Dielectric Relaxation and the Glass Transition in Nematic Liquid Crystals

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Dielectric relaxation studies in nematic liquid crystals with $\vec{E} \parallel \vec{n}$ give the unique opportunity to study a microscopically well-defined kinetic process in a temperature interval extending below T_g. Relaxation is nearly exponential at all temperatures and obeys the Vogel-Fulcher law even below T_g.

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Nematic liquid crystals can often be supercooled to the vitreous state. They then form ideal model systems for the study of kinetic processes in glasses. Usually because of the disorder which exists in a glass a given macroscopic kinetic quantity such as viscosity or diffusion constant is not related to a single well-defined microscopic process but to a superposition of many ill-defined processes. This makes the test of simple model concepts for the description of kinetic processes in supercooled liquids and glasses difficult. Supercooled or glassy nematics are disordered with respect to the center of gravity of the molecules but exhibit a high degree of order with respect to the direction of the molecular axes. As a consequence there exist microscopic kinetic processes which are almost as well defined as in a crystalline solid. An example is dielectric relaxation of an axially symmetric nematogen with a permanent dipole moment in the molecular axis. For the electrical field $\vec{E}$ parallel to the nematic director $\vec{n}$ dielectric relaxation corresponds to a 180° rotation of the molecular axis. Initial and final states and also the barrier are well defined by the nematic order. It is the purpose of this Letter to show that dielectric relaxation experiments on nematogens give important new information on kinetic processes in glass-forming systems.

The compounds studied are shown in Fig. 1. The pure cyanobiphenyl CB5 and solutions of up to 30% of the trinuclear pyrimidine CP4 in CB5 can be supercooled in the form of thin (20 μm) layers to any desired temperature without crystallization for time periods sufficient for a dielectric relaxation experiment. The experimental setup was standard except that we used very thin measurement cells (20 μm) for the low-temperature experiments. For relaxation frequencies 10 Hz $< f_0 <$ 250 MHz f_0 was determined from the complex dielectric function $\epsilon(\omega)$ and for 10^{-4} Hz $< f_0 <$ 100 Hz f_0 was obtained from a polarization decay experiment.

Figure 2 gives the relaxation frequency of CB5 for $\vec{E} \parallel \vec{n}$ as a function of inverse temperature (solid line). The nematic-isotropic transition at 308 K manifests itself in a discontinuity in f_0. The most striking feature, however, is the strong curvature of $f_0(T)$ in the $\ln f_0$ vs $1/T$ plot. Previous experimental studies of dielectric relaxation in nematics[1-8] had been restricted to a small temperature range below T_c in which the inherent curvature was counteracted by effects as-

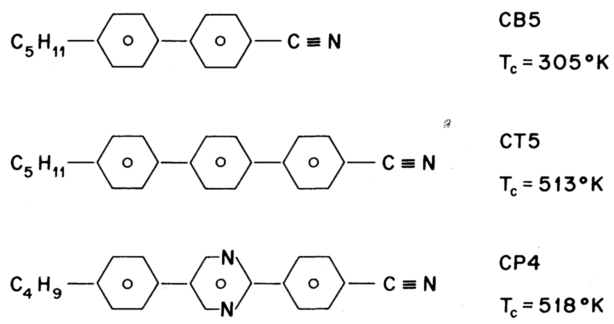

FIG. 1. Chemical structure of the investigated compounds.

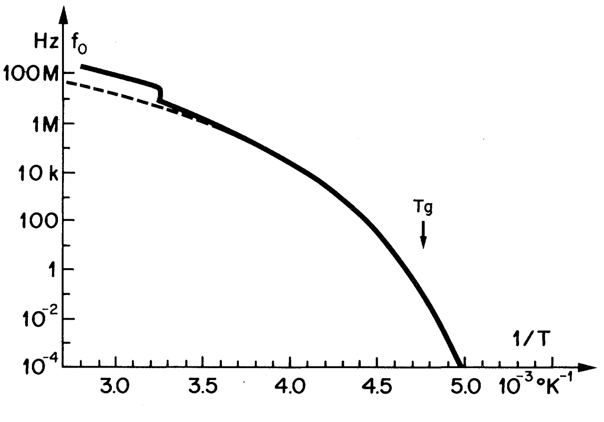

FIG. 2. Relaxation frequency of CB5 as a function of inverse temperature (solid line) and fit of experimental data by Vogel-Fulcher law (dashed line).

sociated with the phase transition (e.g., temperature dependence of the order parameter).

Temperature dependences for kinetic properties of the form shown in Fig. 2 are common for glass-forming systems and can be described by the Vogel-Fulcher law[9, 10]

$$f_0 = CT^{1/2} \exp[A/(T - T_0)] \tag{1}$$

which is universal for glass-forming systems in the sense that the Arrhenius law is universal for ordered systems. I have also carried out specific-heat measurements and for a cooling or heating rate of 5 K/min find a glass transition temperature $T_g = 210$ K for CB5. Typically the Vogel-Fulcher law only holds in a limited temperature interval above T_g. Viscosities of simple liquids for instance tend to be markedly smaller than predicted by (1) in the vicinity of T_g.[11, 12] I find that the Vogel-Fulcher law (dashed line in Fig. 2) describes f_0 within experimental error also below T_g. Deviations occur at the nematic-isotropic phase transition which is obviously not contained in (1).

