Temperature Dependence of Molecular Spinning and Tumbling Fluctuations in the Nematic Phase

M. P. Fontana and B. Rosi
Dipartimento di Fisica and Gruppo Nazionale di Struttura della Materia–Centro Interuniversitario di Struttura della Materia, University of Parma, 43100 Parma, Italy

and

N. Kirov
Institute of Solid State Physics, Sofia, Bulgaria

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We report the first accurate study of the temperature dependence of single-molecule spinning and tumbling correlation times in the nematic phase. Whereas the tumbling diffusion is seen to be an ordinary, Arrhenius-type process, the spinning correlation time actually slows down as temperature increases towards the nematic-isotropic transition point. We discuss our results in terms of the peculiarities of diffusion in anisotropic systems; in particular, we emphasize the possible static or dynamic effects of molecular biaxiality.

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Recently we have shown that band-shape analysis of molecular spectra (infrared[1] and Raman[2]) could be used to study reorientational diffusion of complex molecules in anisotropic fluids, such as liquid-crystalline phases. In this Letter we wish to report an application of our method to the study of the temperature dependence of the spinning (rotations about the main molecular axis) and tumbling (rotations about the short molecular axis) reorientational correlation times $\tau_{\parallel}^{r}$ and $\tau_{\perp}^{r}$ in ordered nematic phases. Our results confirm the peculiarities of rotational diffusion in strongly anisotropic systems, in particular concerning the very different effects that the ordering potential has on the spinning and tumbling motions of the single molecules and their temperature dependence.

The effect seems to be quite general for anisotropic systems, and confirms recent calculations for the case of dielectric relaxation.[3] From the point of view of phase transitions and critical phenomena, our results have some relevance for a still unresolved and debated problem, namely the nature of the nematic-isotropic (N-I) phase transition, for which tricritical behavior has been claimed[4] and disputed.[5]

Our main result is evidence of a perhaps critical slowing down of $\tau_{\parallel}^{r}$ as the temperature in the nematic phase is increased towards $T_{\text{N-I}}$. At the same time, $\tau_{\perp}^{r}$ was found to decrease in the usual Arrhenius-type fashion with increasing temperature up to the isotropic phase, with no appreciable discontinuity at $T_{\text{N-I}}$. Since our experimental technique is somewhat novel in this kind of application, in the following paragraph we shall dwell on its most relevant features.

The static orientational order of the nematic phase may be described by the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$, the two lowest-order coefficients in a series expansion of the nematic distribution function $f(\theta)$, where θ is the angle between the molecular and nematic axes.[6] The dynamics of reorientational diffusion of single molecules is contained in the diffusion tensor, which reduces (to a good approximation in the nematic phase) to the diagonal spinning ($D_{\parallel}^{r}$) and tumbling ($D_{\perp}^{r}$) diffusion coefficients.[7]

We have determined the spinning and tumbling time correlation functions[8] by Fourier analysis of selected infrared and Raman bands of several mesogen molecules in their aligned nematic phase. For conciseness we shall report in this Letter on data obtained for OET (4,*n*-octyl 4′,ethoxytolane), which has a nematic phase between $T_{\text{C-N}} = 47.6\,^{\circ}\text{C}$ and $T_{\text{N-I}} = 74.8\,^{\circ}\text{C}$. To study spinning motion, we chose the 1047-cm^{-1} mode (O-C stretching) in the ir spectrum. Such vibration is associated with a transition dipole moment pointing about 50° away from the long molecular axis, and therefore its band shape may be broadened by both spinning and tumbling diffusion. However, because of the strong anisotropy, the tumbling motion contribution is small compared to the spinning contribution, which is then the only one observed over the whole nematic range.

Tumbling reorientations were studied by use of the 1175-cm^{-1} mode (benzene ring in-plane deformation) in the ir spectrum and the 2224-cm^{-1} mode ($\text{C}\equiv\text{C}$ stretching) in the Raman spectrum. The ir mode is associated with a transition moment which is parallel to the long molecular axis, and the Raman-mode polarizability tensor is strongly uniaxial.

