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Dynamic critical behavior in nematic liquid crystals above the nematic-isotropic transition

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Using the temperature and frequency dependences of proton relaxation rates in *p*-methoxybenzylidene *p*-*n* butylaniline (MBBA), measured in the temperature range of 316.2–350 K and the frequency range of 4–20 MHz, we confirm the necessity of considering critical fluctuations (CF) in two parts—"local" and "nonlocal" as envisaged in a recent theoretical study—characterized by their corresponding correlation times $\tau_{\rm CFL}$ and $\tau_{\rm CFN}$. Both $\tau_{\rm CFL}$ and $\tau_{\rm CFN}$ have also been determined at different temperatures. In such determinations, use has been made of the critical index for $\tau_{\rm CFL}$, the same as observed in light scattering experiments, and our $\tau_{\rm CFL}$ is in reasonable agreement with these results. Like $\tau_{\rm CFL}$, $\tau_{\rm CFN}$ also shows critical behavior but with a slightly higher index. The magnitude of $\tau_{\rm CFN}$ is also appreciably larger than $\tau_{\rm CFL}$ at the same temperature. These observed differences between $\tau_{\rm CFL}$ and $\tau_{\rm CFN}$, and the behavior of nuclear relaxation rate $(T_1)^{-1}_{\rm CFL}$ at T^* predicted by the Landau-de Gennes theory suggest strongly a close similarity between the nematic-isotropic (NI) transition and the Bose-Einstein condensation; T^* is the apparent critical temperature if the IN transition were continuous.

I. INTRODUCTION

Because of the weak first-order phase transition shown by nematic liquid crystals in going from the ordered nematic phase to the disordered isotropic liquid phase (NI) or vice versa, appreciable pretransitional phenomena are observed around the NI transition temperature T_c. Various techniques have been used and are being used to study these pretransitional phenomena and their similarity with the critical behavior (CB), both static (*S*) and dynamic (*D*), shown by systems undergoing a second-order or continuous transition is now well established from both experimental and theoretical considerations.[1–4] The essential aspects of CB[5] are the divergences in the correlation length ξ and the correlation time $\tau_{\rm CF}$ of critical fluctuations (CF) in the order parameter Q with the approach to the critical temperature $T_{\rm CR}$. The order parameter Q, which is a quantity averaged thermodynamically over a macroscopic volume, is nonzero in the ordered phase but zero in the disordered phase. In the case of continuous transition, the vanishing of Q is continuous. But, in the case of a first-order transition, Q vanishes discontinuously at the transition temperature. Even though the long-range order vanishes in the disordered phase, the short-range or local order persists over an appreciable temperature range above T_c. The fluctuations in the order parameter in such a situation can be thought of as fluctuations in this short-range order, or in other words, as the fluctuations around the thermodynamically averaged value of zero. Similar ideas can also be applied in the ordered phase where the fluctuations are considered around the thermodynamically averaged value of nonzero Q. Since Q is zero or close to zero around T_c in systems showing the continuous transition, fluctuations in Q is very prominent both above and below T_c. But since Q is not close to zero and has finite values [$\sim$0.43 at T_c (Ref. 6)], the effects of fluctuations in Q below T_c is expected to be less pronounced than those in the disordered phase. There exists another small but important difference between this weak first-order transition in nematics and the continuous transition; $T_{\rm CR} = T_c$ in the latter, while $T_{\rm CR} = T^*$ in the former. This temperature T^* is in fact a virtual temperature and is higher or lower than T_c depending on the ordered or disordered phase in which CB is being studied. The two parameters ξ and $\tau_{\rm CF}$ mentioned earlier characterize the CF which are manifest in the CB of different physical parameters obeying the universal scaling law[5,7]; ξ describes the SCB, while $\tau_{\rm CF}$ the DCB, although they are not quite unrelated.

It is well known that the nuclear relaxation is a very sensitive probe to any fluctuations[8]—whether in space, in time or in both present in a "lattice" in which the nuclear spins are embedded, and nuclear relaxation studies have been made in widely different systems in understanding the detailed nature of CF with considerable success.[9] This high sensitivity of nuclear relaxation to any fluctuations helps in understanding its detailed nature but at the same time creates the experimental problem of isolating and identifying its contribution to the nuclear relaxation rate measured in an experiment. It is not easy to find a system where the nuclear relaxation arises from a single source of fluctuations. This is very true in studying CF since, even in the most favorable case, the contribution to relaxation rate from this source is not the only one and in many situations may not be the predominant one. From all these considerations, nuclear relaxation studies in nematic liquid crystals have a special interest, particularly for the convenient frequency range of CF,[10–13] which provides a unique opportunity of not only isolating the CF part from other existing ones with sufficient confidence but also of determining the exact magnitude of τ_{CF}. An additional interest exists for those systems for which are present directly measured τ_{CF} (Refs. 10 and 11) offering an independent check on NMR results. To our knowledge, no report has yet been published, including our own,[14,15] where a complete isolation of the CF part has been accomplished.[2]

The main problem of the determination of $(T_1)_{CF}$, the CF part of experimental relaxation time $(T_1)_{expt}$, are the existence of a model relating CF with the nuclear relaxation and its application under proper experimental conditions to extract $(T_1)_{CF}$ from $(T_1)_{expt}$ with sufficient confidence. In what follows, we shall demonstrate that a reliable determination of $(T_1)_{CF}$ can be made and $(T_1)_{CF}$, as envisaged in Ref. 2, needs be divided into two parts corresponding to the two parts of CF. One of these $(T_1)_{CF}$ arises from $\vec{q}=\vec{0}$ mode of CF and the second from all other $\vec{q}$ modes; the former we call "nonlocal" (N) and the latter "local" (L) characterized by their corresponding correlation times τ_{CFN} and τ_{CFL}. To be precise, τ_{CFL}, which is involved in the expressions of nuclear relaxation rates, is the correlation time for $\vec{q}\rightarrow\vec{0}$ mode. It is to be noted that this time is measured in light-scattering techniques,[2,11–13] and no usual scattering experiments measure the $\vec{q}=\vec{0}$ mode, since the scattered beam in this case lies exactly along the direction of the incident beam. But since in relaxation studies no external radiation is used in the sense of scattering experiments, no problem arises in observing the $\vec{q}=\vec{0}$ mode of CF. We shall see later that our results are in good accord with such ideas as suggested in Ref. 2.

Corresponding to the above two parts of CF, the nuclear-spin-lattice relaxation times are denoted by $(T_1)_{CFN}$ and $(T_1)_{CFL}$, and

$$(T_1)^{-1}_{CF}=(T_1)^{-1}_{CFN}+(T_1)^{-1}_{CFL}\ . \qquad (1)$$

The expressions for $(T_1)_{CFN}$ and $(T_1)_{CFL}$ are given in Sec. II [see Eqs. (39) and (40)], where we review briefly the Landau-de Gennes theory of the NI phase transition and its application to the nuclear relaxation as presented in Ref. 2, particularly to bring out the essential assumptions involved. It may be pointed out here that $(T_1)_{CFL}$ is essentially the same as the one obtained earlier by Cabane and Clark[16,17] in understanding ^{14}N relaxation in para-azoxyanisole (PAA); $(T_1)_{CFN}$, on the other hand, has essentially the same BPP form[18] used earlier by us in understanding the proton relaxation in p-methoxybenzylidene p-n butylaniline (MBBA).[14] As noted elsewhere[2] and supported by our present temperature and frequency dependences of the proton relaxation in MBBA, we shall see later that both the parts of CF need be considered.

As we have noted already, one of the intriguing problems in obtaining $(T_1)_{CF}$ from $(T_1)_{expt}$ is to determine the other contribution(s) $(T_1)_O$, since in general

$$(T_1)^{-1}_{expt}=(T_1)^{-1}_{CF}+(T_1)^{-1}_{O} \qquad (2)$$

and since $(T_1)^{-1}_{O}$ may not be negligible compared to $(T_1)^{-1}_{CF}$ even closest to T_c. Since even in the nematic phase many aspects of molecular dynamics, such as rotation about the molecular axis and translational motions of centers of mass of molecules, are close to those of isotropic liquids, it is expected $(T_1)_O$ will be diffusion-controlled. The validity of such an assumption can be checked in two direct ways: (i) by observing an activation energy W identical with that determined from molecular self-diffusion[15,19] D, and (ii) by observing frequency independent $(T_1)_{expt}$. Of

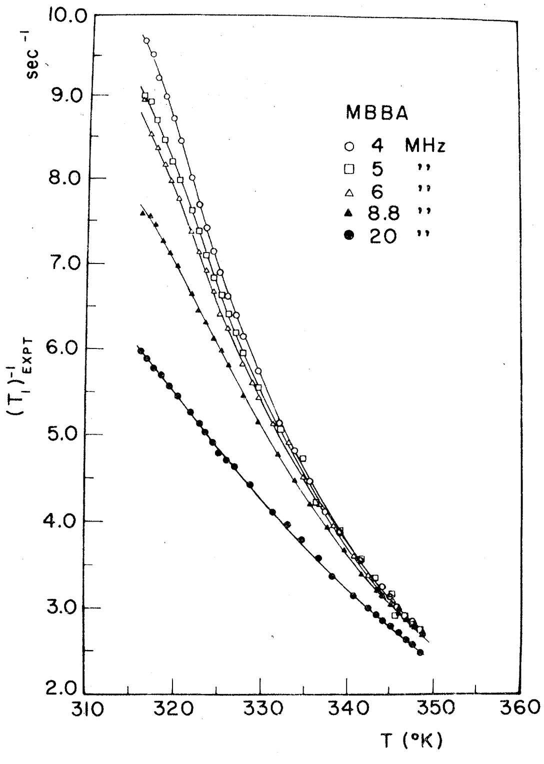

FIG. 1. Experimental proton-spin-lattice relaxation rate $(T_1)^{-1}_{expt}$ vs temperature T in MBBA measured at different frequencies.

