

frequency was applied near f_2 , and there was evidence from the radial dependence of the density fluctuations at the pump frequency that the $m = 2$ mode was being excited. Since $f_2 < f_3 - f_1$, this may account for some of the additional broadening.

An attempt was made to measure the growth rate of the instability by switching off the pump signal and observing the rise time of the instability. These observations indicate that the growth rate was very large, at least as large as the observed instability frequency.

In conclusion, we have observed the suppression of a large-amplitude instability by parametric coupling to a damped normal mode of the plasma column. We obtained qualitative agreement between the experimental observations and a simple theory based on parametric coupling of lumped circuits.

This technique may be applicable to other instabilities and plasma devices. When a large-amplitude oscillation is detrimental to device operation, by using parametric suppression its energy may be transferred to a less detrimental, damped mode. In addition, the energy dissipated in the damped mode may result in particle heating. In contrast to linear feedback stabilization this technique may be used on high-growth-rate, nonlinearly saturated modes. Also since it is a resonant process, it should require less energy than other nonresonant types of dynamic stabilization.

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Interpretation of the Nuclear Spin-Lattice Relaxation-Time Behavior in the Nematic Mesophases*

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We give a coherent quantitative interpretation of both the frequency and temperature behavior of the proton spin-lattice relaxation time T_1 in the nematic phase of *p*-azoxyanisole. The frequency dependence of T_1 is dominated by the long-wavelength thermal fluctuations in the orientational order. The temperature dependence of T_1 has an important contribution from short-range phenomena involved in the motion of methyl protons. The activation energy for this motion is $W \approx 9$ kcal/mole.

About two years ago, Pincus¹ predicted that in nematic liquid crystals the nuclear relaxation arising from the modulation of the dipolar intramolecular energy due to the long-wavelength orientational modes of motion should be competitive with the relaxation arising from the modulation of the intermolecular spin-spin coupling via the translational diffusion. His calculation, as im-

proved by Lubensky,² gives the following expression for the relaxation rate:

$$\frac{1}{T_{1B}} = \omega_D^2 \frac{k_B T S^2}{K} \left[\omega_0 \left(D + \frac{K}{\gamma} \right) \right]^{-1/2} + \frac{1}{T_1'}, \quad (1)$$

where ω_D is a dipolar frequency, ω_0 is the nuclear Larmor frequency, and K , γ , and S are parameters characteristic of the liquid crystal (see

below). The meaning of $1/T_1'$ is given in Ref. 2.

The interpretations given to the experiments carried out to date in order to test this formula have produced a rather confusing situation. While the frequency dependence of the relaxation rate $1/T_1$ given by (1) is accepted,^{3,4} although in most cases with severe modifications,⁵⁻⁸ the general feeling⁴⁻¹³ is that expression (1) cannot account for the observed temperature dependence. However, it has been shown³ that care should be taken in interpreting the experimental results because the model used in the theory^{1,2} is not found to agree with the experimental situations generally involved. This has also been recognized in a recent attempt¹¹ to interpret some experimental data of this author within the framework of a different model for the nematic mesophase. More recently, the relevance of the collective orientational fluctuations to the nuclear relaxation behavior has been questioned, and it was suggested^{9,10} that a quite different interpretation in terms of a diffusion theory designed for the isotropic liquids could be given. Another distinct tentative interpretation of the overall relaxation data is contained in Refs. 12 and 13. So far we have only referred to the literature on *p*-azoxyanisole, but the same confusing situation can be found in the literature concerning the other liquid crystals.

In this Letter we give the main points of a coherent quantitative interpretation of both temperature and frequency dependences of the proton spin-lattice relaxation rate in PAA and PAA-CD₃.¹⁴ The validity of the relaxation theory^{1,2} based on the long-wavelength thermal fluctuations in the molecular orientational order is strongly supported. The present interpretation can be extended¹⁵ to other nematic liquid crystals with equally good results.

Let us start with expression (1) above. We have replaced the original^{1,2} symbol η by γ to stress that this is an *orientational* viscosity coefficient related essentially to the $\gamma_{1,2}$ that appear in the Leslie theory¹⁶ of nematics. This viscosity is related to the molecular order and vanishes in the isotropic phase, sufficiently above the transition point. K is an elastic constant which is also essentially related to the orientational order; it is proportional¹⁷ to S^2 , where S is the degree of order. The temperature dependence anticipated for the factor $T(K/\gamma + D)^{-1/2}$ in expression (1) can be shown to agree with reported³ experiments on PAA-CD₃. This point is not relevant to the present Letter, and so we defer its discussion to a forthcoming paper.¹⁵ Another point we should like

to stress again³ is that *expression (1) only applies to benzene protons of PAA* (note the *B* subscript); methyl protons are in a situation incompatible with the assumptions used in deriving this expression and therefore must be considered separately. Improper consideration of these points has been the cause of most of the confusion referred to above.

