}}' = \overleftrightarrow{\mathrm{A}}(\vec{\mathrm{x}}(t))\cdot\vec{\mathrm{S}} - \vec{\mathrm{B}}(t) . \tag{10}$$

This is analogous to a result obtained in Ref. 2. The vector $\vec{\mathrm{B}}$, which is due to the imaginary term, approaches in time the value of the spin polarization as given by the modified Bloch equations minus $\langle\vec{\mathrm{S}}\rangle_{\theta}^{\text{eq}}$. $\vec{\mathrm{A}}$ is a rotation tensor in terms of complex Euler angles $x_1 = \vartheta$, $x_2 = \psi$, $x_3 = \varphi$. The difference with Ref. 2 is that because $T_{1e} \neq T_{2e}$ the Fokker-Planck equation for the probability law $P(\vec{\mathrm{x}}, \overline{\vec{\mathrm{x}}}, t)$ of $\vec{\mathrm{x}}$ and their complex conjugate $\overline{\vec{\mathrm{x}}}$ is anisotropic, as in Ref. 4. To first order in β, the Fokker-Planck equation has the form

$$\begin{aligned}
\frac{\partial P}{\partial t} &= (\mathfrak{F}_0 + \mathfrak{F}_1 + \mathfrak{F}_2)P ,\\
\mathfrak{F}_0 &= \frac{1}{2T_{1e}}(\vec{\mathrm{K}} + \overline{\vec{\mathrm{K}}})^2 + \left(\frac{1}{T_{2e}} - \frac{1}{T_{1e}}\right)(K_z + \overline{K}_z)^2 ,\\
\mathfrak{F}_1 &= -\Delta\omega(K_z + \overline{K}_z) - \omega_1(K_x + \overline{K}_x) ,\\
\mathfrak{F}_2 &= -\tfrac{1}{2}i\beta\omega_1\Omega(K_y - \overline{K}_y) ,
\end{aligned} \tag{11}$$

where $\vec{\mathrm{K}}$ and $\overline{\vec{\mathrm{K}}}$ are i times of angular momentum in terms of Euler angles and their complex conjugates, respectively.

The transformed Schrödinger equation is

$$\begin{aligned}
i\frac{d\mathcal{W}'(t)}{dt} &= \mathcal{H}'(t)\mathcal{W}'(t) ,\\
\mathcal{H}'(t) &= \gamma_I\gamma_S\vec{\mathrm{I}}\cdot\overleftrightarrow{\Phi}^R(t)\cdot\overleftrightarrow{\mathrm{A}}(x(t))\cdot\vec{\mathrm{S}} .
\end{aligned} \tag{12}$$

The term $\vec{\mathrm{B}}$ is neglected, as it only contributes second- and higher-order terms in β.

V. EQUATION FOR ΔI_z

As the above transformations leave I_z invariant, the dynamic polarization as defined by Eqs. (6) and (8) is equal to the limit for $t \to \infty$ of

$$\Delta I_z(t) = \tfrac{1}{4}\,\mathrm{Tr}\,\{\mathcal{W}'^{\dagger}(t)I_z\mathcal{W}'(t)\}_{\text{av}} . \tag{13}$$

An integral equation for $\Delta I_z(t)$ can be obtained by a double iteration with Eq. (12). This gives

$$\Delta I_z(t) = -\tfrac{1}{4}\,\mathrm{Tr}\int_0^t dt'\int_0^{t'} dt'' \times \{\mathcal{W}'^{\dagger}(t'')[\mathcal{H}'(t''), [\mathcal{H}'(t'), I_z]]\mathcal{W}'(t'')\}_{\text{av}} , \tag{14}$$

where, in view of the non-Hermitian nature of $\mathcal{H}'$, the commutator is defined by

$$[\mathcal{H}', Q] = \mathcal{H}'^{\dagger}Q - Q\mathcal{H}' . \tag{15}$$

The result takes a simple form if one uses unitary spin components

$$I_{\pm 1} = (1/\sqrt{2})(I_x \pm iI_y), \quad I_0 = I_z \tag{16}$$

and likewise for S. In order to decouple the equation for ΔI_z from the corresponding equations for the other spin variables, we first perform a truncation by neglecting the correlation between $\overleftrightarrow{\Phi}$ and the random variables $\overleftrightarrow{\mathrm{A}}$ and $\mathcal{W}'$. Thus the average values of products of $\overleftrightarrow{\Phi}$'s become correlation functions:

$$\{\Phi_{\alpha\mu}^R(t')\Phi_{\alpha'\mu'}^R(t'')\}_{\text{av}} = r^{-6}f_{\alpha\mu}^R(t' - t'')\delta_{\alpha',-\alpha}\delta_{\mu',-\mu} , \tag{17a}$$

where

$$f^R_{\alpha\mu}(t'-t'')=f_{\alpha\mu}(t'-t'')\exp[i(\alpha\omega+\mu\Omega)(t'-t'')] \; . \tag{17b}$$

$f_{\alpha\mu}(t)$ are the autocorrelation functions of the dipole tensor components on the laboratory frame, and r is the electron-proton distance. The cross-correlation functions of Φ disappear because the periodic factors contain t' and t'' separately and not only in the combination $t'-t''$. Neglecting terms of $O(\beta^3)$, Eq. (19) takes the form

$$\Delta I_z(t)=-\tfrac{1}{4}C\int_0^t dt'\int_0^{t'} dt''\sum_{\alpha\mu} f^R_{\alpha\mu}(t'-t'')\Big\{\alpha^2\sum_\gamma \mathrm{Re}\,A_{\mu\gamma}(t')\,\mathrm{Re}\,A_{-\mu-\gamma}(t'')\,\mathrm{Tr}[\mathcal{W}'^{\dagger}(t'')I_z\mathcal{W}'(t'')]$$
$$+\tfrac{1}{2}\alpha\sum_\gamma \mathrm{Re}A_{\mu\gamma}(t')\,\mathrm{Im}A_{-\mu-\gamma}(t'')\,\mathrm{Tr}[\mathcal{W}'^{\dagger}(t'')\mathcal{W}'(t'')]$$
$$+\alpha\sum_{\gamma\gamma'\sigma}\mathrm{Re}A_{\mu\gamma}(t')\,\mathrm{Re}A_{-\mu-\gamma'}(t'')\epsilon_{-\gamma\gamma'\sigma}\,\mathrm{Tr}[\mathcal{W}'^{\dagger}(t'')S_\sigma\mathcal{W}'(t'')]\Big\}_{\mathrm{av}} \; , \tag{18}$$

where

$$C=\tfrac{1}{4}\gamma_I^2\gamma_S^2r^{-6}, \quad \left.\begin{matrix}\mathrm{Re}\\ \mathrm{Im}\end{matrix}\right\}A=\tfrac{1}{2}[A(\vec{\mathrm{x}})\pm A(\bar{\vec{\mathrm{x}}})] \tag{19}$$

and where $\epsilon_{-\gamma\gamma'\sigma}$ is the antisymmetric tensor, $\epsilon_{10-1}=1$.