course, both these checks can be made in the absence of or for negligible $(T_1)_{\mathrm{CF}}^{-1}$. We shall see shortly that similar checks can be reasonably made even though this condition is not rigorously satisified. Further complexity in determining $(T_1)_{\mathrm{CF}}$ arises from the possible frequency-dependent intermolecular contribution[20] to $(T_1)_{\mathrm{expt}}$. The exact frequency dependence of this contribution in nematics is not known with any certainty, but is hoped to be less pronounced at low frequencies. From these considerations, we measured proton T_1 in MBBA at a number of frequencies (4, 5, 6, 8.8, and 20 MHz, a compromise between necessity and availability) over a large range of temperatures above T_c. These results are shown in Fig. 1. All the necessary experimental details are given in Sec. III. In Sec. IV, we present our data analysis to extract the two parts of CF contributions from $(T_1)_{\mathrm{expt}}$ and summarize our results. The results are discussed in Sec. V. Some discussion, both from the theoretical and experimental viewpoints, to establish possible connections between our observations and those made in the ordered phase have been included in Sec. V. Finally, we conclude in Sec. VI.

II. THEORETICAL BACKGROUND

We summarize in this section the basic theoretical background to understand the NI phase transition and its effect on the nuclear relaxation.[1–4] Very essential references are cited only wherever necessary, and Refs. 1–4 are suggested for a more complete list of references.

A. Landau-de Gennes theory of the CB at the NI transition

The order parameter Q in a nematic liquid crystal can be defined by a symmetric traceless second-rank antensor

$$Q_{\alpha\beta}(\vec{r}) = \tfrac{1}{2}\langle(3n_\alpha n_\beta - \delta_{\alpha\beta})\rangle \ , \tag{3}$$

where n_α are the Cartesian components of a unit vector $\vec{n}$ along the symmetry axis of a molecule in its longitudinal direction, and the average is taken in the thermodynamic limit over the molecular ensemble in a small but macroscopic volume around the point $\vec{r}$. This average is nonzero in the nematic phase and zero in the isotropic liquid phase. In a homogeneously ordered system $Q_{\alpha\beta}$ are independent of $\vec{r}$. Any unit vector which can be related to the molecular symmetry axis is equally good in defining the order parameter. But this relation must be known in connecting this order parameter to $\overleftrightarrow{Q}$ defined above from microscopic consideration. It may be pointed out here that the above form of $\overleftrightarrow{Q}$ is consistent with the general symmetry arguments[21] and is independent of any specific source of interaction. Since the order parameter is a traceless symmetric second-rank tensor, it has in general five independent components. Because of the uniaxial nature of ordering in the nematic phase and because of the vanishing trace of the order-parameter tensor, the number of independent components can be reduced to only one similar to that of Maier and Saupe[6] by the proper choice of coordinates. But to consider the fluctuations in the order parameter, we must retain all the components. Under such considerations, the free energy g per unit volume close to the NI transition point is expanded, in accordance with the Landau theory, in a power series correct to the fourth order in $Q_{\alpha\beta}$:

$$\begin{aligned} g = g_0 &+ \tfrac{1}{2}AQ_{\alpha\beta}Q_{\beta\alpha} + \tfrac{1}{3}BQ_{\alpha\beta}Q_{\beta\nu}Q_{\nu\alpha} + \tfrac{1}{4}CQ_{\alpha\beta}^2Q_{\nu\eta}^2 \\ &+ \tfrac{1}{2}D(\nabla_\alpha Q_{\alpha\beta})^2 + \tfrac{1}{6}\chi_a H_\alpha Q_{\alpha\beta} H_\beta \ , \end{aligned} \tag{4}$$

where g_0 is the part of free energy independent of the order parameter. The coefficients A, B, C, and D are constants, but may depend on temperature and pressure. The indices α, β, ν, and η denote the components of $\overleftrightarrow{Q}$ in a Cartesian coordinate system, and the summation over the tensor indices is implied. The temperature dependence of A is assumed to be of the form

$$A = a(T - T^*)^\gamma \ , \tag{5}$$

where γ is an unknown exponent to be determined from experiments; it is unity in a standard molecular-field approximation. The temperature T^* defines the point where the phase transition is to occur if it were not intercepted by the first-order transition at T_c. The presence of the cubic term takes account of this first-order transition. T^* is higher or lower than T_c in accordance with the transition to be N → I or I → N. The remaining coefficients B, C, and D are assumed to be independent or weakly dependent on T. The last term describes the magnetic anisotropy energy due to an applied field H, and χ_a is anisotropic magnetic susceptibility. Close to T_c in the nematic phase, the order parameter is large and the validity of the expansion is questionable. But considering $Q_{\alpha\beta}$ in Eq. (4) as the deviations from their respective thermodynamic average values, such a restriction is expected to be removed.[3] Of course, the general limitations of the molecular-field approximations are still retained. Both from theoretical and experimental viewpoints discussed elsewhere,[2] the Landau-de Gennes theory seems to offer a fair description of the NI transition.

To understand the DCB we have to consider both space and time fluctuations in $\overleftrightarrow{Q}$ and to set up dissipative equations of motion. Using the original idea of Landau and Khalatnikov,[22] de Gennes has derived these equations of motion compatible with rotational invariance and the Onsager relations for a nematic system

$$\tfrac{1}{2}\sigma_{\alpha\beta} = \tfrac{1}{2}\eta e_{\alpha\beta} + \mu \dot{Q}_{\alpha\beta} \ , \tag{6a}$$

$$\varphi_{\alpha\beta} = \mu e_{\alpha\beta} + \nu \dot{Q}_{\alpha\beta} \ . \tag{6b}$$

In deriving these relations, de Gennes has considered two groups of fluxes, $\dot{Q}_{\alpha\beta}$ and $e_{\alpha\beta}$, and the corresponding conjugate forces $\varphi_{\alpha\beta}$ and $\frac{1}{2}\sigma_{\alpha\beta}$. The quantity $\dot{Q}_{\alpha\beta}$ describes the rate of $Q_{\alpha\beta}$, $e_{\alpha\beta}$ is the hydrodynamic-shear-rate tensor, $\frac{1}{2}\sigma_{\alpha\beta}$ is the viscous stress tensor, and

$$\varphi_{\alpha\beta} = -\partial F / \partial Q_{\alpha\beta} \ . \tag{7}$$

The coefficients η, μ, and ν (which should not be confused with the tensor indices used earlier) are the transport coefficients and have the dimension of viscosity. In the absence of external velocity gradient, $e_{\alpha\beta}$ can be neglected. When no space variation in $Q_{\alpha\beta}$ is considered, Eq. (7) reduces to

$$\dot{Q}_{\alpha\beta} = -\Gamma Q_{\alpha\beta}, \ \text{with } \Gamma(T) = \tfrac{1}{2} A(T) \ . \tag{8}$$

$A(T)$ has already been defined in Eq. (5), and

$$\nu = \nu_0 \exp(W/T) \ , \tag{9}$$

where ν_0 is a constant and W is the activation energy.

It is assumed that ν does not show any divergence with the approach of T to T^*. This is perhaps true for microscopic probes in nuclear- or -electron-spin relaxation but may not be true for macroscopic probes. Such a conclusion can be easily arrived at following the simple arguments of coupled-mode theory.[7] This is probably the reason why Rao *et al.*[3] did not observe any divergence from the transport coefficient although direct macroscopic measurement of transport coefficients shows divergence in the nematic phase.[23]

In the above derivation of the relaxation time or the correlation time of order fluctuations, which become critical with T approaching to T^* and hence known as CF, magnetic-anisotropy energy has been neglected. It has an important part to play on the fluctuations in the order parameter in the nematic phase[1] and hence on the nuclear relaxation.[24] Within the experimental accuracy of light-scattering experiments, the Rayleigh line is Lorentzian with a single relaxation time Γ^{-1} independent of the scattering wave vector $\vec{q}$.[11–13]

We shall shortly see that to consider the effect of CF on the nuclear relaxation we need to consider the space variation in $\vec{Q}$ in addition to its time variation. In the presence of space variation in $\vec{Q}$, we have to express the free energy of a sample of volume V as

$$G = G_0 + \tfrac{1}{2}\int d\vec{r}\, [A Q_{\alpha\beta}(\vec{r}) Q_{\beta\alpha}(\vec{r}) + D \nabla_\alpha Q_{\alpha\mu} \nabla_\beta Q_{\beta\mu}] \ , \tag{10}$$

where the integration is extended over the whole volume V. Here we have retained up to quadratic terms, since the space flcutuations in such a case can be decomposed into noninteracting "quasiparticles," although not in the usual sense as they have finite lifetimes, given by the Fourier components

$$Q_{\alpha\beta}(\vec{q}) = V^{-1} \int d\vec{r}\, Q_{\alpha\beta}(\vec{r}) \exp(-i\vec{q}\cdot\vec{r}) \ , \tag{11}$$

$$Q_{\alpha\beta}(\vec{r}) = \sum_{\vec{q}} Q_{\alpha\beta}(\vec{q}) \exp(i\vec{q}\cdot\vec{r}) \ , \tag{12}$$

and

$$\int d\vec{r} \exp[i(\vec{q}-\vec{q}')\cdot\vec{r}] = V\delta(\vec{q}-\vec{q}') \ . \tag{13}$$

It may be pointed out that this is the so-called Gaussian model of phase transition, and it has an exact solution. With the fourth-order term, which is known as the interaction term, the problem is insoluble. The Gaussian model has another advantage, since we do not have to restrict ourselves to the hydrodynamic limit.[7] The model seems appropriate where the microscopic definition of the order parameter is used.

