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SPIN - LATTICE RELAXATION AND TENSOR ORDER PARAMETER FLUCTUATIONS IN NEMATICS

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Abstract The nuclear magnetic resonance spin - lattice relaxation time, both in laboratory and rotating frames, T_1 and $T_{1\rho}$ are calculated for nematic liquid crystal. It is shown that $T_{1\rho}$ has logarithmic frequency dependence, and both of them - a complicated temperature dependence.

INTRODUCTION

Many theoretical and experimental works are devoted to the problem of nuclear spin-lattice relaxation in nematic liquid crystals. Nematic order fluctuations are known to play an important role in the NMR relaxation of molecules. It is well known that the order parameter in nematics is a symmetric traceless second rank tensor $Q_{\alpha\beta}$. Thus, fluctuations of a new degree of freedom include the longitudinal, transverse and biaxial fluctuations. First of them is connected with fluctuations of order parameter modulus and the second - with director fluctuations. Another important peculiarity of nematics, as well as of any other degenerate system, is the presence of singular longitudinal fluctuations which are connected with a transverse fluctuations.[1] In this paper we examine the influence of the tensor order parameter fluctuations on the frequency and temperature dependences of the

nuclear spin-lattice relaxation rate in nematics.

THE NEMATIC - ISOTROPIC PHASE TRANSITION

The free energy density in the de Gennes model has the form ($\nabla_\alpha = \partial / \partial x_\alpha$)

$$F = \frac{1}{2} AQ_{\alpha\beta}Q_{\beta\alpha} - \frac{1}{3} BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \frac{1}{4} C(Q_{\alpha\beta}Q_{\beta\alpha})^2 - \frac{1}{2}\chi_a H_\alpha H_\beta Q_{\alpha\beta} + \frac{1}{2} L \nabla_\alpha Q_{\beta\gamma} \nabla_\alpha Q_{\beta\gamma} , \quad (1)$$

where $A=a(T-T^*)$, B and C are constants, χ_a is the anisotropy of the diamagnetic constant, H is the magnetic field. Since of the equivalence between the tensor $Q_{\alpha\beta}$ and the spinor Q_1^m with l=2, one can rewrite (1) over the scalar order parameter $Q=\langle Q_1^o \rangle$ and fluctuations of Q_1^m in the Gauss approximation

$$F = \frac{1}{2} AQ^2 - \frac{1}{3} BQ^3 + \frac{1}{4} CQ^4 - hQ + \frac{1}{2} (r_o + L\nabla^2) Q_2^o Q_2^o + (h/Q + L\nabla^2) Q_2^1 Q_2^{-1} + (h/Q + 3BQ + L\nabla^2) Q_2^2 Q_2^{-2}, \quad (2)$$

where $h=1/3\,\chi_a H^2$, $H=(0,0,H)$, $r_o = Q_c B(t+t^{1/2})$, $t=(T^+-T)/(T^+-T^*)$, $Q_c=(B/3C)(1+(1-h/h_c)^{1/2})$, $h_c=B^3/27C^2$, $T^+=T^*+B^2/3aC$, T^+ is the temperature of the continuous phase transition. The temperature of the first order phase transition is $T_c=T^*+(2B^2/9aC)(1+h/2h_c)$ and there is no phase transition for $h>h_c$, $T_c(h_c)=T^+$. If h=0, then T^+ must be replaced by $T^{**} = T^*+B^2/4aC$, which determines the superheating temperature of nematic phase. Further we will show how the fluctuations $\langle |Q_2^m|^2 \rangle$ can be used to calculate nuclear relaxation rate in the nematic phase of liquid crystals.