Next the averages appearing in Eq. (18) are approximated by moving $A(t')$ backward in time to t'' as if it had followed the most probable path (cf. Ref. 2), i.e.,

$$A(t')\rightarrow\exp[(t'-t'')(\mathfrak{F}_0+\mathfrak{F}_1)]A(t'') \; . \tag{20}$$

We have omitted the term $\mathfrak{F}_2$ in the exponent because we calculate only to order β. $\mathfrak{F}_0+\mathfrak{F}_1$ is a linear operator in the space of $A_{\mu\gamma}$ with fixed γ:

$$(\mathfrak{F}_0+\mathfrak{F}_1)A_{\mu\gamma}=\textstyle\sum_\kappa D_{\mu\kappa}A_{\kappa\gamma} \; , \tag{21}$$

$$\overleftrightarrow{\mathrm{D}}=\begin{pmatrix}-1/T_{2e}-i\Delta\omega & i\omega_1/\sqrt{2} & 0\\ i\omega_1/\sqrt{2} & -1/T_{1e} & -i\omega_1/\sqrt{2}\\ 0 & -i\omega_1/\sqrt{2} & -1/T_{2e}+i\Delta\omega\end{pmatrix} . \tag{22}$$

Therefore, Eq. (20) gives

$$A_{\mu\gamma}(t')\rightarrow\textstyle\sum_\nu[\exp(t'-t'')\overleftrightarrow{\mathrm{D}}]_{\mu\nu}A_{\nu\gamma}(t'') \; . \tag{23}$$

Substituting this into Eq. (18) allows one to use the orthogonality relations and product relations for real rotations, i.e.,

$$\textstyle\sum_\gamma \mathrm{Re}A_{\nu\gamma}(t)\,\mathrm{Re}A_{-\mu-\gamma}(t)=\delta_{\nu\mu} \tag{24}$$

and

$$\sum_{\gamma\gamma'}\epsilon_{-\gamma\gamma'\sigma}\,\mathrm{Re}A_{\nu\gamma}(t)\,\mathrm{Re}A_{-\mu-\gamma'}(t)=\sum_\kappa\epsilon_{-\nu\mu\kappa}\,\mathrm{Re}A_{\kappa\sigma}(t) \; . \tag{25}$$

With this the A's disappear in the first term of Eq. (18), leaving

$$\tfrac{1}{4}\{\mathrm{Tr}[\mathcal{W}'^{\dagger}(t'')I_z\mathcal{W}'(t'')]\}_{\mathrm{av}}=\Delta I_z(t'') \; .$$

The third term contains

$$\tfrac{1}{4}\{\mathrm{Tr}[\mathcal{W}'^{\dagger}(t'')\textstyle\sum_\sigma A_{\kappa\sigma}(t'')S_\sigma\mathcal{W}'(t'')]\}_{\mathrm{av}}=\Delta S_\kappa(t'') \; ,$$

which has the physical meaning of the deviation of S_κ from its value in the modified Bloch equations [cf. Eqs. (6) and (10) and Ref. 2]. In the second term, where $\mathrm{Im}A$ is already of order β, $\mathcal{W}'^{\dagger}(t'')\times\mathcal{W}'(t'')$ can be replaced by the unit matrix, leaving expressions of the form

$$J_{\nu\mu}=\{\textstyle\sum_\gamma \mathrm{Re}A_{\nu\gamma}(t'')\,\mathrm{Im}A_{\mu-\gamma}(t'')\}_{\mathrm{av}} \tag{26}$$

to be calculated.

Substituting into Eq. (18) gives

$$\Delta I_z(t)=-\int_0^t dt'\int_0^{t'} dt''[M(t'-t'')\Delta I_z(t'')$$
$$+\textstyle\sum_\kappa M_\kappa(t'-t'')\Delta S_\kappa(t'')-R(t'-t'')] \; , \tag{27}$$

where

$$M(t)=C\textstyle\sum_{\alpha\mu}\alpha^2f^R_{\alpha\mu}(t)[e^{t\overleftrightarrow{\mathrm{D}}}]_{\mu\mu} \; , \tag{28a}$$

$$M_\kappa(t)=C\textstyle\sum_{\alpha\mu}\alpha f^R_{\alpha\mu}(t)\sum_\nu\epsilon_{-\nu\mu\kappa}[e^{t\overleftrightarrow{\mathrm{D}}}]_{\mu\nu} \; , \tag{28b}$$

$$R(t)=-\tfrac{1}{2}C\textstyle\sum_{\alpha\mu}\alpha f^R_{\alpha\mu}(t)\sum_\nu J_{\nu-\mu}[e^{t\overleftrightarrow{\mathrm{D}}}]_{\mu\nu} \; . \tag{28c}$$

Equation (27) contains the variable $\Delta S_\kappa(t)$ for which similar equations are easily derived. However, ΔS_κ is the change in electron-spin polarization with respect to the modified Bloch equations produced by the electron-proton interaction. As we assume that this interaction is very small compared to either $\mathcal{H}_1$ or $\mathcal{H}_L$, ΔS_κ is small and can be neglected. This is just as well, because the frequent replacement of protons in the solvation layer is likely to invalidate a calculation of ΔS_κ in our model. With this approximation the asymptotic value of $\Delta I_z(t)$ for large t can now finally be obtained. One has

$$\Delta I_z=\int_0^\infty R(t)\,dt\Big/\int_0^\infty M(t)\,dt=R^L(0)/M^L(0) \; , \tag{29}$$

where the superscript L indicates the Laplace transform.

VI. EVALUATION OF M AND R

We assume that all the components of the dipole tensor have the same autocorrelation function

$$f_{\alpha\mu}(t) = f_{\alpha\mu} F(t) \ , \tag{30}$$

where $f_{\alpha\mu}$ have the well-known values

$$f_{\alpha\mu} = \frac{1}{5}\begin{pmatrix} 6 & 3 & 1 \\ 3 & 4 & 3 \\ 1 & 3 & 6 \end{pmatrix} . \tag{31}$$

We will write $F(t)$ as a Laplace integral, $F(t) = \int_0^\infty \bar{F}^L(p) e^{-pt} dp$. This gives

$$M^L(0) = C \sum_{\alpha\mu} \alpha^2 f_{\alpha\mu} \int_0^\infty dp\, \bar{F}^L(p) \times [(\overleftrightarrow{\mathrm{D}} + i\alpha\omega + i\mu\Omega - p)^{-1}]_{\mu\mu} \ , \tag{32}$$

$$R^L(0) = -\tfrac{1}{2} C \sum_{\alpha\mu\nu} \alpha f_{\alpha\mu} J_{\nu-\mu} \int_0^\infty dp\, \bar{F}^L(p) \times [(\overleftrightarrow{\mathrm{D}} + i\alpha\omega + i\mu\Omega - p)^{-1}]_{\mu\nu} \ . \tag{33}$$

For given $\bar{F}^L(p)$ the integrals are easily computed. For the constants $J_{\nu\mu}$ defined by Eq. (26) we find

$$J_{\nu\mu} = -\tfrac{1}{4} i \sqrt{2}\, \beta\omega_1 \Omega \sum_{\gamma\kappa} \kappa \epsilon_{\nu\mu\gamma} D^{-1}_{-\gamma\kappa} \ , \tag{34}$$

where $\overleftrightarrow{\mathrm{D}}^{-1}$ is the inverse of $\overleftrightarrow{\mathrm{D}}$. Equation (34) is derived in Appendix A.