With the above definitions of $Q_{\alpha\beta}(\vec{r})$, we can get

$$G = G_0 + \tfrac{1}{2} VA \sum_{\vec{q}} (1 + \xi^2 q^2) Q_{\alpha\beta}(-\vec{q}) Q_{\beta\alpha}(\vec{q}) \ , \tag{14}$$

where

$$\xi = (D/A)^{1/2} \tag{15}$$

and is known as the correlation length. Under the approximation of the model, the relaxation time or the correlation time of the $\vec{q}$ mode is

$$\tau_{\vec{q}}^{-1} = A(T)(1 + q^2\xi^2)/\nu \ , \tag{16}$$

Hence the light-scattering experiments measure[11–13]

$$\tau_0 = \nu / A(T) \ , \tag{17}$$

for $q\xi << 1$. It is to be noted that both ξ and τ_0 diverge at T, since $A(T) \rightarrow 0$ with $T \rightarrow T^*$, the latter for the mode with $\vec{q} \rightarrow \vec{0}$ [see Eqs. (15) and (16)]. The constant D and hence ξ is not defined for the model with $\vec{q} = \vec{0}$; but the constant A, which determines the CB of both ξ and τ_0, can still be defined.

B. Nuclear dipolar relaxation in the presence of CF

Here we restrict ourselves, following Ref. 2, to the nuclear dipolar relaxation in the isotropic phase and in the absence of fine structures. Whether the system is in the isotropic or in the nematic phase, the problem of nuclear relaxation in the presence of fine structures is much more complex both from theoretical and experimental viewpoints.[25] It may be noted here that, although our treatment is restricted here to dipolar interaction, this can be easily extended to quadrupolar interaction when the single-line approximation is valid.

To consider the nuclear dipolar relaxation, the most convenient form to express the dipolar interaction is

$$\mathcal{H}_d=\sum_{p=-2}^{2}\sum_{j>k}F_{jk}^{(-p)}A_{jk}^{(p)}\ , \tag{18}$$

where

$$F_{jk}^{(0)}=(3\cos^2\theta_{jk}-1)/R_{jk}^3\ , \tag{19}$$

$$F_{jk}^{(\pm1)}=\sin\theta_{jk}\cos\theta_{jk}\,\exp(\pm i\varphi_{jk})/R_{jk}^3\ , \tag{20}$$

$$F_{jk}^{(\pm2)}=\sin^2\theta_{jk}\exp(\pm2i\varphi_{jk})/R_{jk}^3\ , \tag{21}$$

$$A_{jk}^{(0)}=\gamma^2\hbar^2[I_{jz}I_{kz}-\tfrac{1}{4}(I_{j+}I_{k-}+I_{j-}I_{k+})]\ , \tag{22}$$

$$A_{jk}^{(\pm1)}=\tfrac{2}{3}\gamma^2\hbar^2(I_{jz}I_{k\pm}+I_{j\pm}I_{kz})\ , \tag{23}$$

$$A_{jk}^{(\pm2)}=\tfrac{2}{3}\gamma^2\hbar^2I_{j\pm}I_{k\pm}\ . \tag{24}$$

$F_{jk}^{(p)}$ depend only on the lattice coordinates determined by the radius vector $\vec{R}_{jk}$ joining a spin pair $\vec{I}_j$ and $\vec{I}_k$, θ_{jk} and φ_{jk} are the polar and azimuthal angles, respectively, defining $\vec{R}_{jk}$ in a coordinate system, the z axis of which is in the direction of applied magnetic field H. The nuclear-spin selection rules give nonvanishing matrix elements for $A_{jk}^{(p)}$ only when $\Delta m=p$, where $m=m_j+m_k$; m denotes eigenvalues of $I_{jz}+I_{kz}$. The nuclear-spin-lattice relaxation rate arising from the fluctuations of $\mathcal{H}_d$ in time is given by[8]

$$(T_1)^{-1}=\tfrac{3}{2}\gamma^4\hbar^2I(I+1)\sum_k{}'\sum_{p=1}^{2}J_{jk}^{(p)}(p\omega)\ , \tag{25}$$

where

$$J_{jk}^{(p)}(p\omega)=\int_{-\infty}^{\infty}\langle F_{jk}^{(-p)}(t)F_{jk}^{(p)}(0)\rangle \times\exp(-ip\omega t)\,dt\ . \tag{26}$$

ω is the nuclear resonance frequency given by $\omega=\gamma H$, and the bracket $\langle\cdots\rangle$ indicates the statistical average over the lattice the time fluctuations of which cause the time fluctuations in $\mathcal{H}_d$ through $F_{jk}^{(p)}$. The prime on the summation sign indicates that $k=j$ is to be excluded. The above result has been obtained by various methods[8] for systems with the nuclear dipolar interaction in the absense of fine structures.

Now to include the time fluctuations in $\mathcal{H}_d$ due to the CF, we can write

$$\langle F_{jk}^{(-p)}(t)F_{jk}^{(p)}(0)\rangle =V^{-1}\int\langle F_{jk}^{(-p)}(\vec{r},t)F_{jk}^{(p)}(\vec{r},0)\rangle\,d\vec{r}\ . \tag{27}$$

For each spin pair jk or for similar pairs, we can define a microscopic-order parameter related to $F_{jk}^{(p)}$ by

$$F_{jk}^{(0)}=(2/R_{jk}^3)Q^{(0)}\ ,$$

$$F_{jk}^{(\pm1)}=(2/3R_{jk}^3)Q^{(\pm1)}\ ,$$

and

$$F_{jk}^{(\pm2)}=(2/3R_{jk}^3)Q^{(\pm2)}\ , \tag{28}$$

where

$$Q^{(0)}=Q_{zz},\quad Q^{(\pm1)}=Q_{zx}\pm iQ_{yz}$$

and

$$Q^{(\pm2)}=Q_{xx}-Q_{yy}\pm2iQ_{xy}\ . \tag{29}$$

All these components of $\overleftrightarrow{Q}$ are defined by a unit vector along $\vec{R}_{jk}$. It may be pointed out here that the jk spin pairs include both intramolecular and intermolecular ones.

In principle, one expects to include all liquidlike motions—such as the rotation about the symmetry axes of molecules, the rotation of any atomic group, molecular translations, etc.—in the above treatment. But such a treatment including the couplings of all liquidlike motions and the CF will be extremely complex. To simplify the problem, we assume that all liquidlike motions contributing to the relaxation rates can be incorporated in $(T_1)_0^{-1}$ of Eq. (2) and that the CF contribution can be considered separately. This assumption may not be as strong as it appears when we consider the many couplings, not so weak from other aspects, between different molecules or between atomic groups even in the same molecule can essentially be neglected from the point of view of the nuclear relaxation, and the individual motions can be treated separately. For example, consideration of the rotational and translational motions individually and neglecting their coupling yields acceptable relaxation rates in simple liquids; even in the ordered nematic phase of PAA-d_6, both intramolecular and intermolecular relaxation rates show identical frequency dependence.[26] Hence we do not expect to introduce serious errors in treating the CF contribution to the nuclear relaxation rate in isolation of all other liquidlike motions.

Under these simplifying assumptions and using Eqs. (11)–(13), we can reduce Eq. (27) to

$$\langle F^{(-p)}(t)F^{(p)}(0)\rangle=\sum_{\vec{q}}\langle F^{(p)}(-\vec{q},t)F^{(p)}(\vec{q},0)\rangle\ . \tag{30}$$

Here we have suppressed the indices jk for simplicity. It should be noted that the above relation is valid for each spin pair to be considered.

We can interpret $\langle F^{(p)}(-\vec{q},t)F^{(p)}(\vec{q},0)\rangle$ in Eq. (30) as the time correlation between two "quasiparticles" of wave vectors $\vec{q}$ and $-\vec{q}$. But such an interpretation cannot be made for the "quasiparticle" with $\vec{q}=\vec{0}$. Under this situation, we can rewrite Eq. (30)

$$\langle F^{(-p)}(t)F^{(p)}(0)\rangle=\langle F^{(p)}(\vec{0},t)F^{(p)}(\vec{0},0)\rangle + \sum_{\vec{q}\neq 0}\langle F^{(p)}(-\vec{q},t)F^{(p)}(\vec{q},t)\rangle \ . \tag{31}$$

It may be noted here that $\vec{q}=\vec{0}$ mode appears also in scattering intensity,[27] but no importance is attached to it since this mode is not observed in the usual scattering experiments. Also to note, the $\vec{q}=\vec{0}$ mode has certain similarity with the condensate in the problem of Bose-Einstein condensation, and is expected to have similar problems in its exact treatment.[28] But we can make the following simplifying approach.