SPIN - LATTICE RELAXATION

Let us consider well known model of two nuclear spins 1/2 located on the long axis of nematic molecule. The spin-lattice relaxation arises from order parameter fluctuations in intramolecular dipolar interaction, and relaxation rates in the laboratory frame and in the rotating frame are [2]

$$T_1^{-1} = \frac{9}{8}\gamma^4\hbar^2 r^{-6}\left[G_1(\omega_o) + G_2(2\omega_o)\right]\left(\frac{\mu_o}{4\pi}\right)^2, \qquad (3)$$

$$T_{1\rho}^{-1} = \frac{9}{8}\gamma^4\hbar^2 r^{-6}\left[\frac{1}{4}G_o(2\omega_1)+\frac{5}{2}G_1(\omega_o)+\frac{1}{4}G_2(2\omega_o)\right]\left(\frac{\mu_o}{4\pi}\right)^2, \qquad (4)$$

where $\omega_1=\gamma H_1$, H_1 is the r.f. field, r is the fixed separation between spins, $G_i(\omega)$ are the spectral densities of corresponding correlation functions. This functions are easy to obtain from (2) in q - space

$$G_o(q)=(r_o+Lq^2)^{-1}, \quad G_1(q)=\frac{1}{2}(h/Q+Lq^2)^{-1}, \qquad (5ab)$$

$$G_2(q)=\frac{1}{2}(h/Q+3BQ+Lq^2)^{-1}, \qquad (5c)$$

which are the correlation functions of longitudinal, transverse and biaxial fluctuations of the tensor order parameter. The gap in the spectrum of longitudinal fluctuations r_o decreases strongly for $T \to T_c$ in comparison with the gap in the spectrum of biaxial fluctuations

$$\Delta = \frac{3}{4}\,Q_c(h=0)\,B\left[1+t^{1/2}+\frac{4h}{9h_c}(1+t^{1/2})^{-1}\right], \qquad (6)$$

note, that for $h=0$ $\Delta(T^*)/\Delta(T_c)=3/2$. Nevertheless,

both of them are of the same order of magnitude. The transverse fluctuations (5b) are suppressed only by external magnetic field.

Together with fluctuations of the modulus Q (5a) we shall consider the longitudinal fluctuations caused by strong transverse fluctuations. Such connection due to the modulus retain principle exists in any degenerated system[1]: $2QQ_2^o=-Q_2^1Q_2^{-1}$. For the correlation function $G_o=\langle Q_2^oQ_2^o\rangle$ one can get in q- space

$$G_o(\vec{q})=\frac{1}{4Q^2}\int\frac{d\vec{p}}{(2\pi)^3}G_1(\vec{p})G_1(\vec{p}+\vec{q})\ . \qquad (7)$$

The function like this had been calculated[1], where the influence of the order parameter fluctuations on the light scattering in nematics had been investigated. One can show that fluctuations (7) prevail over the order parameter modulus fluctuations for $q\leqslant q_o$, what corresponds to the wave length 5000 Å. Using the Landau-Khalatnikov equation for the Fourier component $Q_2^o(q)$ the corresponding order parameter relaxation time can be obtained $\tau_q^{-1}=L\eta^{-1}(q^2+\xi^{-2})$, where the coherence length is defined as $\xi=\xi_o(t+t^{1/2})^{-1/2}$, and $\xi_o=(3LC/2B^2)^{1/2}$, η -effective viscosity coefficient. Then the complete expression for $G_o(\omega)$ in (4) including both kinds of fluctuations is

$$G_o(\omega)=\mathcal{K}\left[\frac{\pi}{4}\left(\frac{\omega_c}{\omega_\xi}\right)^{1/2}u_{c,\xi}-1\right]+\frac{T^2\tilde{\gamma}}{64Q^2L^3}\left[\frac{1}{2}\ln\frac{1+u_c}{1-u_c}-u_c\right], \qquad (8)$$

$$u_{c,\xi}=2^{1/2}\frac{\omega_{c,\xi}}{\omega}\left(\left(1+\omega^2/\omega_{c,\xi}^2\right)^{1/2}-1\right)^{1/2},$$

$$\mathcal{K}=T\eta^{1/2}/\pi^2L^{3/2}\omega_c^{1/2}\ ,\quad \omega_\xi=L\xi^{-2}/\eta\ ,\quad \omega_c=Lq_c^2/\eta,$$