It remains to choose $\bar{F}^L(p)$. For a Markoffian process one has

$$F(t) = e^{-t/\tau}, \quad \text{i.e.,} \quad \bar{F}^L(p) = \delta(p - 1/\tau) \ . \tag{35}$$

This was assumed in Ref. 2 but the data analyzed in Paper I strongly suggest that this is inadequate for the systems under study. A Gaussian distribution for $\ln\tau$ was found to give an accurate fit to the relaxation data. This can indeed be construed as the Laplace transform of $F(t)$, but another interpretation is possible and perhaps more plausible. This is that the spin pairs producing relaxation as well as dynamic polarization are inequivalent, each having a correlation function of the type (35) but forming an ensemble which can adequately be represented by a distribution of $\ln\tau$ as obtained. The electron-induced proton relaxation does not allow one to distinguish between these possibilities, because in our samples each electron-proton pair contributes separately and linearly to the observed relaxation rate. This is not so for dynamic polarization which, according to Eq. (29), is the ratio of two quantities each containing the correlation function. The question then is whether to average (29) as a whole or to average numerator and denominator separately.

In order to decide if one of these two extreme interpretations accounts for the data we have made sample calculations for both, taking averages over τ with the distribution function

$$G(\tau) = \frac{1}{\tau\sigma(2\pi)^{1/2}} \exp\left(-\frac{1}{2}\frac{(\ln\tau - \ln\tau^*)^2}{\sigma^2}\right) , \tag{36}$$

to which corresponds in Eqs. (32) and (33)

$$\bar{F}^L(p) = p^{-2} G(1/p) \ . \tag{37}$$

In each case we have optimized τ^*. For comparison we have also made a calculation with a Markoffian homogeneous model, optimizing τ.

VII. RESULTS

The values of T_{1e} and T_{2e} are taken from experiment and the width σ is taken from the analyses of the proton relaxation data as obtained in Paper I. Only τ^* is used as an adjustable parameter. In order to choose between the alternatives we have selected two well-defined features of the experimental curves for ΔI_z as a function of $\Delta\omega$, to wit, the maximum of the absolute value and the ratio p of the extreme values. The latter is a sensitive function of the temperature and varies between zero at high θ (pure inverted Overhauser effect) and 1 at low θ (solid effect). We have evaluated ΔI_z as a

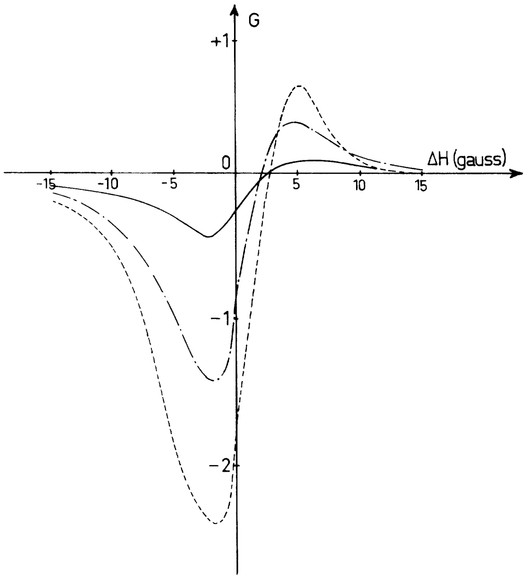

FIG 1. Values for one hyperfine component of the dynamic polarization of tanone in isopropanol at $\theta = -75\,^\circ\mathrm{C}$ calculated with three different models using $T_{1e} = 7.8 \times 10^{-7}$ sec, $T_{2e} = 3.7 \times 10^{-8}$ sec, $\omega_1 = 1.3 \times 10^7\ \mathrm{sec}^{-1}$. $G = A/A_0 - 1$, where A is the enhanced and A_0 the unenhanced signal amplitude. Dashed line: inhomogeneous model ($\sigma = 1.84$); dash-dot line: non-Markoffian model ($\sigma = 1.84$); solid line: Markoffian case ($\sigma = 0$).

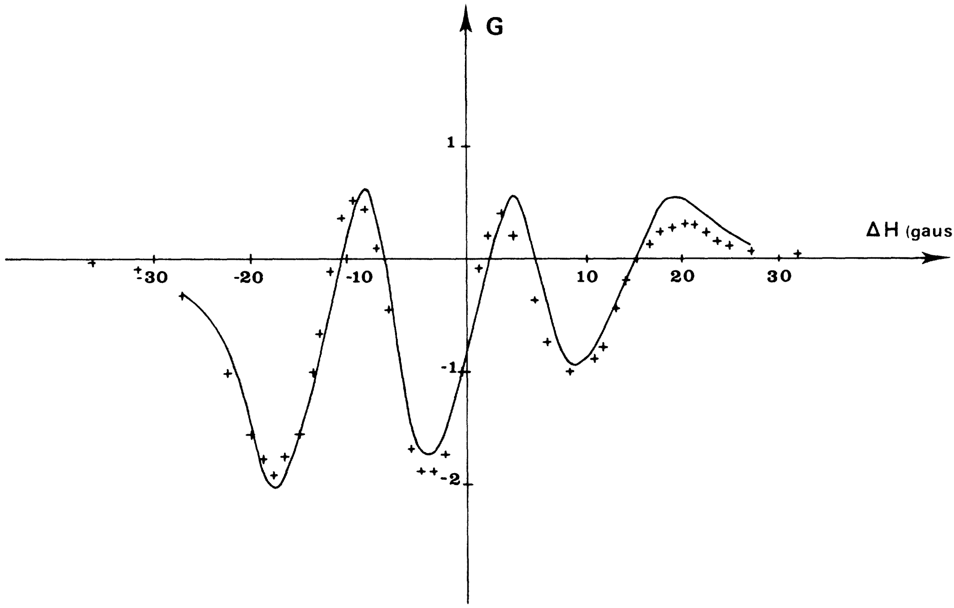

FIG. 2. Dynamic polarization of the tanone solution at $\theta = -75\,^{\circ}\mathrm{C}$. The drawn curve is calculated with $T_{1e} = 7.8\times10^{-6}$ sec, $T_{2e} = 3.7\times10^{-8}$ sec, $\sigma = 1.8$, $\tau^* = 1.49\times10^{-9}$ sec, $\omega_1 = 1.31\times10^{7}\ \mathrm{sec}^{-1}$.