According to Landau and Khalatnikov,[22] we can write for the modes with $\vec{q}\neq\vec{0}$

$$\langle F^{(p)}(-\vec{q},t)F^{(p)}(\vec{q},0)\rangle=\langle F^{(p)}(-\vec{q},0)F^{(p)}(\vec{q},0)\rangle \times\exp(-|t|/\tau_{\vec{q}}) \ , \tag{32}$$

where $\tau_{\vec{q}}$ is the relaxation time of the q mode when $q\neq 0$, and is given by Eq. (16). In analogy with Eq. (32), we can express

$$\langle F^{(p)}(\vec{0},t)F^{(p)}(\vec{0},0)\rangle=\langle F^{(p)}(\vec{0},0)F^{(p)}(\vec{0},0)\rangle \times\exp(-|t|/\tau_{\mathrm{CFN}}) \ , \tag{33}$$

where τ_{CFN} is the relaxation time for $\vec{q}=\vec{0}$ mode, and may be different from $\tau_{\vec{q}}$ for $\vec{q}\rightarrow\vec{0}$ mode; this is to be verified by experiments.

Our assumption is based on the following facts: It is well known that the Landau-Khalatnikov theory cannot be rigorously applied to the $\vec{q}=\vec{0}$ mode since this is the equilibrium state. But a close similarity between Eq. (33) and the well-known BPP form for time correlation, which has been proved so successful, can be easily noticed. This becomes particularly apparent when we write

$$\langle F^{(p)}(\vec{0},0)F^{(p)}(\vec{0},0)\rangle = V^{-2}\int\langle F^{(-p)}(\vec{r},0)F^{(p)}(\vec{r}\,',0)\rangle\, d\vec{r}\, d\vec{r}\,' \ . \tag{34}$$

In writing this expression, we have used Eq. (11) with $\vec{q}=\vec{0}$. Eq. (34) can be written

$$\langle F^{(p)}(\vec{0},0)F^{(p)}(\vec{0},0\rangle = V^{-1}\int\langle F^{(-p)}(\vec{r},0)F^{(p)}(\vec{r},0)\rangle\, d\vec{r} \ , \tag{35}$$

where we have used

$$\langle F^{(-p)}(\vec{r},0)F^{(p)}(\vec{r}\,',0)\rangle=\langle F^{(-p)}(\vec{r},0)F^{(p)}(\vec{r},0)\rangle \times\delta(\vec{r}-\vec{r}\,') \ .$$

Substituting Eq. (35) in Eq. (33), the BPP form can be recovered.

This problem can also be viewed from another angle if we assume that the Landau-Khalatnikov model is also applicable to $\vec{q}=\vec{0}$ mode. This is compatible with the idea that the $\vec{q}=\vec{0}$ mode fluctuates also in time, and as a result no long-range order is observed even at $T^*$where occurs a large increase of $\vec{q}=\vec{0}$ modes. Again drawing an analogy with the Bose-Einstein condensation for interacting particles,[28] the condensate or the number of modes with $\vec{q}=\vec{0}$ does not become infinite at T^* (i.e., at the ground state); appreciable number of $\vec{q}\neq\vec{0}$ modes, depending on the strength and nature of interaction, remain at the ground state. To approach the problem from this point of view will require not only the knowledge of the lifetimes of different $\vec{q}$ modes but also their number densities, particularly of the mode $\vec{q}=\vec{0}$ and modes with $\vec{q}\neq\vec{0}$. Such a problem is still unresolved, and its complexity can be envisaged from the almost analogous problem of estimating the condensate in superfluid ^{4}He.[29] Hence we follow here the former approach leaving the two constants [C_N and C_L in Eqs. (39) and (40)] to be determined from experiments.

Using the expression for the free energy given in Eq. (14), and Eqs. (28) and (29), we get for $q\neq 0$ modes

$$\langle F_{jk}^{(0)}(-\vec{q})F_{jk}^{(0)}(\vec{q})\rangle=\frac{8kT}{3AV(1+q^2\xi^2)R_{jk}^6} \ , \tag{36}$$

$$\langle F_{jk}^{(1)}(-\vec{q})F_{jk}^{(1)}(\vec{q})\rangle=\frac{2kT}{9AV(1+q^2\xi^2)R_{jk}^6} \ , \tag{37}$$

$$\langle F_{jk}^{(2)}(-\vec{q})F_{jk}^{(2)}(\vec{q})\rangle=\frac{8kT}{9AV(1+q^2\xi^2)R_{jk}^6} \ . \tag{38}$$

It is now straightforward to obtain the relaxation rate arising from the CF using the Eqs. (25), (26), and (32)–(38). The two parts of $(T_1)_{\mathrm{CF}}$ arising from the modes with $\vec{q}=\vec{0}$ and from the modes with $\vec{q}\neq\vec{0}$ are given by, respectively,

$$(T_1)^{-1}_{\mathrm{CFN}}=C_N\omega^{-1}x[(1+x^2)^{-1}+4(1+4x^2)^{-1}] \ , \tag{39}$$

$$(T_1)^{-1}_{\mathrm{CFL}}=C_L T\nu^{1/2}\omega^{-1/2}y^{1/2} \times\{[1+(1+y^2)^{1/2}]^{-1/2} +4[1+(1+4y^2)^{1/2}]^{-1/2}\} \ , \tag{40}$$

where $x=\omega\tau_{\mathrm{CFN}}$ and $y=\omega\tau_{\mathrm{CFL}}$, C_N and C_L are constants independent of ω and T, and ν is defined in Eq. (9). The temperature dependences of τ_{CFN} and τ_{CFL}, in accordance with the Landau-de Gennes theory,[1,2] are given by

$$\tau_{\mathrm{CFN}}=\tau^{(0)}_{\mathrm{CFN}}\exp(W/T)(T-T^*)^{-\gamma} \ , \tag{41}$$

$$\tau_{\mathrm{CFL}}=\tau^{(0)}_{\mathrm{CFL}}\exp(W/T)(T-T^*)^{-\gamma'} \ , \tag{42}$$

where γ and γ' are the critical indices to be determined from experiments; both are equal to unity in a standard molecular-field approximation. On the background of our earlier discussions on $\vec{q}=\vec{0}$ mode and all other modes with $\vec{q}\neq\vec{0}$, we have left the two critical indices unequal; we shall see later that our experimental results do also suggest this. It may be pointed out here that Eq. (42) is identical with Eq. (17), while Eq. (41) in an assumed form in analogy with τ_{CFL}.

It is to be mentioned that, in deriving Eq. (40), the summation over $\vec{q}$ has been replaced by an integration over the whole $\vec{q}$ space excluding the point $\vec{q}=\vec{0}$, the density of states in the $\vec{q}$ space has been assumed uniform, and the upper limit of integration has been taken as ∞ without introducing a cutoff. Because of the presence of the factor $\exp(-|t|/\tau_{\vec{q}})$ in the integrand, no appreciable error is introduced in extending the upper limit of $\vec{q}$ to ∞.

III. EXPERIMENTAL DETAILS

As we have noted already, the main problem of studying the DCB is to determine $(T_1)_{\mathrm{CF}}$ from experimental $(T_1)_{\mathrm{expt}}$ with sufficient confidence. We have also noted there our motivation of selecting the number of frequencies for measuring proton T_1 in MBBA over a large temperature range above T_c ($\sim$316 K). The highest temperature tried in our measurements was motivated to observe frequency independent T_1 within our experimental accuracy ($\sim$1% for absolute values). During such measurements, we kept always a check on our sample to ensure that it did not deteriorate. This check was made by repeating T_1 measurements for some lower-temperature point at the same frequency used. Measurements of T_1 were made by a modified version of the three-pulse method[30,31] which enable us to determine relative T_1 at any frequency within a few parts in 10^3 and the absolute magnitudes within 1%. Limitations of achieving higher accuracy were mainly from the consideration of experimental time and the consequent stability in the temperature control. The temperature control was done by a Bruker air-flow cryostat (model B-ST 100/700), but its stability was monitored by a digital millivoltmeter connected in parallel to the temperature deviation meter in conjunction with another Chromel-Alumel thermocouple reading the temperature to about 0.03 K. This latter thermocouple was used also to calibrate the Bruker temperature-control unit with the temperature deviation read by the millivoltmeter mentioned above. In this way, we were ensured of the sample temperatures remaining constant within ±0.1 K during measurement at any temperature point. The temperature of the sample was taken as that at the sample center. This was accomplished from the Bruker thermocouple reading the correspondence of which with the temperature of the sample center was established previously by a blank experiment with a sample of MBBA not vacuum sealed. Such a procedure ensured us also of the temperature gradient existing inside a sample. No appreciable temperature gradient was observed over the sample volume except for temperatures around T_c ($\sim$0.2 K).

The sample of MBBA used in the present measurements was commercial grade, distilled and degassed several times prior to sealing it under vacuum. All the data presented here were taken on a single sample. It might be noted here that some of our samples used earlier to this set of data showed deterioration on taking to high temperatures as revealed by repeating some lower temperature T_1 measurements, but no observable change in T_c (within about 0.2 K) could be detected. These data have not been included here.