where ω_c is the critical cutoff frequency, q_c - cut-

off wave vector, $\tilde{\gamma}$ - viscosity coefficient. For nematic phase of MBBA $a=5.3\cdot10^5$erg/Kcm^3, $B = 5.1\cdot10^6$erg/cm^3, $C=1.1\cdot10^7$erg/cm^3 ^{3}, $L=0.5\cdot10^{-6}$erg/cm $\eta\sim\tilde{\gamma}\sim0.1$P, $\lambda_c=2\cdot10^{-7}$cm, and thus $\omega_c=3\cdot10^9$s^{-1}, $\omega_\xi=5\cdot10^7$s^{-1}. In the typical spin-relaxation technique in rotating frame $\omega_1 \ll \omega_\xi, \omega_c$, therefore, one finds the ratio of the second term to the first in the right-hand side of eq. (8) $0.5\ln(4\omega_c/e\omega_1) > 1$. This estimation indicates that the longitudinal order parameter fluctuations induced by the transverse fluctuations gives essential contribution to the $T_{1\rho}^{-1}$. The transverse correlation function (5b) is nothing more than director fluctuations in nematic. If we shall neglect terms of the order of $\omega_H/\omega \ll 1$, $\omega_H = h/Q\eta$, then for the spectral density G_1 it is easy to obtain well known expression

$$G_1(\omega) = \frac{\pi}{4\sqrt{2}} \varkappa \, (\omega_c/\omega)^{1/2}. \qquad (9)$$

Neglecting of the ω_H/ω terms in deriving (9) is a good approximation on the frequency range of NMR relaxation experiments (10^4-10^8Hz). Really, for $\chi_a=10^{-7}$, $H=10^4$G we have $\omega_H=10^2$Hz. That is why the frequency dependence of G_1 is not the same as for the first term in the right-hand side of eq. (8). The case $\omega_H \simeq \omega$ in the real magnetic fields may be realized in a paramagnetic liquid crystals with a large magnetic susceptibility. But in the known to date paramagnetic liquid crystals [4] the susceptibility is not so large. For the same reason we shall neglect the field dependent term in (6), and after that the calculations for G_2 lead to

$$G_2(\omega) = \frac{\pi}{8}\varkappa\,(\omega_c/\omega_\Omega)^{1/2}\,u_\Omega\,, \qquad (10)$$

where u_Ω has the form like in (8) with $\omega_\Omega=\Omega(1+t^{1/2})$, $\Omega=3Q_cB/4\eta$. The estimation for Ω gives $1{,}2\cdot10^7\,s^{-1}$. Finaly, from (8)-(10) in the limit $\omega_1 \ll \omega_\xi, \omega_c$ we find out

$$T_{1\rho}^{-1}=\frac{9}{8}\gamma^4\hbar^2 r^{-6}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\pi\varkappa}{16\sqrt{2}}\left(\frac{\omega_c}{\Omega}\right)^{1/2}\left\{\left(\frac{3}{2}\right)^{1/2}(t+t^{1/2})^{-1/2}\right.$$
$$+(1+t^{1/2})^{-1/2}\left[1+\left(1+\left(\frac{2\omega_0}{\Omega}\right)^2(1+t^{1/2})^{-2}\right)^{1/2}\right]^{-1/2} \qquad (11)$$
$$\left.+10\,\left(\frac{\Omega}{\omega_0}\right)^{1/2}\right\}+\frac{9}{8}\gamma^4\hbar^2 r^{-6}\left(\frac{\mu_0}{4\pi}\right)^2\frac{T^2\tilde{\gamma}}{64Q^2L^3}\,\ln\frac{2\omega_c}{e\omega_1}$$

and

$$T_1^{-1}=\frac{9}{8}\gamma^4\hbar^2 r^{-6}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\pi\varkappa}{4\sqrt{2}}\left(\frac{\omega_c}{\Omega}\right)^{1/2}\left\{\left(\frac{\Omega}{\omega_0}\right)^{1/2}\right.$$
$$\left.+(1+t^{1/2})^{-1/2}\left[1+\left(1+\left(\frac{2\omega_0}{\Omega}\right)^2(1+t^{1/2})^{-2}\right)^{1/2}\right]^{-1/2}\right\}. \qquad (12)$$

The temperature and frequency dependences of obtained eqs. (11), (12) are complicated enough and strongly depend on the ratio ω_0/Ω. Equation (12) reduces in the limits $\Omega \ll \omega_0$ and $\Omega \gg \omega_0$ to $T_1 \sim \omega_0^{1/2}$, whereas in the case $\omega_0 \sim \Omega$ the full expression (12) has to be retained.

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