function of $\Delta\omega$ for a temperature where the experimental curve is very asymmetrical, using parameters as we have found them in Paper I for the tanone sample at $\theta = -75\,^{\circ}\mathrm{C}$, i.e., $T_{1e} = 7.8\times10^{-7}$ sec, $T_{2e} = 3.7\times10^{-8}$ sec, $\sigma = 1.8$ (and $\omega_1 = 1.31\times10^{7}\ \mathrm{sec}^{-1}$). At this temperature our measurements gave, for each of the three curves into which the dynamic polarization can be decomposed, a ratio $p = 0.25$. Figure 1 shows the result for the three models. In each case τ^* (or τ) has been chosen to make $p = 0.25$. The inhomogeneous interpretation is strongly favored, as it gives very nearly the observed magnitude. The non-Markoffian model gives a 40% discrepancy in magnitude and the homogeneous Markoffian case is completely ruled out. The values of τ^* are, respectively, 2.3, 0.34, and 1.5 times the value obtained from proton relaxation.

For the sample of tetrachlorosemiquinone, the inhomogeneous model also gives the best results, although the differences are less pronounced. This could be expected because the width σ is much smaller.

A complete set of curves has been calculated only for the inhomogeneous case, i.e., by using (32), (33), and (35) in (29) and averaging afterwards with (36). Figures 2 and 3 show the sum of contributions from the three equidistant hyperfine components for tanone in isopropanol at −75 and −85 °C, respec-

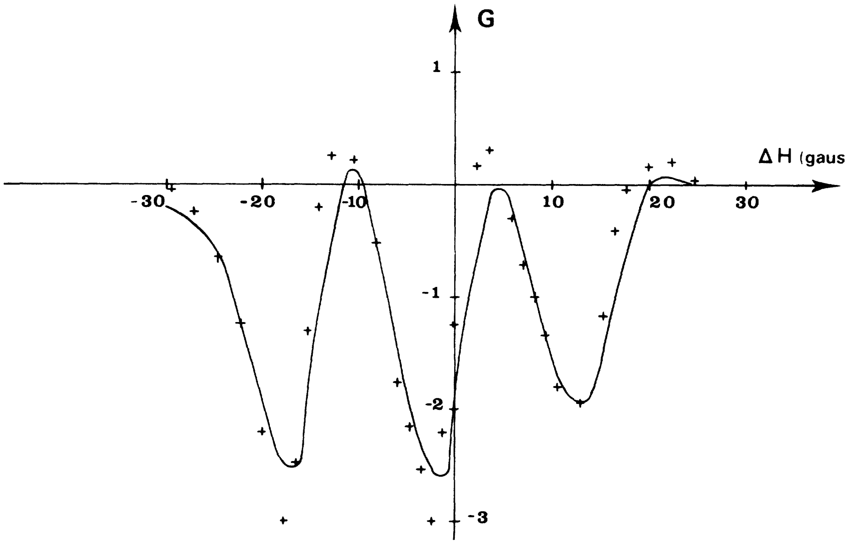

FIG. 3. Dynamic polarization of the tanone solution at $\theta = -85\,^{\circ}\mathrm{C}$. The drawn curve is calculated with $T_{1e} = 1.1\times10^{-6}$ sec, $T_{2e} = 2.4\times10^{-8}$ sec, $\sigma = 1.8$, $\tau^* = 2.86\times10^{-9}$ sec, $\omega_1 = 1.31\times10^{7}\ \mathrm{sec}^{-1}$.

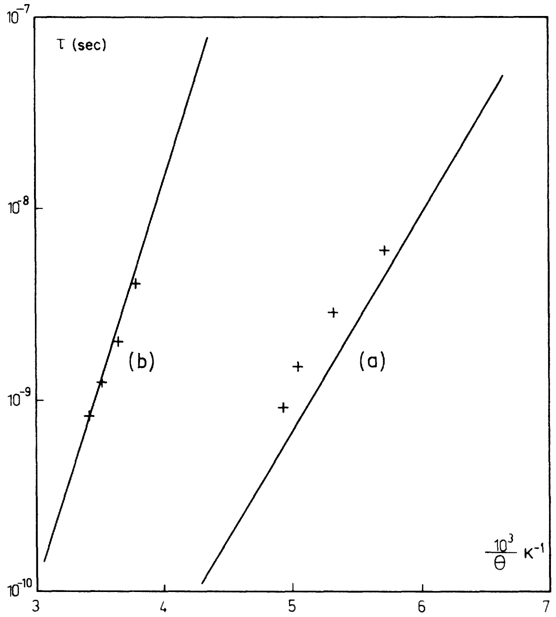

FIG. 4. Values of τ^* as a function of temperature from dynamic polarization (pluses) and from proton relaxation (solid line): (a) tanone, (b) semiquinone.

tively. Figure 4 gives the value of τ^* at four temperatures. For comparison, τ^* from relaxation has also been plotted. Figures 5 and 6 show results for tetrachlorosemiquinone in tetraethyleneglycol. The best values of τ^* and their counterparts from relaxation have been included in Fig. 4.

VIII. CONCLUSIONS

The quantitative agreement between calculation and experiment shows that the dynamic polarization in our samples is adequately described by a simple stochastic model which agrees with and was essentially obtained from an analysis of proton and electron relaxation data. Where the latter left an ambiguity as to the origin is a distribution of correlation times, the dynamic polarization favors an inhomogeneous model, ascribing the distribution to the presence of inequivalent electron-proton pairs, all contributing to the proton relaxation and to the dynamic polarization. In view of what is known of the materials used and because electron spin-orbit relaxation does not require a distribution, this result could have been expected, and it is safe to conclude that the rather similar distribution needed to account for the proton relaxation in the pure solvents describes an analogous situation.

