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Critical fluctuations and random-anisotropy glass transition in nematic elastomers

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We carry out a detailed deuterium nuclear magnetic resonance (NMR) study of local nematic ordering in polydomain nematic elastomers. This system has a close analogy to the random-anisotropy spin glass. We find that, in spite of the quadrupolar nematic symmetry in three dimensions requiring a first-order transition, the order parameter in the quenched "nematic glass" emerges via a continuous phase transition. In addition to this remarkable effect, by a careful analysis of the NMR line shape, we deduce that the local director fluctuations grow in a critical manner around the transition point. This could become an essential experimental evidence for the quenched disorder changing the order of discontinuous transition.

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I. INTRODUCTION

The debate over the nature of the spin-glass phases is still vibrant in the modern literature.[1–3] The key question is about the nature of the symmetry that is broken by the spin-glass transition. In the mean-field or continuum models, this is in fact the Parisi "replica symmetry."[4] Therefore, in the mean field, one expects and indeed finds a true phase transition even in nonzero field—the celebrated de Almeida-Thouless (AT) line.[5]

There has been relatively little study on how the quenched disorder influences the systems, whose pure versions undergo a first-order phase transition. Imry and Wortis[6] first showed that inhomogeneities may cause local variations of the transition temperature inside the sample. In some cases, there can be no phase coexistence at the transition and, therefore, no latent heat; such systems are expected to always exhibit a continuous transition. The influence of quenched impurities has been extensively studied by Cardy.[7] It was found that, depending on the specific values of parameters of the pure system, such as the latent heat and the surface tension, the disorder-affected phase transition is fluctuation driven and can either be first or second order. In both cases of spin-glass and quenched first-order systems, the experimental measurement of equilibrium transition characteristics is difficult and only few indirect results are available. Most of the studies, such as neutron spin-echo experiments,[8] only access dynamic quantities and correlation functions.

A physical system in which the sources of quenched disorder can be coarse grained to a weak random field is liquid crystalline elastomers.[9] Disorder is intrinsically present in all elastomers as a direct result of their crosslinking with typical separation between sources ~ 3 nm in our system. Once the polymer network is formed, the configuration of the crosslinks remains quenched and the underlying nematic[10] or smectic[11] phase transition takes place with their effect in the background. The nematic correlation length is ~ 10 nm. In this work, we carry out deuterium nuclear magnetic resonance (DNMR) experiments to measure the local nematic order parameter in the "polydomain" nematic elastomer system, that is, the equilibrium symmetry-broken state with the orientational texture analogous to the spin glass. Strictly, the nematic order parameter is a tensor with quadrupolar symmetry, arising from the averaging of axes ($\hat{\boldsymbol{u}}$) of rodlike molecular groups $Q_{ij}=\langle \hat{u}_i\hat{u}_j-\frac{1}{3}\delta_{ij}\rangle=S(T)[n_in_j-\frac{1}{3}\delta_{ij}]$ in three dimensions. In the system with quenched disorder, one must distinguish between the time and the ensemble averaging since the principal axis $\boldsymbol{n}$ (the local nematic director) randomly varies in space. Nuclear magnetic resonance (NMR) is the only technique we know that can access the local value of the scalar order parameter $S(T)$ in spite of the powder averaging over the $\boldsymbol{n}(\boldsymbol{x})$ orientations.[12]

There have been many measurements of the nematic order parameter in aligned nematic elastomers, in which case, a variety of experimental techniques are available.[13] The alignment in these materials can be installed in two ways: (1) by applying a uniaxial field (usually mechanical stress) to an original polydomain texture and passing through the polydomain-monodomain transition;[14] or (2) by crosslinking the network in a state that is uniformly aligned by a mechanical, electric, or surface field.[15,16] In both cases, one does not expect a true phase transition, and indeed finds the varying degrees of supercritical crossover and the "paranematic" order remaining above the transition (see Refs. 17 and 18 and references therein).

In contrast, we deliberately devise a system that is as close as possible to the equilibrium "nematic glass" state. Apart from crosslinking in a fully isotropic state, carefully avoiding any stray aligning influences, we also choose the type of crosslinking that is creating as weak as possible orientational effect. There are two key results we report here. First, after careful analysis of the DNMR signal, we are able to obtain the temperature dependence of the equilibrium local order parameter $S(T)$, which has a clear critical behavior $S\propto|T-T_c|^{0.22}$ according to our best fit. In addition, we found that the NMR linewidth (which reflects the local mobility) has a very clear λ-shaped peak at the transition point T_c. We

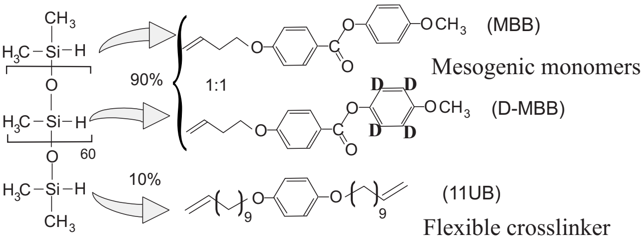

FIG. 1. The components of polysiloxane nematic elastomer.

associate this peak with the critical growth of correlation length of fluctuations on both sides of the transition, which further supports the conclusion about the continuum transition from the isotropic into the nematic glass phase.