IV. DATA ANALYSIS AND RESULTS

A. Preliminary considerations

In Fig. 1, we show our directly measured proton T_1 in MBBA obtained over a temperature range of about 316–350 K and for a number of frequencies. It can be noted there that $(T_1)_{\mathrm{expt}}$ becomes frequency independent within our experimental error above about 340 K for the lowest three frequencies (4, 5, and 6 MHz), but not so when the data of the other two frequencies (8.8 and 20 MHz) are also considered. These suggest three possibilities for the source or sources of the observed frequency dependence in this temperature range: (i) appreciable $(T_1)_{\mathrm{CF}}$ exists at these high temperatures, and both x and y are $<<1$ for the lowest three frequencies, (ii) the frequency dependence is due to diffusion mechanism[20] as some authors have suggested earlier from studies in the nematic phase,[32] and (iii) the frequency dependence is due to both of the above sources. In order to check these possibilities, we have determined the apparent W(W_A) from the data of the lowest three frequencies, from those of 8.8 and of 20 MHz in this temperature range. These three W_A are 4.4, 4.0, and 3.7×10^3 K, respectively, shown in Fig. 2. All these W_A are fairly large compared to real W (3.0×10^3 K),[19] although differences between the apparent ones and the real one decrease with increasing frequency. From these observations and from the observed frequency independence of $(T_1)_{\mathrm{expt}}$ for the lowest three frequencies, one can easily conclude that the frequency dependence, if any, from the diffusion mechanism[20] is to be negligible in this temperature range for all frequencies measured. Such a conclusion one can arrive at without going into the details of diffusion mechanism in nematics. This is because

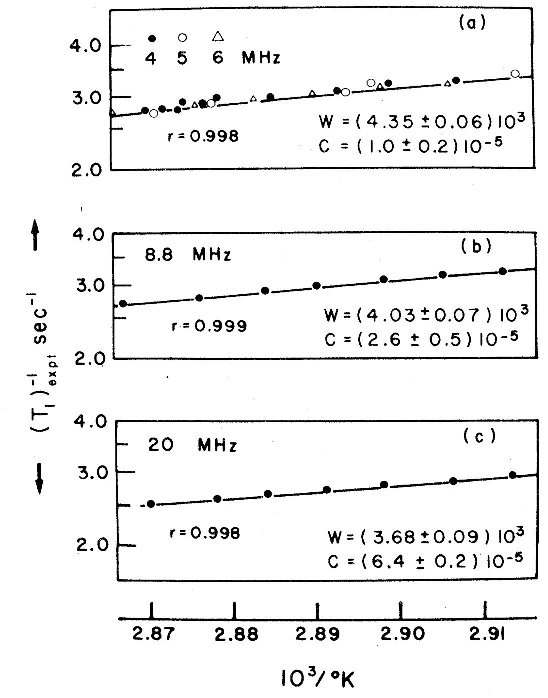

FIG. 2. (a)–(c) Semilog plots of experimental relaxation rates vs $1/T$. The straight lines are obtained by the LSF to the relation: $(T_1)^{-1}_{\rm expt} = C\exp(W/T)$. The data points are from Fig. 1 for T above about 340 K.

the diffusion mechanism noted above is expected to lower W_A rather than to increase it for any fixed frequency. Similar lowering of W_A is also expected in the presence of appreciable exchange diffusion[33] since the observed relaxation rate at any frequency should also increase with increasing temperatures flattening the relaxation rate curve. It is also to be noted that we do not normally expect this mechanism of exchange diffusion to be present in MBBA for its chemical nature. We can then exclude the possibility of exchange diffusion playing any significant role in our observed relaxation rates. With these observations and considering only a factor of 2.5 variation of D in the whole temperature range of our measurements,[19] the frequency dependence from the diffusion mechanism can be excluded completely from our $(T_1)_{\rm expt}$. This is also supported by our earlier observations on our data above 340 K that the frequency dependence from the diffusion mechanism, if any, is negligible for a variation of frequency from 4 to 20 MHz, a factor of 5. We conclude from all these observations that the frequency dependence we observe in our $(T_1)_{\rm expt}$ comes from the CF and not from the frequency-dependent diffusion mechanism.[20] To emphasize this point, we shall henceforth denote $(T_1)_O$ by $(T_1)_D$; assuming all the frequency-independent contributions to $(T_1)_{\rm expt}$ are diffusion controlled.

B. Determinations of $(T_1)_{\rm CF}$ and its two components, $(T_1)_{\rm CFL}$ and $(T_1)_{\rm CFN}$

First, we describe the method we followed to determine $(T_1)_{\rm CF}$ from $(T_1)_{\rm expt}$ at different temperatures for each of the frequencies used. Two methods have been used earlier[14,15,34] for the purpose, and both of them are based on the idea of separating $(T_1)_O^{-1}$ from $(T_1)^{-1}_{\rm expt}$ by knowing its value first at some temperature and then by extrapolating it to other temperatures on the assumption that

$$(T_1)_O^{-1} = (T_1)_D^{-1} = K\exp(W/T) \ , \qquad (43)$$

where K is a constant independent of frequency and is to be determined from some known T and $(T_1)_D^{-1}$. One of them is based on extrapolating low temperature $(T_1)^{-1}_{\rm expt}$ to T^* where $(T_1)^{-1}_{\rm CFN}$ [$(T_1)^{-1}_{\rm CF}$ in our earlier notation[14]] is to be zero for each frequency. Such an extrapolation cannot be reasonably done here particularly on the low-frequency data for which the variation of $(T_1)^{-1}_{\rm expt}$ is large. The second method,[15,34] which is based on determining $(T_1)_D^{-1}$ from $(T_1)^{-1}_{\rm expt}$ at high temperatures where $(T_1)^{-1}_{\rm CF}$ is negligible. This cannot also be applied in our present case since $(T_1)^{-1}_{\rm CF}$ is not negligible at our highest temperatures measured. Still higher temperatures were not tried because of the apprehension of having the sample deteriorate.

We have also used here the above form of $(T_1)_O$ given by Eq. (43), but it has been determined in a slightly different way for reasons noted earlier. Our present method is based on the following considerations.

For the lowest three frequencies in Fig. 1, we can note strong frequency dependence of $(T_1)_{\rm expt}$ at temperatures close to T_c while a little or no frequency dependence at high temperatures. On the other hand, $(T_1)_{\rm expt}$ for the highest two frequencies show appreciable frequency dependence at both low and high temperatures. These suggest that we can reasonably assume both x and y to be $>>1$ at $T = T_L$, the closest temperature to T_c measured. Under these conditions, we expect $(T_1)_{\rm expt}$ at $T = T_L$ for all frequencies to satisfy the relation

$$(T_1)^{-1}_{\rm expt} = A + B\omega^{-1/2} + C\omega^{-2} \ . \qquad (44)$$

The first term on the right-hand side can be identified with the frequency independent $(T_1)_D^{-1}$ given by Eq. (43), the second with $(T_1)^{-1}_{\rm CFL}$ given by Eq. (40) for $y >> 1$, and the third with $(T_1)^{-1}_{\rm CFN}$ given by Eq. (39) for $x >> 1$. For any fixed frequency ω, since $(T_1)^{-1}_{\rm CFL}$ approaches its maximum while $(T_1)^{-1}_{\rm CFN}$ approaches its minimum (zero) with $T \rightarrow T^*$, we assume further that the third term is negligible at $T = T_L = 316.2$ K (compare $T_c \sim 316$ K). Such an assumption may not be completely justified, and may introduce some errors in A and B. But in view of our earlier measurements in MBBA,[14] where $(T_1)^{-1}_{\rm CFL}$ was essentially approximated to be diffusionlike,[2] and in view of errors involved in absolute $(T_1)_{\rm expt}$ ($\sim$1%), we expect these errors in A and B not to be very serious. This is well supported by the excellent least-squares fit (LSF) of our data to Eq. (44) without the third term. These results are shown in Fig. 3. We shall call this approximation the "slow-motion" or "low-temperature" approximation, in contrast to the "fast-motion" or "high-temperature" approximation under which $(T_1)_{\rm CF}$ becomes frequency independent, as for the lowest three frequencies at temperatures above about 340 K.

Under the "fast-motion" approximation and using Eq. (1) with Eqs. (39)–(42), we can write

$$(T_1)^{-1}_{\rm CF}=B'T(T-T^*)^{-\gamma'/2}\exp(W/T)$$
$$+C'(T-T^*)^{-\gamma}\exp(W/T)\ , \qquad (45)$$

where B' and C' are constants independent of T and ω, and are related to B and C of Eq. (44), respectively; these relations can be easily established with the help of Eqs. (39)–(42). The frequency-independent data for the lowest three frequencies were fitted to Eq. (45) by the LSF with $\gamma=\gamma'=1$, and $W=3.0\times10^3$ K, for different choices of T^*. The value of $\gamma'=1$, was taken from light-scattering results.[11–13] One of these fits is shown in Fig. 4. In obtaining $(T_1)^{-1}_{\rm CF}$ from $(T_1)^{-1}_{\rm expt}$, use has been made of Eq. (43), with $K=A\exp(-W/T_L)$, A determined from the low-temperature fit shown in Fig. 3. We must note here that these frequency-independent data, when fitted alone to $(T_1)^{-1}_{\rm CFL}$ or $(T_1)^{-1}_{\rm CFN}$, did not yield any realistic result. Similar unrealistic results were also obtained when these frequency-independent $(T_1)^{-1}_{\rm expt}$ were fitted to $(T_1)^{-1}_D$ and any one of $(T_1)^{-1}_{\rm CFL}$ and $(T_1)^{-1}_{\rm CFN}$. It may be pointed out that the correlation coefficient r of these fits (shown in Fig. 4) are not very good. This may be due to particular choices of variables necessitated for the two-parameter fits. Considering the reproducibility of data within our experimental accuracy the LSF are reasonably good. As we shall see shortly, a marked improvement in these fits is observed when γ is taken to be different from γ'.