The origin of the difference between τ^* as obtained from relaxation and from dynamic polarization can be explained as follows: It is seen from Eq. (29) that ΔI_z for a given spin pair is the ratio of two quantities and that, to the extent that the proton is in the solvation layer of the electron's radical, the distance r between the two spins divides out. The average over all spin pairs is thus an average over correlation times of random motion only. The electron-induced proton relaxation rate, on the other hand, is linear in the correlation function and, as shown in Appendix B, closely related to the denominator of Eq. (29). Averaging it means taking the average, over correlation times and relative distances simultaneously, of a function of orientation divided by r^6. Since one can expect a spread in r of a factor of approximately 2, the two averaging procedures differ widely. Having kept

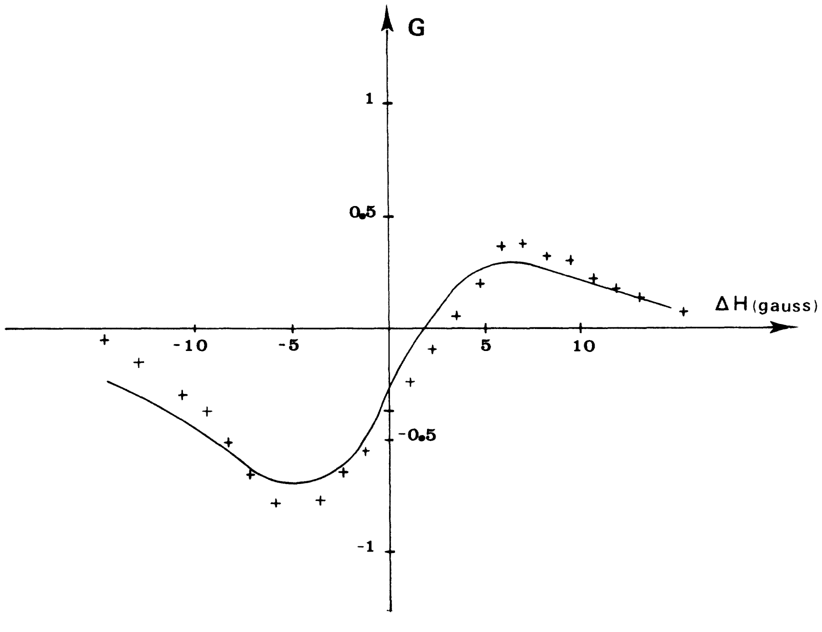

FIG. 5. Dynamic polarization of the semiquinone solution at $\theta = 20\,°\mathrm{C}$. The drawn curve is calculated with $T_{1e} = 2.5 \times 10^6$ sec, $T_{2e} = 1.0 \times 10^{-7}$ sec, $\sigma = 0.9$, $\tau^* = 0.82 \times 10^{-9}$ sec, $\omega_1 = 1.31 \times 10^7$ sec^{-1}.

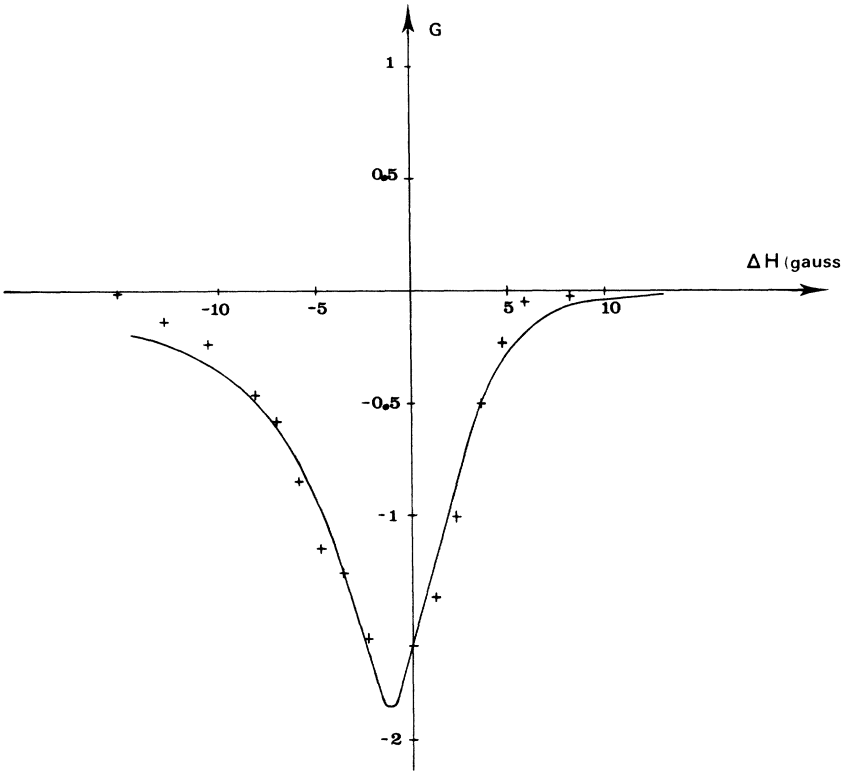

FIG. 6. Dynamic polarization of the semiquinone solution at 0 °C. The drawn curve is calculated with $T_{1e}=6.8\times10^{-6}$ sec, $T_{2e}=4.9\times10^{-8}$ sec, $\sigma=0.9$, $\tau^*=2.02\times10^{-9}$ sec, $\omega_1=1.31\times10^{7}$ sec^{-1}.

the variance σ of the distribution constant, the results appear as a difference in τ^*. This explanation is consistent with the fact that, as reported in Paper I, the EPR requires no distribution, showing that the ion, at least, experiences a Markoff-type motion. One must conclude that the molecules of the solvation layer move with respect to the ion, of which motion the NMR and the DNP give two distinct measures, the first including a weighting factor r^{-6} and the second being independent of r. It is in this connection of interest that the dynamic polarization is much more sensitive to the choice of τ^* than the relaxation.

One finds in this manner a new method for studying molecular motion through the introduction of radicals and the measurement of dynamic polarization. This opens possibilities for "radicular probes" to reveal the dynamics of molecular motion in viscous substances, inhomogeneous media, smectic and nematic liquids, colloids, and polymers. Perhaps it would even be possible to use dynamic polarization in the study of phase transitions near a critical point.

As for the theory, its essential limitation is that the electron spin-spin interaction is small and that the nuclear-spin relaxation is dominated by the electron-nuclear coupling. We have also used the fact, verified for our samples, that the electron-spin relaxation comes primarily from the spin-lattice coupling term $\mathcal{H}_L(t)$ of the Hamiltonian. This allowed us to identify the parameters T_{1e} and T_{2e} of the Fokker-Planck equation with the experimentally observed relaxation times. Our method can easily be extended to cases where this is not true and can thus be made to include the "bottle-neck" effect in dynamic polarization.[7] To this end one must derive a complete set of equations for total electronic and nuclear relaxation rates on the basis of our model, dropping the term $\mathcal{H}_1(t)$ from the Hamiltonain. They will contain four parameters, viz., T_{1e}, T_{2e}, τ^*, and σ. The former two are relaxation times in the absence of $\mathcal{H}_d$, and therefore unknown. All four should be optimized by fitting the equations to the experimental relaxation data. The values of T_{1e} and T_{2e} thus found should be used in Eq. (29), but for reasons discussed above, τ^* (and preferably also σ) in the equations for dynamic polarization should not be identified with the values obtained from relaxation. The equations required to carry out this program are given in Appendix B.