Dielectric relaxation in nematics for $\vec{E} \parallel \vec{n}$ can be described by a single relaxation time[1, 6-8] which is equivalent to a semicircle in the ϵ_2 vs ϵ_1 (Cole-Cole) plot or an exponential polarization decay. This fact had been noticed in previous experiments at temperatures not far from T_c but the surprising thing is that even below T_g the decay is still nearly exponential as can be seen from Fig. 3. (In fact a small admixture of a faster decay component exists. The importance of the fast component varies somewhat from sample to sample. We do not believe it is intrinsic in origin.) Dielectric relaxation in other than nematic liquids invariably shows marked deviations from single-relaxation-time behavior at $T \cong T_g$.[13]

I have measured dielectric relaxation not only in pure CB5 but also in solutions of trinuclear compounds [CT5 (Ref. 8) and CP4] in CB5. For concentrations not too far from the eutectic, CP4 in CB5 could be kept supercooled for long time periods without crystallization. In a previous paper[8] it was shown that mixtures of a binuclear and a trinuclear compound show two relaxation processes, a fast one due to the binuclear compound and a slow one due to the trinuclear compound. The dielectric response of the mixtures studied can be described by two δ functions in the distribution of relaxation times. At low temperatures the fast component shows traces of nonexponential decay qualitatively similar to Fig. 3. The low-frequency process is strictly exponential.

The experimental results were fitted by Eq. (1) and resulted in all cases in fits of excellent quality except for processes connected with the nematic-isotropic phase transition. However, in some cases f_0 could not be measured in a sufficiently large temperature interval to allow a unique determination of the three parameters C, A, and T_0 in Eq. (1). I therefore fitted the results for pure CB5 by Eq. (1) and found $T_g - T_0 = 42$ K. I then assumed $T_g - T_0 = 42$ K to hold for all other systems too which allows an independent determination of T_0 by a specific-heat experiment. For pure CP4 T_g was determined by extrapolation since it was not possible to quench it into the vitreous state.

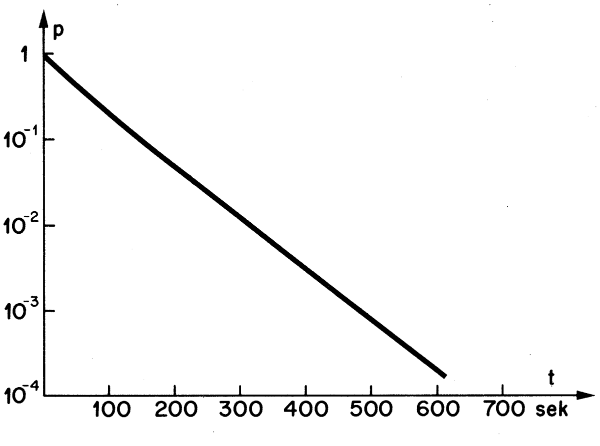

FIG. 3. Decay of polarization for CB5 at a temperature of 205 K. Except for a small sample-dependent faster component the decay is exponential.

TABLE I. Parameters of the fit of Eq. (1) to the experimental results (all concentrations are molar).

Molecule	Medium	C (Hz $K^{1/2}$)	A (K)	T_0 (K)
CB5	pure	6×10^8	1070	168
	20% CP4 in CB5	4×10^8	1070	173.2^a
	30% CP4 in CB5	4×10^8	1070	176^a
	50% CP4 in CB5	4×10^8	1070	181.8^a
	14% CT5 in CB5	5×10^8	1100	170^a
	21% CT5 in CB5	4×10^8	1100	171^a
CT5	14% CT5 in CB5	5×10^8	1450	170^a
	21% CT5 in CB5	3×10^8	1450	171^a
CP4	pure	4×10^7	1250	194.7^a
	50% CP4 in CB5	1.2×10^8	1250	181.8^a
	30% CP4 in CB5	1.2×10^8	1250	176^a
	20% CP4 in CB5	1.2×10^8	1250	173.3^a

[a] Values derived from specific-heat experiments.

The results of the fit are shown in Table I. As discussed above except for pure CB5 only A and C are free parameters. Surprisingly A and C show little or no variation across a concentration series. In other words in many cases dielectric relaxation frequencies can be directly predicted from specific-heat experiments and are a function of $T - T_g$ only. T_g determined by a specific-heat experiment samples all structural relaxation processes in the liquid. The close relation between dielectric relaxation and T_g indicates that the different relaxation processes scale with each other. For the viscosities η of polymers[14] it is found that $\eta(T)/\eta(T_g)$ is only a function of $T - T_g$ and is of the functional form of Eq. (1) with $T_g - T_0 \cong 52$ K and $A \cong 2070$ K.[15]

The Vogel-Fulcher law [Eq. (1)] is usually discussed in terms of free-volume arguments. A derivation of Eq. (1) based on a free-volume model has first been given by Cohen and Turnbull.[11] A recent review can be found in Ref. 12. The reorientation of a rigid elongated molecule requires free volume if the process is a single-particle process but not necessarily if it is a many-body or almost hydrodynamic process. I observe experimentally two relaxation processes for two molecules of different length in solution which shows that relaxation is a single-particle process and that the free-volume concept applies.