As shown experimentally in a previous paper,³ the increase of T_1 with the temperature, for PAA (see, for instance, Fig. 1 of Doane and Visintainer¹⁸), is due to the CH₃ protons. When deuterons are substituted for these protons, $T_1(T)$ becomes constant within the experimental error.³ For the analysis given below, we separate the protons of PAA in two groups: the benzene-ring protons, characterized by the relaxation time T_{1B} , and the methyl groups whose characteristic relaxation time is denoted by T_{1M} . The experimentally observed $T_1(T)$ dependence for PAA, as contrasted to the temperature independence of T_{1B} for PAA-CD₃, implies that for a general (ω, T) point we have $T_{1B} \neq T_{1M}$. In practice, experimentalists have generally not observed this two-time relaxation behavior. Let us show why.

In a spin-echo experiment, the relaxation of the longitudinal component of the nuclear magnetization to its equilibrium value can be observed after a 180° - t - 90° pulse sequence.¹⁹ The observed signal is given by

$$M(t) = M_0 [1 - (2/N) \sum_i n_i \exp(-t/T_{1i})] \quad (2)$$

when i uncoupled groups of spins are present with populations n_i ($\sum_i n_i = N$) and relaxation times T_{1i} . When processing the experimental data, what matters is the derivative $dy(t)/dt$ of $y(t) \equiv \ln \{ [M_0 - M(t)] / 2M_0 \}$. Calculating it and substituting $T_{1i}^{-1} = T_{10}^{-1}(1 \pm \epsilon_i)$, where ϵ_i is a measure of the deviation of the relaxation rate T_{1i}^{-1} from some intermediate value T_{10}^{-1} , we find that a single-exponential decay of $M(t)$ will be *observed* with a relaxation rate given by

$$(T_1^{-1})_{\text{ob}} = (1/N) \sum_i n_i / T_{1i} \quad (3)$$

if the condition $\epsilon_i t \ll T_{10}$ is fulfilled. Conversely, in order to *measure* a relaxation rate given by (3), it is sufficient in practice to limit the observation of the decay of $M(t)$ to times t such that $\epsilon_i t \ll T_{10}$. In the case of PAA, the two groups of spins are practically uncoupled (this will be discussed in detail elsewhere¹⁵). So, expression (3), together with the experimentally observed fact of single-exponential decay of $M(t)$, shows that within the frequency range studied (10–60 MHz) we

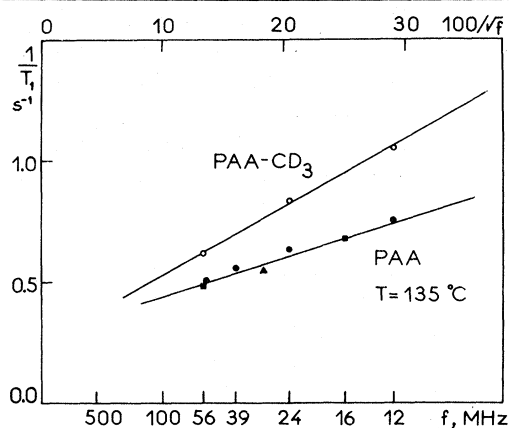


FIG. 1. Plot of the measured spin-lattice relaxation rate against $\omega^{-1/2}$ for PAA and PAA-CD₃. The data concerning PAA-CD₃ are from the present author (partially in Ref. 3). For PAA, we have: full circles, from Ref. 18; triangles, from Ref. 4; squares, from the present author.

must have $T_{1M}^{-1} \approx T_{1B}^{-1}$. The relaxation rate observed in experiments with PAA is, accordingly, given by

$$T_1^{-1} = \frac{3}{7} T_{1M}^{-1} + \frac{4}{7} T_{1B}^{-1}. \quad (4)$$

We plotted in Fig. 1 the frequency dependences of $1/T_{1B}$ (PAA-CD₃) and $1/T_1$ (PAA) at 135°C. They show the behavior given by the expression (1). The values of T_{1B} have already been partially given in a previous paper.³ We will remember that they do not depend on the temperature within the experimental error. From Eq. (4) and the values of $1/T_{1B}$ and $1/T_1$ given in Fig. 1, we find $1/T_{1M} = 0.32$ sec at any frequency between 12 and 60 MHz, and $T = 135^\circ\text{C}$. Writing $(1 + \epsilon)/T_{10} = 1/T_{1B}$ and $(1 - \epsilon)/T_{10} = 1/T_{1M}$, and solving this system of equations, we find very good justification for the approximations (3) and (4) within this frequency range. The values of t used in experiments are well in the range established by the condition $\epsilon t \ll T_{10}$. For frequencies sufficiently below 12 MHz we predict that a two-time decay of the nuclear magnetization will be observed. However, it should be noted that this prediction does not extend to very low frequencies, where expression (1) cannot be valid because it gives an infinitely high relaxation rate. Another check on the above theory is the following: According to expression (4), the slopes of the straight lines given in Fig. 1 are related by $\partial(T_1^{-1})/\partial(\omega^{-1/2}) = \frac{4}{7} \partial(T_{1B}^{-1})/\partial(\omega^{-1/2})$, where the frequency independence of $1/T_{1M}$ is taken into account. This feature is displayed by Fig. 1 with remarkable accuracy (better than 1%).