These same equations are also needed in the analysis of experiments in weaker fields H_0, for which $\tau\Omega_0\approx1$. In that case double spin flips contribute essentially to the proton relaxation and the corresponding terms are modified by the electron spin-lattice relaxation. This effect was discussed in Paper I where it was shown that it is negligible in the present experiments.

After this there remains a very weak restriction of the strength of H_0 demanding only that an oscillating field of frequency $\gamma_s H_0$ be replaced by its resonant rotating comment $H_1(t)$. This means $H_0 \gg H_1$, i.e., fields larger than 10 G. Low-field experiments[8] are thus within the range of our theory.

Finally, with regard to the allowed amplitudes of the field H_1, and apart from the obvious requirement that the lattice remain in thermal equilibrium at the temperature θ, we have imposed only one restriction. This was introduced when the terms proportional to ΔS in Eq. (27) for ΔI_z were neglected. As discussed there, this presupposes that the influence of the I-spin on the S-spin polarization is negligible either compared to the influence of $\mathcal{H}_L$ or $\mathcal{H}_1$. If this is not the case, one would need two coupled equations for ΔI_z and ΔS_z similar to those for relaxation in Appendix B and easily derived. In contrast to the case of relaxation, this generalization would be meaningful only if the I-S spin pair were permanently coupled, unlike in our present samples. With this exception, therefore, our equations should correctly describe the saturation curves as well as the dynamic polarization for complete saturation.

APPENDIX A: EVALUATION OF $J_{\nu\mu}$

From the definition (26) one has

$$J_{\nu\mu} = -\tfrac{1}{4}\left\{\textstyle\sum_\gamma [A_{\nu\gamma}(\vec{\mathrm{x}})A_{\mu-\gamma}(\vec{\bar{\mathrm{x}}}) - A_{\mu-\gamma}(\vec{\mathrm{x}})A_{\nu\gamma}(\vec{\bar{\mathrm{x}}})]\right\}_{\mathrm{av}} . \tag{A1}$$

The average is over time, the evolution of $\vec{\mathrm{x}}(t)$ and $\vec{\bar{\mathrm{x}}}(t)$ being given by the Fokker-Planck equation. The right-hand side of (A1) will be expressed linearly in eigenfunctions of $\mathfrak{F}$ of Eq. (11), calculated to first order in the perturbation $\mathfrak{F}_2$. It follows from Eq. (11) that the functions $\psi_{\alpha\beta} = \sum_\gamma A_{\alpha\gamma}(\vec{\mathrm{x}})A_{\beta-\gamma}(\vec{\bar{\mathrm{x}}})$ transform mutually under the operators $\mathfrak{F}_0$, $\mathfrak{F}_1$, and $\mathfrak{F}_2$. An orthogonal basis in the linear space of $\psi_{\alpha\beta}$ can be found by defining an inner product through

$$(\phi_1(\vec{\mathrm{x}}, \vec{\bar{\mathrm{x}}}),\ \phi_2(\vec{\mathrm{x}}, \vec{\bar{\mathrm{x}}})) = \int \phi_1^*(\vec{\mathrm{x}}, \vec{\bar{\mathrm{x}}})\phi_2(\vec{\mathrm{x}}, \vec{\bar{\mathrm{x}}})\, d^3\vec{\mathrm{x}}\, d^3\vec{\bar{\mathrm{x}}} ,$$

where $\vec{\mathrm{x}}$ and $\vec{\bar{\mathrm{x}}}$ are treated as independent real variables and where the volume element for Euler angles is taken as $d^3\vec{\mathrm{x}} = \sin\vartheta\, d\vartheta\, d\varphi\, d\psi$. That makes the angular momentum operators $-i\vec{\mathrm{K}}$ and $-i\vec{\bar{\mathrm{K}}}$ Hermitian, and therefore the simultaneous eigenfunctions of the commuting operators $\mathfrak{F}_0$ and $L_z = -i(K_z + \bar{K}_z)$ orthogonal. These are $\phi_{00} = \sum_\alpha \psi_{\alpha,-\alpha}$, with eigenvalue zero of $\mathfrak{F}_0$, L_z, and of $\mathfrak{F}_1$; $\phi_{\sigma 1} = \sum_{\alpha\beta} \epsilon_{-\sigma\alpha\beta}\psi_{\alpha\beta}$ with eigenvalues $-1/T_{1e} - \sigma^2(1/T_{2e} - 1/T_{1e})$ for $\mathfrak{F}_0$ and σ for L_z and similarly $\phi_{\lambda 2}$ with eigenvalues $-3/T_{1e} - \lambda^2(1/T_{2e} - 1/T_{1e})$ for $\mathfrak{F}_0$ and λ for L_z. In terms of these functions, one has

$$\sum_{\nu\mu} \epsilon_{-\sigma\nu\mu} J_{\nu\mu} = -\tfrac{1}{2}\{\phi_{\sigma 1}\}_{\mathrm{av}} , \tag{A2}$$

while

$$(\mathfrak{F}_0 + \mathfrak{F}_1)\phi_{00} = 0 , \tag{A3}$$

$$(\mathfrak{F}_0 + \mathfrak{F}_1)\phi_{\sigma 1} = \textstyle\sum_\kappa D_{\sigma\kappa}\phi_{\kappa 1} . \tag{A4}$$

Let ϕ'_{00}, $\phi'_{\sigma 1}$, and $\phi'_{\lambda 2}$ be defined as functions in the linear space of $\psi_{\alpha\beta}$ which are the same linear combinations of the eigenfunctions of $\mathfrak{F}_0 + \mathfrak{F}_1 + \mathfrak{F}_2$ as ϕ_{00}, $\phi_{\sigma 1}$, and $\phi_{\lambda 2}$ are of the eigenfunctions of $\mathfrak{F}_0 + \mathfrak{F}_1$. Writing

$$\phi_{\sigma 1} = A_{\sigma 00}\phi'_{00} + \textstyle\sum_\kappa A_{\sigma\kappa 1}\phi'_{\kappa 1} + \sum_\lambda A_{\sigma\lambda 2}\phi'_{\lambda 2} , \tag{A5}$$

one has $A_{\sigma 00} = O(\beta)$, $A_{\sigma\lambda 2} = O(\beta)$, $A_{\sigma\kappa 1} = \delta_{\sigma\kappa} + O(\beta)$, while $\{\phi'_{\kappa 1}\}_{\mathrm{av}} = \{\phi'_{\lambda 2}\}_{\mathrm{av}} = 0$. Using the orthogonality of the unprimed ϕ's, (A5) gives

$$\{\phi_{\sigma 1}\}_{\mathrm{av}} = -\{\phi_{00}\}_{\mathrm{av}}(\phi_{00}, \phi'_{\sigma 1})/(\phi_{00}, \phi_{00}) + O(\beta^2) . \tag{A6}$$