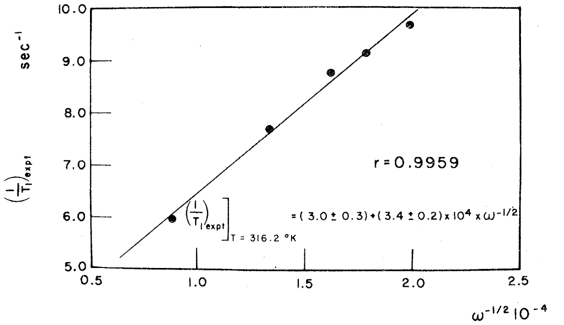

FIG. 3. Least-squares fit of $(T_1)^{-1}_{\rm expt}$ at $T=T_L=316.2$ K, measured at different frequencies, to the relation: $(T_1)^{-1}_{\rm expt}=A+B\omega^{-1/2}$, obtained under the "slow-motion" approximation. Note that the relation is identical with Eq. (44) with the last term dropped. See the text for details.

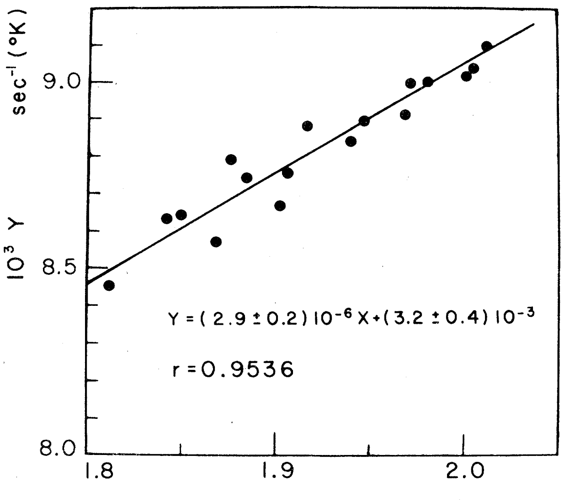

FIG. 4. Least-squares fit of the frequency-independent $(T_1)_{\rm CF}$ observed for the lowest three frequencies (4–6 MHz) to the relation: $Y=B'X+C'$, where $Y=(T_1)^{-1}_{\rm CF}(T-T^*)\exp(-W/T)$ and $X=T(T-T^*)$, obtained under the "fast-motion" approximation [see Eq. (45)]; $W=3\times10^3$ K, and $T^*=315.2$ K for this particular set. $(T_1)^{-1}_{\rm CF}$ at different T have been obtained using Eqs. (2) and (43) with $K=A\exp(-W/T_L)$, W and T_L have the values shown in Fig. 3. See the text for details.

Using B and B' determined from the low- and high-temperature fits, we obtained $C_L\,\nu_0^{1/2}$ and $\tau^{(0)}_{\rm CFL}$, the constants necessary to determine $(T_1)^{-1}_{\rm CFL}$ and $(T_1)_{\rm CFL}$ at different temperatures, the former also at different frequencies [see Eqs. (40) and (42)]. Using $(T_1)^{-1}_{\rm CF}$ and $(T_1)^{-1}_{\rm CFL}$ obtained as above, we determined $(T_1)^{-1}_{\rm CFN}$ at different temperatures and at different frequencies with the help of Eq. (1). Such a procedure was followed to determined $(T_1)^{-1}_{\rm CFN}$ for each choice of T^* ranging between 315–316 K at intervals of 0.1 K. One such set of results is shown in Fig. 5. As expected from Eq. (39), the following three features can immediately be noted: (i) maxima, (ii) maxima shifted to higher temperatures with higher frequencies, and (iii) reduced heights of these maxima with higher frequencies. We shall discuss each of these features in relation to our Eq. (39).

According to Eq. (39), these maxima should occur at $x=0.616$. Using this value of x and the relation $x=\omega\tau_{\rm CFN}$, we determined $\tau_{\rm CFN}$ at different T corresponding to the observed maxima at different frequencies and for a chosen T^*. These values of $\tau_{\rm CFN}$ with their corresponding T were fitted to Eq. (41) by

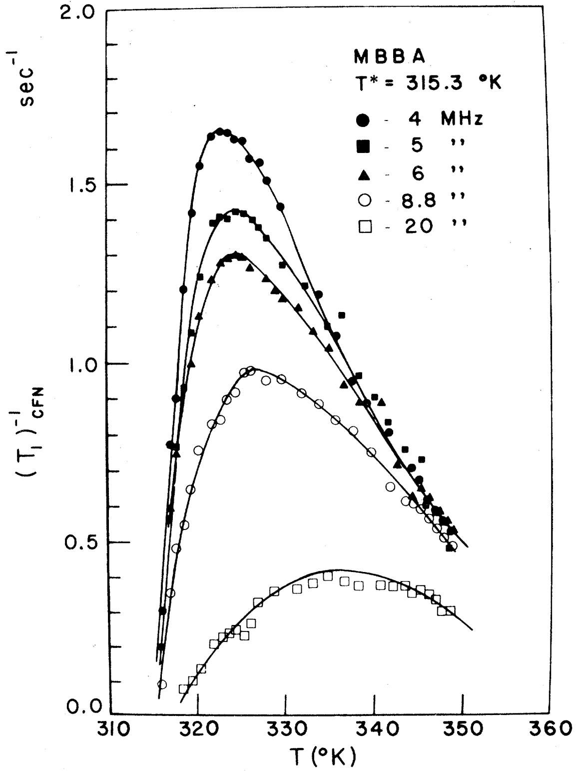

FIG. 5. Typical set of $(T_1)^{-1}_{\mathrm{CFN}}$ vs T plots obtained at different frequencies and for the choice of $T^* = 315.3$ K. The solid lines are to aid the eye to locate the maxima.

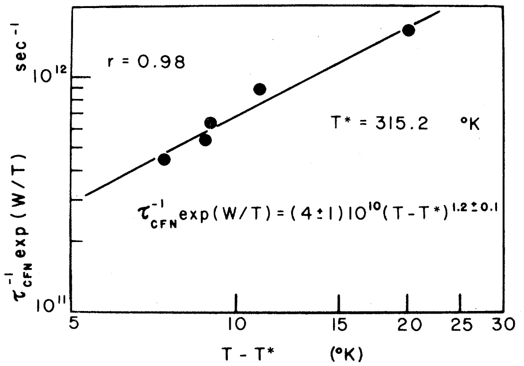

FIG. 6. Log-log plot of $\tau^{-1}_{\mathrm{CFN}}\exp(W/T)$ vs $T-T^*$ with $T^* = 315.2$ K and $W = 3\times10^3$ K; τ_{CFN} and the corresponding T were determined from the maxima similar to those shown in Fig. 5; $\omega\tau_{\mathrm{CFN}} = 0.616$ at the maxima. The straight line shows the least-squares fit to Eq. (41). See the text for details.

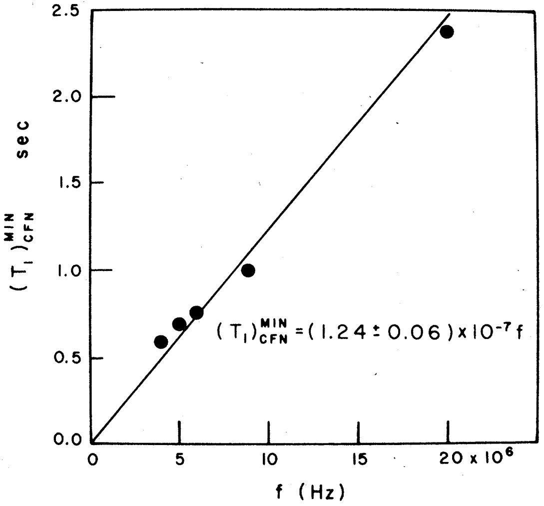

FIG. 7. Observed $(T_1)^{-1}_{\mathrm{CFN}}$ (max) for $T^* = 315.2$ K similar to those shown in Fig. 5, or $(T_1)^{\mathrm{MIN}}_{\mathrm{CFN}}$ vs frequency f $(=\omega/2\pi)$. The straight line shows the least-squares fit to Eq. (46).

the LSF, and this procedure was followed for each choice of T^*. The best fit, defined by the maximum r, was obtained for $T^* = 315.2$ K. These results are shown in Fig. 6. It should be pointed out that we obtain $\gamma = 1.2 \pm 0.1$ instead of the value 1 used for the high-temperature fits, one of which is shown in Fig. 4. Using this value of γ, the high-temperature fit was redone with the data for $T^* = 315.2$ K and a marked improvement in the fit was observed, as indicated by an increased r (from 0.95 to 0.98). Since this new fit increased $(T_1)^{-1}_{\mathrm{CFL}}$ marginally, no appreciable changes in observed maxima of $(T_1)^{-1}_{\mathrm{CFN}}$ were expected, and the procedure was not followed for all different T^* used earlier. Corrections to $(T_1)^{-1}_{\mathrm{CFN}}$ at different temperatures and at different frequencies due to the new fit were not also incorporated since they were well below our estimated errors shown.

Using Eq. (39), we can get the frequency dependence of the maximum of $(T_1)^{-1}_{\mathrm{CFN}}$ or the minimum of $(T_1)_{\mathrm{CFN}}$ as

$$(T_1)^{-1}_{\mathrm{CFN}}(\max) = (T_1)^{\mathrm{MIN}}_{\mathrm{CFN}} = M\omega\ , \tag{46}$$

where M is a constant independent of frequency. The LSF of $(T_1)^{\mathrm{MIN}}_{\mathrm{CFN}}$ to Eq. (46) is shown in Fig. 7 for the data with $T^* = 315.2$ K. The agreement is excellent in spite of different complex steps in extracting the data from the directly measured quantities.