For light propagating in the y direction, and polarized along the x or z directions, where z is the nematic axis direction, we determine the dichroic spectrum $A_x(\omega)/A_z(\omega)$ and then take its Fourier transform. This procedure automatically factors out the vibrational relaxation contribution and yields the reorienta-

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tional-time correlation function.[1] This method is novel, but of course its applicability is limited to aligned anisotropic systems. In the Raman case, we construct the isotropic ($I_{\mathrm{iso}}=I_{\mathrm{pol}}-\frac{4}{3}I_{\mathrm{dep}}$) and anisotropic ($I_{\mathrm{anis}}=I_{\mathrm{dep}}$) spectra from the experimental polarized (I_{pol}) and depolarized (I_{dep}) bands. We then take their Fourier transforms and again obtain the reorientational part of the polarizability-fluctuation correlation function from their ratio.[2] Our method allows us to obtain simultaneously static and dynamic parameters such as $\langle P_2\rangle$, $\langle P_4\rangle$, $D^r_\parallel$, and $D^r_\perp$, by fitting the data to the solution, in the short-time ($tD^r \ll 1$) limit, of the rotational diffusion equation in the framework of irreducible tensor formalism.[9] In our previous work we selected, as the most reasonable approximation to the reorientational dynamics of the molecules, the small-step rotational diffusion model.[10] Our calculations yield relations linking the time derivatives of the Fourier transforms of the spectra to the order parameters and the diffusion coefficients. In the ir case we have only one equation, and therefore in order to determine the diffusion coefficient we need to obtain $\langle P_2\rangle$ independently from the dichroic ratio of a strongly longitudinally polarized band. In the Raman case, because of the tensorial nature of the response function, we obtain three equations corresponding to three different scattering geometries, from which we can derive values for $\langle P_2\rangle$, $\langle P_4\rangle$, and $D^r_\perp$.

For the purpose of the present Letter, it is convenient to avoid theoretical manipulation in order to gain in generality. Thus we chose to use as our basic experimental information the relaxation times $\tau^r_\parallel$ and $\tau^r_\perp$, which may be obtained directly from the exponentially decaying part of the experimental reorientational-time correlation function, which we found to be exponential in the range $0.2 \lesssim t \lesssim 3$ psec (ir case) or $0.1 \lesssim t \lesssim 1.5$ psec (Raman case). For $\Delta t \rightarrow 0$, inertial effects dominate the motion, and therefore the correlation function approaches the expected t^2 behavior.[8] For long times noise and finite ($\sim 1\ \mathrm{cm}^{-1}$ for ir spectra; $\sim 2\ \mathrm{cm}^{-1}$ for Raman spectra) experimental resolution made the data unreliable.

Oriented samples were prepared by our rubbing the optical KBr windows, heating to the isotropic phase, and then slowly cooling. Temperature in the cell was stable to within 0.02 °C. Temperature uniformity throughout the cell was estimated to be better than 0.2 °C; this, of course, may have created a problem in the case of ir spectra, where the light beam was of the order of the window dimensions ($10\times 5\ \mathrm{mm}^2$). For Raman spectroscopy uniformity in the illuminated volume was much better, given the very small size of the excitation beam ($2\times 0.1\ \mathrm{mm}^2$, with cylindrical focusing in backscattering geometry). Sample thickness was 10 μm (ir) and 10, 25, 50, or 75 μm (Raman). Several sample thicknesses were necessary in the Raman case to correct for the polarization scrambling due to molecular director fluctuations in the nematic phase.[11] For other experimental and data-handling details we refer to our previous papers.[1,2] A more complete and comprehensive report is also in preparation.[12]

In Fig. 1 we show typical temperature dependences of $\tau^r_\perp$ and $\tau^r_\parallel$. The tumbling diffusion is seen to follow an ordinary, temperature-activated, Arrhenius-type behavior, typical of a Debye diffusional process. In fact, the $D^r_\perp$ coefficient obtained from the $\tau^r_\perp$ data by use of the small-step diffusion model obeys well the Nernst-Einstein connection with the average rotational viscosity in the nematic phase.[13]

Quite different is the behavior of $\tau^r_\parallel$, which actually increases as $T \rightarrow T_{\mathrm{N\text{-}I}}$. Such a slowing down is predicted by our calculations[1,2]; for the ir case, for instance, we find that

$$\tau^r_\parallel \sim [D^r_\parallel \langle P_2\rangle]^{-1}. \qquad (1)$$

Thus, as T increases and $\langle P_2\rangle$ decreases, $\tau^r_\parallel$ is expect-