The inner product $(\phi_{00}, \phi'_{\sigma 1})$ is obtained from the equation

$$(\mathfrak{F}_0 + \mathfrak{F}_1 + \mathfrak{F}_2)\phi'_{\sigma 1} = \textstyle\sum_\kappa D_{\sigma\kappa}\phi'_{\kappa 1} + O(\beta^2) \tag{A7}$$

which follows from the fact that the diagonal elements of $\mathfrak{F}_2$ are at most of order β^2. Equation (A7) can be written in tensor notation as

$$(\mathfrak{F}_0 + \mathfrak{F}_1 - \overleftrightarrow{\mathrm{D}})\vec{\phi}'_{,1} = -\mathfrak{F}_2\phi'_{,1} , \tag{A8}$$

from which

$$\begin{aligned}(\phi_{00}, \phi'_{,1}) &= -(\phi_{00}, (\mathfrak{F}_0 + \mathfrak{F}_1 - \overleftrightarrow{\mathrm{D}})^{-1}\mathfrak{F}_2\phi'_{,1}) \\ &= -((\mathfrak{F}_0 - \mathfrak{F}_1 - \overleftrightarrow{\mathrm{D}}^*)^{-1}\phi_{00}, \mathfrak{F}_2\phi'_{,1}) \\ &= \overleftrightarrow{\mathrm{D}}^{-1}(\phi_{00}, \mathfrak{F}_2\phi'_{,1})\end{aligned}$$

or

$$(\phi_{00}, \phi'_{\sigma 1}) = \textstyle\sum_\kappa (D^{-1})_{\sigma\kappa}(\mathfrak{F}_2\phi_{00}, \phi_{\kappa 1}) + O(\beta^2) . \tag{A9}$$

One has furthermore

$$(K_y - \bar{K}_y)\phi_{00} = \sqrt{2}(\phi_{-11} - \phi_{11}) , \tag{A10}$$

while the explicit form of $A_{\mu\gamma}$ in terms of Euler angles,

$$A_{\mu\gamma} = e^{i(\mu\psi + \gamma\varphi)}C_{\mu\gamma} ,$$

$$C_{\mu\gamma} = \begin{pmatrix} (1+c)/2 & -is/\sqrt{2} & (1-c)/2 \\ -is/\sqrt{2} & c & is/\sqrt{2} \\ (1-c)/2 & is/\sqrt{2} & (1+c)/2 \end{pmatrix} ,$$

$$c = \cos\vartheta, \quad s = \sin\vartheta \tag{A11}$$

gives $\{\phi_{00}\}_{\mathrm{av}} = 3$, $(\phi_{00}, \phi_{00}) = 4(2\pi)^4$, $(\phi_{11}, \phi_{11}) = \frac{8}{3}(2\pi)^4$. Combining (A2), (A6), and (A9), one gets

$$J_{\nu\mu} = -\tfrac{1}{4}\sqrt{2}\, i\beta\omega_1\Omega \sum_{\kappa\gamma} \kappa\epsilon_{\nu\mu-\gamma}(D^{-1})_{\gamma\kappa} . \tag{A12}$$

APPENDIX B: RELAXATION, GENERAL EQUATIONS

Equations for two-spin relaxation for the underlying model have been derived earlier[9] under the simplifying assumption $T_{1e} = T_{2e}$. The general equations are obtained as follows: With $\mathcal{H}_1 = 0$ ($\omega_1 = 0$) and choosing $\Delta\omega = 0$, the interaction Hamiltonian has the form as in Eq. (12), but A is now real. In Eq. (11), $\mathfrak{F}_1$ and $\mathfrak{F}_2$ are zero and, correspondingly, the matrix $\overleftrightarrow{D}$ of Eq. (22) is diagonal:

$$\mathfrak{F}_0 A_{\mu\nu} = \lambda_\mu A_{\mu\nu}, \quad \lambda_{\pm 1} = -1/T_{2e}, \quad \lambda_0 = -1/T_{1e} \ , \tag{B1}$$

where T_{1e} and T_{2e} are the S-spin relaxation times in absence of the dipole coupling. The deviation of the spin polarization from thermal equilibrium is given by

$$\Delta I_\gamma(t) - \Delta I_\gamma(0) = \tfrac{1}{4}\,\mathrm{Tr}\{\mathcal{W}'^{\dagger}(t)\, I_\gamma\, \mathcal{W}'(t)\}_{\mathrm{av}} \ , \tag{B2}$$

$$\Delta S_\gamma(t) - e^{\lambda_\gamma t}\Delta S_\gamma(0) = \tfrac{1}{4}\,\mathrm{Tr}\{\mathcal{W}'^{\dagger}(t) \textstyle\sum_\nu A_{\gamma\nu}(t) S_\nu \mathcal{W}'(t)\}_{\mathrm{av}} \ , \tag{B3}$$

where $\mathcal{W}'(t)$ satisfies Eq. (12) but with arbitrary initial $\mathcal{W}(0)$ and corresponding $\Delta I_\gamma(0)$ and $\Delta S_\gamma(0)$. (The subscript zero is synonymous with z.) The right-hand side of Eqs. (B2) and (B3) can be expressed as the integral of a double commutator, as in Eq. (14), where $\mathcal{H}'$ is now Hermitian. With the approximation of Eq. (20) for $A(t')$ in (B2) and the corresponding

$$A_1(t')A_2(t) \rightarrow e^{(t'-t'')\mathfrak{F}}[A_1(t'')e^{(t-t')\mathfrak{F}}A_2(t'')] \tag{B4}$$

in (B3), and with the truncation that averages of $\vec{\phi}(t'')\vec{\phi}(t')$ are taken separately, the double commutator can be evaluated. Using the relations between $A_{\mu\nu}$ of Eqs. (24) and (25), we obtain

$$\Delta I_\gamma(t) - \Delta I_\gamma(0) = -C\int_0^t dt' \int_0^{t'} dt'' \Big(\sum_{\alpha\mu} (1-\delta_{\alpha\gamma}) \tilde{f}_{\alpha\mu}(t'-t'')\Delta I_\gamma(t'') + \delta_{\gamma 0}\sum_{\alpha\mu} \alpha\mu \tilde{f}_{\alpha\mu}(t'-t'')\Delta S_0(t'') \Big) \ , \tag{B5}$$

$$\Delta S_\gamma(t) - e^{\lambda_\gamma t}\Delta S_\gamma(0) = -C\int_0^t dt' \int_0^{t'} dt'' \Big(\delta_{\gamma 0}\sum_{\alpha\mu} \alpha\mu \tilde{f}_{\alpha\mu}(t'-t'')\Delta I_0(t'') + \sum_{\alpha\mu} (1-\delta_{\mu\gamma}) \tilde{f}_{\alpha\mu}(t'-t'')\Delta S_\gamma(t'') \Big) e^{\lambda_\gamma (t-t')} \ , \tag{B6}$$

where

$$\tilde{f}_{\alpha\mu}(t) = f_{\alpha\mu}(t) e^{(i\alpha\omega + i\mu\Omega + \lambda_\mu)t} \ . \tag{B7}$$

$f_{\lambda\mu}(t)$ is defined in Eq. (17), and C in Eq. (19).