C. Summary of experimental results

(i) Proton spin-lattice relaxation time $(T_1)_{\mathrm{expt}}$ has been measured in MBBA as a function of temperature above T_c (~316 K) over a range of 316.2–350 K at frequencies 4–6, 8.8, and 20 MHz.

(ii) Even at the highest temperatures, appreciable contribution to the nuclear relaxation rates arising from the CF remains for all the frequencies used.

(iii) Frequency dependence of the spin-lattice relaxation rate arising from the diffusion mechanism, if any, in the temperature and frequency ranges studied here is negligible within the experimental accuracy; all the observed frequency dependence can be attributed to the part arising from the CF.

(iv) From the temperature and frequency dependences of the nuclear relaxation rate, it has been shown that the proton relaxation consists broadly of two parts—one arising from the diffusion-controlled mechanisms and independent of frequency, and the other from the CF dependent on frequency. The frequency-dependent $(T_1)_{\mathrm{CF}}$ needs be divided into two parts as envisaged in Ref. 2; no one component of the CF is capable of explaining the observed temperature and frequency dependences.

(v) The two parts of $(T_1)_{\mathrm{CF}}$, $(T_1)_{\mathrm{CFL}}$, and $(T_1)_{\mathrm{CFN}}$, have been determined over a wide temperature range at a number of frequencies.

(vi) The correlation times τ_{CFL} and τ_{CFN} characterizing these two part of CF have also been determined over a large range of temperatures. In such determinations, the CB of τ_{CFL} has been taken the same as observed in the light-scattering experiments.[11–13] Like τ_{CFL}, τ_{CFN} shows also CB but with a slightly higher index. The best fit values are $\tau_{\mathrm{CFL}}^{(0)} = (1.2 \pm 0.2) \times 10^{-11}$ sec with $\gamma' = 1$ (taken from light-scattering results), $\tau_{\mathrm{CFN}}^{(0)} = (2.5 \pm 0.6) \times 10^{-11}$ sec with $\gamma = 1.2 \pm 0.1$, $T^* = 315.2$ K. It should be noted that we have taken $T - T^*$ in Eqs. (41) and (42) as pure numbers in expressing $\tau_{\mathrm{CFN}}^{(0)}$ and $\tau_{\mathrm{CFL}}^{(0)}$ in seconds.

(vii) The heights of $(T_1)_{\mathrm{CFN}}^{-1}$ (max) or $(T_1)_{\mathrm{CFN}}^{\mathrm{MIN}}$ versus frequency follows a linear relation in agreement with the theory.

V. DISCUSSIONS

Since the work of Cabane and Clark[16] in PAA, a number of reports[14,15,17,34,35] have appeared on the CB in nematics above T_c studied through nuclear relaxation. As we have noted earlier, none of these reports have considered the total CF contribution to nuclear relaxation rates usually measured in an experiment. The main experimental problem is to determine this contribution from other existing ones with sufficient confidence. Mainly for the limited nature of the data, the separation of $(T_1)_{\mathrm{CF}}$ has been partial in earlier studies, although both the essential features of the two components, $(T_1)_{\mathrm{CFN}}$ and $(T_1)_{\mathrm{CFL}}$, have been observed there. With the more elaborate frequency and temperature dependences of proton-spin-lattice relaxation rates, it has been possible here to separate not only $(T_1)_{\mathrm{CF}}$ from $(T_1)_{\mathrm{expt}}$ but also its two components.

From the frequency and temperature dependences of our high-temperature data, it could be convincingly shown that the frequency dependence of $(T_1)_{\mathrm{expt}}$ arising from the diffusion mechanism[20] could be neglected in the temperature and frequency ranges of our measurements. Once the frequency independence of this contribution $[(T_1)_O$ in Eq. (2)$]$ is known, this part could be determined from the frequency dependence of low-temperature $(T_1)_{\mathrm{expt}}$. Here we have neglected the contribution from $(T_1)_{\mathrm{CFN}}$. Such an assumption, although not rigorously justified, seems well satisfied in view of the excellent fit shown in Fig. 3. Combining the high- and low-temperature fits, it has been possible to determine τ_{CFL}, the temperature dependence of which is assumed to be the same as observed in the light-scattering experiments.[11–13] In other words, we have used the critical index for τ_{CFL}, the same as derived in light-scattering experiments. The exact values of τ_{CFL} observed in those experiments have not been used here for two reasons: (i) Although the nature of the CB is not dependent on the purity of the sample but the absolute value of a parameter does.[11] (ii) Nuclear relaxation utilizes a microscopic-order parameter while the light-scattering experiments the macroscopic one; such difference may introduce some unforeseen error in determining $(T_1)_{\mathrm{CFL}}$, and hence in $(T_1)_{\mathrm{CFN}}$.

We compare our τ_{CFL} with those obtained by the two different light-scattering techniques.[11–13] For a meaningful comparison of the different results, we have also computed $\tau_{\mathrm{CFL}}^{(0)}$ from light-scattering results with $W = 3.0 \times 10^3$ K instead of 2.8×10^3 K used by both groups and with T^* reported. These are 3.5×10^{-11} and 4.8×10^{-11} sec, respectively, obtained from Refs. 11 and 13.

Considering the simplifications of the Landau-de Gennes model as applied to the NMR relaxation and to the light-scattering techniques, the observed discrepancies between our result and the light-scattering results may not be as great as they appear. Besides theoretical simplifications, there exist experimental problems on the exact separation of the CF contribution to the nuclear relaxation, the purity of the sample, etc. From the theoretical viewpoint, particular mention should be made to the fact that the correlation times of fluctuations in different components of the order-parameter tensor $\vec{\mathrm{Q}}$ are not equal as de Gennes has considered,[1,2] and we have used in our theory. In fact, it can be easily shown from the Landau-de Gennes expression of free energy [see Eq. (14)] that the nondiagonal components of $\vec{\mathrm{Q}}$ decay twice as fast as the diagonal components. From these considerations alone, a factor of two discrepancies between NMR and light-scattering results can be accounted for. Another important point in this connection needs also be mentioned is the local-field effects,[1(b)] which play a considerable role in the optical but not in NMR results. It is well known that because of the local-field effects the macroscopic and microscopic $\vec{\mathrm{Q}}$ are not strictly proportional, as has also been recently stressed by Hanson and Shen.[36] Furthermore considering the complex molecular structure of MBBA, the contributions of different nuclear dipole pairs to the relaxation rate may be more complex than that treated in the theory [see Eqs. (36)–(39)]. It is not clear yet how all these simplifications contribute to the observed discrepancy.

We have no existing results to compare with our $(T_1)_{\mathrm{CFN}}$ and with τ_{CFN} obtained here. But both from theoretical and experimental viewpoints discussed earlier, the necessarity of considering the CF in two parts seems well established by our results. The essential features of $(T_1)_{\mathrm{CFN}}$ noted earlier can be readily observed, and the agreement between the theory and experiment is reasonably good.

The validity of separating the CF contribution to the nuclear relaxation rate as we have done here can also be understood by the following simple arguments. It is well known in the relaxation theory that the two most important factors in determining the relaxation rate by the direct process[37] are: (i) the existence of coupling between the spin system and the bath or the lattice to which the former gives up its excess energy, and (ii) the spectral density of the lattice centered around the frequency of nuclear resonance ω. The former is the required condition for any relaxation process, while the latter is typical for the direct process. The spectral density contributing to the nuclear relaxation rate can then be defined by the number of modes with frequency ω and the correlation or the relaxation time of this particular mode. For simplicity, we shall restrict our discussions to the number of modes with frequency ω. Under this simple consideration, we expect the increase or the decrease in the relaxation rate at a particular frequency of nuclear resonance with the corresponding increase or decrease of these modes. Keeping these considerations in our view, let us look at our Eqs. (14)–(16) and (36)–(40). One can easily note the following facts with T approaching to T^*: (i) the number of modes with $\vec{q}\rightarrow\vec{0}$ increases with the corresponding increase of their relaxation times, i.e., the spectral density of the mode increases for increasing numbers as well as for getting narrower; (ii) the lower the $|\vec{q}|$, the lower the energy; (iii) $(T_1)_{\mathrm{CFL}}^{-1}$ tends to a constant but increasing with the lowering of ω at T^*, since $y\rightarrow\infty$ for any finite ω; and (iv) $(T_1)_{\mathrm{CFN}}^{-1}$ tends to zero at T^*, since $x\rightarrow\infty$ for any finite ω. At $T=T^*$, point (iv) can be easily understood, since the number of modes with $\vec{q}=\vec{0}$ and frequency ω becomes zero, and hence the relaxation rate is also zero. But it is difficult to understand point (iii), particularly its frequency dependence, if we consider all the modes with different $\vec{q}$ condense to the mode $\vec{q}\rightarrow\vec{0}$ at $T=T^*$. Moreover, the spectral density reduces to a δ function with the center at zero frequency since the relaxation time becomes also infinite. In such a case, we would expect $(T_1)_{\mathrm{CFL}}^{-1}$ to be also zero at $T=T^*$ for any finite ω. The frequency dependence of $(T_1)_{\mathrm{CFL}}^{-1}$ can also be well understood from our qualitative arguments when we draw an analogy with the ground state of an interacting Bose gas.[28] Such a ground state (in our case it is at T^* as noted earlier) is not a pure $\vec{q}=\vec{0}$ state, but a mixture of $\vec{q}=\vec{0}$ and $\vec{q}\neq\vec{0}$ states. In other words, appreciable number of $\vec{q}\neq\vec{0}$ modes or particles exist in the ground state, and their numbers are expected to increase with decreasing $\vec{q}$. In such a situation, we expect increasing relaxation rates with decreasing ω as observed in our experimental results. As we know from the problem of Bose-Einstein condensation that the modes with $\vec{q}=\vec{0}$ need separate considerations from those modes with $\vec{q}\neq\vec{0}$, we expect similar distinctions are to be made for the CF. Our experimental results are in good accord with these ideas.