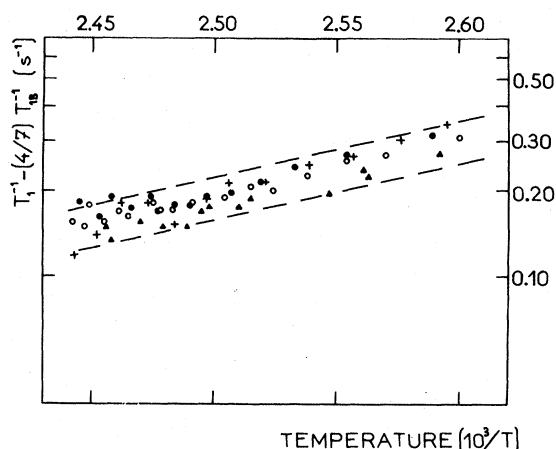


FIG. 2. Experimental display of Eq. (5) in the text. All data refer to PAA: crosses, from Ref. 18, at 12 MHz; full circles, from Ref. 18, at 24 MHz; triangles, from Ref. 4, at 30 MHz; open circles, from Ref. 18, at 39 MHz.

The derivative of (4) implies also that the representations of T_1^{-1} ($\omega^{-1/2}$) at different temperatures are parallel straight lines because of the observed³ independence of $1/T_{1B}$ on temperature. This is not shown on the figure to avoid overcharge, but it can be readily verified from the published data.²⁰

The frequency independence of $1/T_{1M}$ suggests further that we may write $1/T_{1M} \propto \tau_c$, where $\tau_c = \tau_0 \exp(W/kT)$ is a correlation time for the motion of the methyl protons. This assumption might be valid for intra- or intermolecular interactions of any type.²¹ It allows us to convert expression (4) to the following form:

$$\ln(1/T_1 - 4/7 T_{1B}) = C + W/kT, \quad (5)$$

where C is a constant, from which we find the value of the activation energy W . This representation is given in Fig. 2 with published data for several frequencies. Taking into account the structure of expression (5) and the accuracy of the relaxation-time measurements, the agreement between theory and experimental data is again rather good. Note that each set of points fits Eq. (5) with a dispersion much less than the overall dispersion. We find $W \approx 9$ kcal/mole from the plot. However, expression (5) gives no information on whether we are concerned with rotational motion or with diffusion (translation). The relation $1/T_{1M} \propto \tau_0 \exp(W/kT)$ is to be interpreted with caution until a theoretical treatment of the motion of the methyl protons is worked out for the present case. These points, together with the

foregoing results, have interesting implications on the structural static and dynamic properties of the nematic phases. We intend to discuss them in detail in a future work.

In conclusion, we think we have shown that the theory^{1,2} of spin-lattice relaxation in nematic liquid crystals is essentially correct, but in practice the systems are generally more complex than assumed and therefore must be "prepared" (cf. PAA-PAA-CD₃) in order to be treatable within the conditions considered by the theory. Or, if not, the "deviations" from the theoretical assumptions must be properly taken into account.

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²¹Ref. 19, Chap. VIII.

Simple Lattice Gas with Realistic Phase Changes*

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A simple lattice gas with a phase diagram similar to that of argon is described.

It is of interest to find and study simple model systems that can exist in three distinct phases, associated with coexistence regions that show the features typical of systems of real molecules—in particular, the liquid-gas transition with a critical point, the first-order solid-fluid transition, and the triple point.

We wish to report here the discovery of a family of such systems¹ and to give a preliminary

description of the properties of the simplest of these. It is a lattice gas defined on a regular infinite two-dimensional triangular lattice; each site has six nearest-neighbor (nn) sites. The interaction potential is a sum of pair terms $v(\vec{r}_{ij} \equiv \vec{r}_i - \vec{r}_j)$, where $v(\vec{r}_{ij})$ is defined to be infinite between particles i and j occupying the same site or nn sites, while between particles that are further apart, $v(\vec{r}_{ij})$ is taken to be a