The nematic long-range order greatly simplifies the phenomenological description of relaxation in that for $\vec{E} \parallel \vec{n}$ jump reorientation processes only are of importance whereas rotational diffusion processes are dominant for $\vec{E} \perp \vec{n}$. Jump reorientation processes are usually described in terms of defect diffusion models[13] in which it is assumed that long-lived structural defects (e.g., vacancies) exist in the liquid which undergo Brownian motion. Relaxation at a site $\vec{x}$ exclusively occurs when a defect has arrived at $\vec{x}$ and is then instantaneous and complete. The model predicts a nonexponential polarization decay because the system becomes spatially inhomogeneous on the scale of the defect spacing. Also the model predicts a single relaxation process for mixtures. Both predictions are inconsistent with experiment. Agreement with experiment is obtained by assuming that the probability of relaxation upon arrival of a defect at a given site is small. If interdiffusion of defects is faster than polarization decay then the system stays spatially homogeneous at all times and an exponential decay results. Also the probability of relaxation depends on molecular size and two processes are predicted for a binary mixture.

Anderson[16] has pointed out that the concept of a structural defect as a quasipermanent entity is opposed to the classical free-volume concept in which holes are accidental fluctuations which can occur anywhere. The two concepts can be brought together by dividing up the total free volume into basically atomic-size quasipermanent defects and fractional free volume with size of a fraction of an atomic volume. In the present example the fractional free volume is a rate determining factor and classical free-volume concepts may be applied to the fractional free volume.

In the vicinity of the glass transition temperature the total relaxation amplitude $\epsilon_0 - \epsilon_\infty$ is virtually temperature independent. Together with the exponential polarization decay this means that the percolation type models in which solid or liquidlike regions exist with lifetimes of the order or longer than f_0^{-1} can be excluded. In fact the range of validity of the Vogel-Fulcher law extends below T_g determined from specific-heat experiments which means that T_g is completely determined by the Vogel-Fulcher law and time-scale arguments[17] and no new physical concepts have to be introduced.

In conclusion I have shown that nematic liquid crystals are a unique model system for the study of kinetic processes in the vicinity of the glass transition. Dielectric relaxation for $\vec{E} \parallel \vec{n}$ in a nematic is a well-defined microscopic process and is described by the Vogel-Fulcher law in a much wider temperature range than other microscopically less defined properties (e.g., viscosity in isotropic systems). I give evidence that a correct model for the Vogel-Fulcher law has to be based on a combination of a defect diffusion model and the statistical mechanics of fractional free volume (free volume of different than atomic size).

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Synchrotron X-Ray Diffraction Study of Silicon during Pulsed-Laser Annealing

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Time-resolved x-ray diffraction measurements of lattice strain in silicon during pulsed-laser annealing have been made with nanosecond resolution by using synchrotron radiation. Analyses of the strain in pure and boron-implanted silicon in terms of temperature indicate high temperatures and evidence for near-surface melting, in qualitative agreement with the melting model of laser annealing.

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Time-resolved x-ray diffraction measurements, with nanosecond resolution, have been carried out on silicon during pulsed-laser annealing, through the use of single pulses from the Cornell High Energy Synchrotron Source (CHESS). These real-time measurements represent the first nanosecond-resolution structural measurements to be performed with use of x rays, and further represent the first real-time measurements during pulsed-laser annealing that probe below the crystal surface. These measurements provide direct information on the time duration and depth distribution of near-surface lattice strains associated with laser annealing of silicon. When analyzed in terms of thermal expansion they provide the first determination of the lattice temperatures below the surface. The lattice temperature has been one of the central issues in an ongoing controversy[1] as to whether a "melting" or "plasma-fluid" model describes the lattice structure during the laser annealing process in semiconductors. The melting model[2] provides for surface melting (temperatures $\geqslant 1410\,^{\circ}\mathrm{C}$); whereas in the plasma model the lattice temperature is predicted to rise only a few hundred degrees.[3]

In this study, we have made use of the extended Bragg scattering intensity[4,5] that is found in the vicinity of Bragg reflections as a result of Bragg-like scattering from near-surface strains. The attributes of this scattering necessary for understanding the essential points of this work are shown in Fig. 1. The effects of a thermally induced strain gradient are shown for a pure silicon crystal and for a boron-implanted (laser-annealed) crystal in which the thermal strain is superposed on the static contraction caused by the substitutional boron. The present study draws on the results of previous studies of near-surface strain (see Refs. 4 and 5 for details of the analyses) and differs only in that the measure-