It is interesting to seek some connections, if there is any, between our observations and those made in the ordered phase.[38] With this in view, we include here a brief discussion on these aspects, a more detailed connection we hope to establish in a future publication where we apply our model in the ordered phase. A number of mechanisms have been suggested in the literature[38] for the relaxation in the ordered phase. These can be grouped broadly under the following three headings: (a) order fluctuations (OF), (b) translational diffusion, and (c) diffusive rotational motion or rotational diffusion; some couplings among these mechanisms have also been considered. Various models have been developed to consider these mechanisms with some success in understanding the experimental results, but not always without ambiguity both from the theoretical and experimental points of view. Many conflicting results exist in the literature,[38] and it is not clear yet how far different theoretical and experimental factors have contributed to these. Our theory takes the mechanisms noted above also into consideration, but in a slightly different way. We have considered the fluctuations in the order parameter and not simply the order director fluctuations (ODF). Furthermore, our order parameter is microscopic and fluctuations in it are not limited to the hydrodynamic model of OF, as we have noted earlier. These two aspects of OF, the microscopic and macroscopic, may be compared with the lattice and elastic vibrations in a solid,[39] respectively; the former under the long-wavelength limit is expected to yield the latter and vice versa. It may be pointed out that the results obtained by Doane *et al.*[40] under the ODF approximation and latter extended by Blinc *et al.*[41] do not seem right. These results have been criticized also by Freed[42] who has essentially treated all the three mechanisms in a composite way under the approximation of stochastic Markov process, retaining the features of the hydrodynamic model; he recovers under his lowest-order approximation the ODF results of Doane *et al.*[40] The limitations of the ODF treatments can be easily noted by considering the situation where the order director is aligned along the direction of H. The nuclear relaxation treated with ODF or with fluctuations of the dipole-pair vector under the long-wavelength approximation is to be exactly equivalent, since the two situations are physically indistinguishable. One can easily convince oneself in such case that the latter yields all the spectral densities $J_0(0)$, $J_1(\omega)$, and $J_2(2\omega)$, not simply $J_1(\omega)$ as obtained by ODF. Furthermore, an immediate consequence of the ODF results[40,41] is to have different relaxation rates for different spectral lines and the measurements of the relaxation rates with a single exponential are questionable. No less a serious objection is to the conclusion that T_1 is independent of ODF from the observed angular dependence of $T_{1\rho}$ as Blinc *et al.*[40(c)] have done, since $T_{1\rho}$ is expected to have similar angular dependence due to the change in the dipolar field or dipolar splittings caused by the shifting of the order director away from the direction of H and since $T_{1\rho}$ is not expected to be completely determined by the spin-lattice relaxation.[43]

The mechanism (b) and a part of (c), namely the diffusive rotational motion around the long molecular axis, which is ordinary liquidlike, are included in our $(T_1)_{\bar{D}}^{-1}$. The other parts of (c), the diffusive rotational motions around the axes normal to the long molecular axis are essentially included in our local parts of (a) for large $\vec{q}$. In other words, the contributions from these two parts of (c) are included in our $(T_1)_{\rm CFL}^{-1}$. These diffusive rotational motions cannot be ordinary liquidlike since they are restrictive and limited to small deviations from the equilibrium positions of the long axis of the individual molecule. The large deviations can be excluded by the argument that such motions would cause the multiplets in the nematic phase to vanish. This is the physical basis of the dipole-field averaging in solids and liquids.[44] Similar considerations are expected to hold good also in the critical regime where the short-range order still persists. Contrary to the above observations, if we assume the maxima of our $(T_1)_{\rm CFN}^{-1}$ are due to some frequency-dependent mechanism other than the one considered, such as the rotational diffusion around the two normal axes as suggested by certain authors,[38] particularly Graf *et al.*,[45] we end up with unphysical results. These can be noted in Fig. 8 where we show the same $\tau_{\rm CFN}$ used in Fig. 6 versus $1/T$ together with the LSF to the relation: $\tau_R = \tau_R^{(0)} \exp(W/T)$; to avoid confusion, we have used τ_R instead of $\tau_{\rm CFN}$ in this figure. It should be noted that both W ($\sim 14 \times 10^3$ K) and $\tau_R^{(0)}$ ($\sim 10^{-26}$ sec) are unrealistic. Similar unrealistic values are also given by other $\tau_{\rm CFN}$ obtained for different T^*. It is to be noted that the taking of τ_R equal to $\tau_{\rm CFN}$ is not rigorously justified since $(T_1)_{\rm CFN}$ are obtained under different conditions discussed earlier. These are taken equal here since we do not expect appreciable variations of temperatures at which these maxima occur. Such an expectation is based on our experience with $\tau_{\rm CFN}$ obtained for different T^* noted above and also on reasons similar to those discussed earlier in connection with the high-temperature fit with unequal γ. Here we may point out that any realistic fit should yield the parameters $\tau_R^{(0)}$ and W mutually compatible since these should not be unrelated; of course, their exact relation is expected to be model dependent. From the straightforward meaning of the correlation time and with simple arguments based either on the classical[46] or the quantum-mechanical viewpoint of lifetime broadening, we can consider $\tau_R^{(0)}$ to be the residence time of a relaxing particle (for example, a molecule here) in a potential well of depth W. Obviously, the parameters derived above do not stand these and so are unphysical. Similar or almost similar unphysical values are also obtained from the best fit parameters of Graff *et al.*[45] The authors have also noted some of these, but from different viewpoints apparently not giving sufficient stress. Particular mention should also be made of their parameter ϵ, the strong temperature dependence of which is hard to justify. Moreover, it is not clear how far their parameter values have been influenced by the neglect of a term similar to our $(T_1)_{\rm CFN}$ in their relaxation rate equation. In fact, we expect in the nematic phase terms similar to our $(T_1)_{\rm CFL}$ and $(T_1)_{\rm CFN}$ in the relaxation rate equation both for the nematic-solid and the nematic-isotropic transitions. We do not know yet their relative weights in the relaxation rate for any specific system from the theoretical considerations. It may be interesting to point out that the maxima of the spin-lattice relaxation rates in a low-temperature nematic reported recently by Ukleja and Doane[47] may be the first direct observation of $(T_1)_{\rm CFN}^{-1}$ for the solid-nematic transition. The data

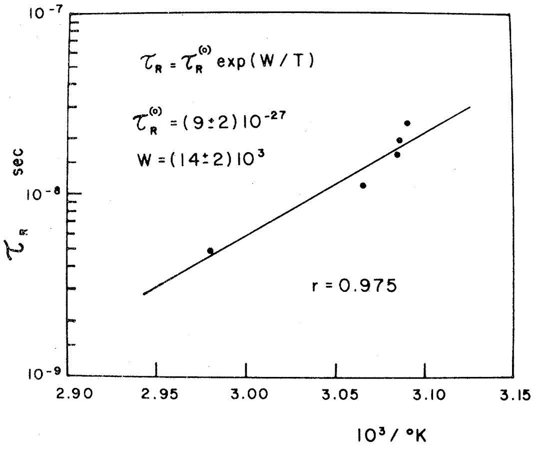

FIG. 8. Semilog plot of τ_R vs $1/T$ with the straight line showing the LSF to the relation $\tau_R = \tau_R^{(0)} \exp(W/T)$. The data points are the same as those of Fig. 6. See the text for details.

shown in their Fig. 4, which is similar to our Fig. 8, yield similar unphysical results discussed earlier. Preliminary analysis shows that this unphysical behavior is completely removed with our model if we assume that the nematic-solid transition is also critical.

VI. CONCLUSIONS

We have shown here that the nuclear relaxation rate arising from the CF, $(T_1)_{\text{CF}}^{-1}$, needs be divided into two parts, one arising from the modes with $\vec{q}=\vec{0}$, $(T_1)_{\text{CFN}}^{-1}$, and the other from all the remaining modes with $\vec{q}\neq\vec{0}$, $(T_1)_{\text{CFL}}^{-1}$, as envisaged in Ref. 2. The Landau-de Gennes model gives a fair description of $(T_1)_{\text{CFL}}$, and τ_{CFL} derived is in reasonable agreement with results obtained by quite different techniques. A reasonable extension of the Landau-de Gennes model can also be made for describing $(T_1)_{\text{CFN}}$, although τ_{CFN} derived shows appreciable differences from τ_{CFL} in both magnitude and temperature dependence. It would be interesting to extend such studies to other nematic systems, preferably in a wider frequency range and with higher precision in measurements, to see particularly whether similar variations in τ_{CFL} and τ_{CFN} are the general features of the NI transition. The observations on τ_{CFL} and τ_{CFN} together with the predicted frequency dependence of $(T_1)_{\text{CFL}}$ at T^* suggest strongly the close similarity of the NI phase transition and the Bose-Einstein condensation.

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