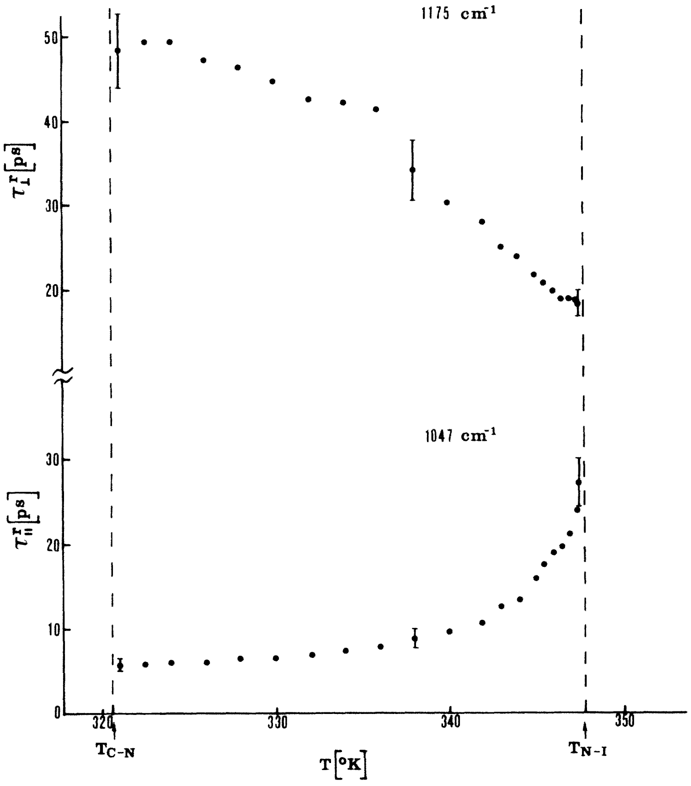

FIG. 1. Reorientational relaxation times for spinning ($\tau^r_\parallel$) and tumbling ($\tau^r_\perp$) motions in the nematic phase of OET [similar behavior was also found in other nematics (Ref. 12)]. Note the break in the ordinate scale. Near $T_{\mathrm{N\text{-}I}}$, the relaxation times are essentially the same within the experimental error.

ed to increase. However, the size of the variation of $\tau^r_\parallel$ in the nematic phase is too large to be accounted for by Eq. (1), even if we assume that $D^r_\parallel$ is independent of temperature. The more general model proposed in Ref. 3 also does not seem to provide a quantitative check of our data on $\tau^r_\parallel$. In particular, an increased role of memory or inertial effects would seem to work in the opposite direction (i.e., to favor a less strong increase of $\tau^r_\parallel$ with increasing temperature).

A possible contribution to the observed slowing down—a static contribution due to the anisotropic, ordered nature of the nematic fluid—could be due to deviations of the molecular shape from the hitherto assumed cylindrical symmetry. In fact, the spinning motions must be very sensitive to such deviations. Preliminary calculations, using the small-step diffusion model with a biaxial potential, do indicate that the vibrations which are sensitive to spinning motion (i.e., the ones with a strong projection of the transition dipole moment in the plane of the second axis) could yield relaxation times which behave as $\langle P_2 \rangle^{-2}$; this would go in the right direction toward explanation of the strong temperature variation of $\tau^r_\parallel$, although it would require the occurrence of a delicate equilibrium between the "uniaxial" and "biaxial" contributions.

Although temperature-induced changes in internal molecular conformations could influence the spinning dynamics, we do not believe they could be the main cause of the slowing down. In a recent work, in fact, we have shown that at a given temperature in the nematic phase alkyl tail and central molecular core are characterized by different relaxation times[14]; however, the difference is relatively small (about 30%), and determination of its temperature dependence (unpublished results) indicates that it is not too sensitive to temperature.

Molecular biaxiality could also have a dynamical effect, besides the static one connected with the presence of a biaxial term in the nematic potential. In this case the observed slowing down of $\tau^r_\parallel$ could be considered as evidence of critical "biaxial fluctuations" in the pretransitional region of the N-I transition. Our data for $\tau^r_\parallel$ in fact seem to obey a law of the type

$$1/\tau^r_\parallel = (T - T_0)^\gamma \nu^{-1}, \tag{2}$$

where ν is an average, weakly temperature-dependent, viscosity coefficient, and $\gamma \sim 1$.[15,16] At this point, however, our experimental accuracy is not sufficient to allow an unambiguous determination of pretransitional "critical" exponents such as γ, or of the superheating temperature T_0. Great accuracy is in fact needed, particularly in this case, if data such as ours are to be used to discriminate among current descriptions of the N-I transition.[4,5] Thus at this time we cannot arrive at any definitive conclusion on this point. Furthermore, the role of biaxial terms in the nematic potential (the "static" effect) in the determination of the ir and Raman band shapes must be fully explored, as well as the concomitant peculiarities of molecular diffusion in a strongly anisotropic potential; we are presently working on this problem. However, we wish to point out that our method is particularly well suited to study these problems, since it is specifically sensitive to eventual biaxial effects (both static and dynamic), and allows the simultaneous determination of static and dynamic order parameters; this latter feature is particularly useful in the study of eventual critical effects.

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