A Laplace transform gives

$$\Big(p + C\sum_{\alpha\mu}(1-\delta_{\alpha\gamma})\tilde{f}^L_{\alpha\mu}(p)\Big)\Delta I^L_\gamma(p) + C\delta_{\gamma 0}\sum_{\alpha\mu}\alpha\mu \tilde{f}^L_{\alpha\mu}(p)\Delta S^L_0(p) = \Delta I_\gamma(0) \ , \tag{B8}$$

$$C\delta_{\gamma 0}\sum_{\alpha\mu}\alpha\mu\tilde{f}^L_{\alpha\mu}(p)\Delta I^L_\gamma(p) + \Big(p - \lambda_\gamma + C\sum_{\alpha\mu}(1-\delta_{\mu\gamma})\tilde{f}^L_{\alpha\mu}(p)\Big)\Delta S^L_\gamma(p) = \Delta S_\gamma(0) \ . \tag{B9}$$

When Eqs. (30) and (35) apply, $\tilde{f}^L_{\alpha\mu}(p)$ takes the form

$$\tilde{f}^L_{\alpha\mu}(p) = f_{\alpha\mu}(p + i\alpha\omega + i\mu\Omega + \lambda_\mu - 1/\tau)^{-1} \ . \tag{B10}$$

The characteristic times are given by

$$1/T_i = -p_i \ , \tag{B11}$$

where p_i are the zeros of the determinant of Eqs. (B8) and (B9). The equations fall apart in two simultaneous equations for ΔI_0 and ΔS_0 and four separate equations for ΔI_γ and for ΔS_γ, $\gamma = \pm 1$. One has

$$\Big(p + C\sum_{\alpha\mu}\alpha^2\tilde{f}^L_{\alpha\mu}(p)\Big)\Big(p + \frac{1}{T_{1e}} + C\sum_{\alpha\mu}\mu^2\tilde{f}^L_{\alpha\mu}(p)\Big) = C^2\Big(\sum_{\alpha\mu}\alpha\mu\tilde{f}^L_{\alpha\mu}(p)\Big)^2 \ , \tag{B12}$$

the two (real) roots giving the characteristic times for the simultaneous decay of ΔI_0 and ΔS_0,

$$p + C\sum_{\alpha\mu}(1-\delta_{\alpha,\pm 1})\tilde{f}^L_{\alpha\mu}(p) = 0 \ , \tag{B13}$$

giving the decay of $\Delta I_\pm$, respectively, and

$$p + \frac{1}{T_{2e}} + C\sum_{\alpha\mu}(1-\delta_{\mu,\pm 1})\tilde{f}^L_{\alpha\mu}(p) = 0 \tag{B14}$$

for the decay of $\Delta S_\pm$. The roots of (B13) and (B14) have a nonvanishing imaginary part.

Equation (B12) shows that longitudinal relaxation times for the spins individually can be defined only if the right-hand side is small. One then has

$$p + C\sum_{\alpha\mu}\alpha^2\tilde{f}^L_{\alpha\mu}(p) = 0 \tag{B15}$$

for the relaxation of ΔI_0 and

$$p + \frac{1}{T_{1e}} + C\sum_{\alpha\mu}\mu^2\tilde{f}^L_{\alpha\mu}(p) = 0 \tag{B16}$$

for the relaxation of ΔS_0. Typically, this can be expected when the rates $1/T_{1e}$ and $1/T_{2e}$ are much larger than the rates produced by the dipole interaction, or when the spins have quite different Larmor frequencies, $\Omega \gg \omega$, and the field is "high" so that $\Omega\tau \gg 1$, where τ is the correlation time of the dipole term. When the former condition holds and more generally when the dipole rates are small compared with $1/\tau + 1/T_e$, Eqs. (B13)–(B16) can be solved by iteration. Thus the familiar expressions from the I-spin relaxation are obtained by putting $p=0$ as the argument of $\bar{f}^{L}_{\alpha\mu}$ in Eqs. (B13) and (B15), and the first-order corrections to the S-spin relaxation follow from (B14) and (B16) by taking $p=-1/T_{2e}$ and $p=-1/T_{1e}$ in $\bar{f}^{L}_{\alpha\mu}$, respectively. In order to apply the Eqs. (B10) and (B13)–(B16) to an inhomogeneous system, they must, in principle, first be solved for p which is then to be averaged over an appropriate ensemble for the values of C and τ. In the above approximation this amounts to averaging the equations, which makes this case indistinguishable (as far as relaxation is concerned) from the case of a homogeneous system with a nonexponential correlation function.

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High-Frequency Electrostatic Plasma Instabilities

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A description of the stability properties of a plasma under the influence of an external electric field oscillating near the plasma frequency is presented.

I. INTRODUCTION

We investigate the stability properties of a homogeneous plasma under the influence of an alternating electric field oscillating at frequencies near the plasma frequency. Describing the stability properties of this system represents a first step in the understanding of a mechanism for absorption of energy in a plasma from laser radiation. This problem has been studied by many authors[1-6] using various analytic expansion techniques. The basic results of their work have been the discovery of two distinct instabilities which occur when the driving frequency is either slightly above or below the Bohm-Gross frequency. It is our aim in this paper to consolidate and expand upon their work by solving the equations numerically, thereby obtaining solutions for a wide range of parameters. From these results it is possible to obtain a relatively simple picture of the structure of the two fundamental unstable modes.

II. THEORY

In the collisionless approximation the equations governing the behavior of a homogeneous plasma under the influence of an electric field

$$\vec{\mathrm{E}}_{\mathrm{ext}} = \vec{\mathrm{y}} E_0 \sin\omega_0 t$$

are

$$\frac{\partial f_j}{\partial t} + v\frac{\partial f_j}{\partial y} + \frac{q_j}{m_j} E \frac{\partial f_j}{\partial v} = 0 ,$$

$$\frac{\partial E}{\partial y} \equiv -\frac{\partial^2 \phi}{\partial y^2} = \frac{1}{\epsilon_0}\sum_j q_j \int f_j \, dv , \tag{1}$$

where j is e for electrons and i for ions. The oscillating solution about which we linearize is given by $f_j = f_j(v_j^*)$, where

$$v_j^* = v + (q_j E_0 / m_j \omega_0)\cos\omega_0 t \equiv v + v_j^0 .$$

We shall take f_j to be a Maxwellian:

$$f_j(v_j^*) = (N_0/\pi^{1/2} v_{Tj}) \exp[-(v^*/v_{Tj})^2] .$$

We consider perturbations of the form

$$Q(y, v, t) = Q(v, t) e^{iky} .$$