II. EXPERIMENT

All starting materials and samples of side chain siloxane liquid crystalline elastomers were prepared in the Cavendish Laboratory, following the hydrosilation procedures developed by Finkelmann.[19] The polymethylhydrosiloxane backbone with approximately 60 Si-H units per chain was obtained from ACROS Chemicals. The pendant mesogenic groups were 4′-methoxyphenyl-4-(1-buteneoxy) benzoate (MBB), as illustrated in Fig. 1. For good quality DNMR signal, we used 50% of the MBB units with the fully deuterated outer benzene ring, symmetrically to preserve the molecular symmetry. All networks were chemically crosslinked with the flexible difunctional crosslinking group 1, 4 di(11-undeceneoxy)benzene (11UB) (also shown in Fig. 1). The crosslinking density was calculated to be 10 mol % of the reacting bonds in the siloxane backbone.

Our aim is to obtain a true polydomain state of the nematic phase, which can only be generated when the crosslinking is fully random and no internal stresses of entanglements are frozen into the resulting network. For this, we have completed the crosslinking reaction in the highly swollen (in toluene) isotropic phase of the polymer. After the reaction, the samples were slowly deswollen so that the dry elastomer network will not end up overentangled.

The NMR data were collected on a BRUKER AVANCE III 300 MHz spectrometer using the solid echo sequence with a $\pi/2$ pulse width of 5 μs and a pulse separation of 20 μs. Measurements were performed at 1 K intervals on cooling from well within the isotropic phase. A cooling rate of 1 K/min and a stabilization delay of 10 min at each temperature were used. 4000 scans (with a recycle delay of 500 ms) were collected at each temperature.

III. DEUTERIUM NMR ANALYSIS

The spin Hamiltonian for deuterium in a high magnetic field is dominated by the Zeeman and quadrupolar interactions.[20] A carbon-bound deuterium in the fast motion limit generates a doublet spectra with an orientationally dependent splitting w (Ref. 20) proportional to the time-averaged quadrupolar coupling constant $\bar{\nu}_Q$, which has a rigid limit of $\nu_Q \approx 185$ kHz for sp^2 bonds.[21] In a three-dimensional polydomain sample, the contributions from all orientations generate a “Pake pattern,”[22] which allows a direct measurement of the time-averaged $\bar{\nu}_Q$ that is directly proportional to the nematic order parameter $S(T)$ (Ref. 23).

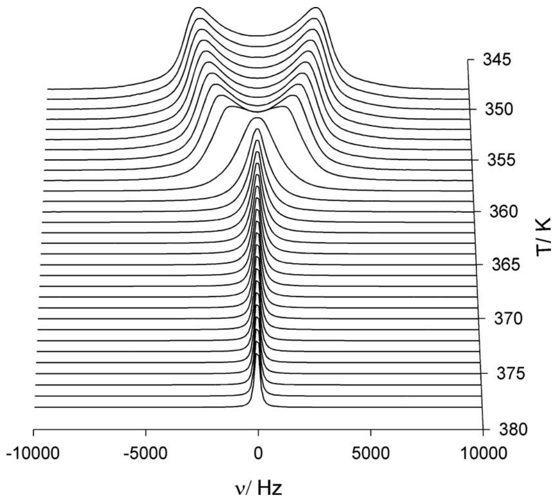

FIG. 2. Composite representation of Pake spectra evolution on cooling the system from the isotropic state. Note the absence of phase coexistence around the transition point.

The doublet and powder spectra cited above are formed by pairs of structured lines with a structure determined by the transverse relaxation occurring in the system.[24] Two limiting cases, corresponding to small and large correlation times τ_c of the fluctuating quadrupolar interaction $\tau_c \nu_Q \ll 1/(2\pi)$ and $\tau_c \nu_Q \gg 1/(2\pi)$, give rise to well-known line structures, respectively, of Lorentzian and Gaussian forms.[20,24] Figure 2 gives the composite view of the sequence of spectra on cooling from the isotropic phase, showing the widening of the central peak, and then the emergence of the nematic splitting. It is important to note the absence of any coexistence, which is a necessary feature of a first-order transition and has been observed in previous NMR experiments on nematic elastomers.[17,18]

The high-temperature isotropic phase has a narrow line that closely matches the Lorentzian form, as expected in a classical process of fast rotational diffusion. In the nematic phase, molecular motion slows down and the correlation time of orientational motion increases significantly. Measurements of rotational viscosity γ_1 (Ref. 25), which is proportional to the orientational correlation time,[26] show an increase of over 4 orders of magnitude in elastomers, relative to the low-molecular weight nematics. This suggests that the correlation time of rodlike groups becomes close to the characteristic NMR time $(2\pi\nu_Q)^{-1}$ as soon as the nematic mean field sets in. Indeed we find that a Gaussian form describes the line structure better in the nematic phase.

In order to test the fitting of the NMR spectra across the whole temperature range, we have applied a model for the line structure, allowing it to vary between the Lorentzian and Gaussian forms through a variable exponent $\alpha(T)$ that can take values in between one and two. The line structure is obtained by numerically Fourier transforming $\exp[-(t\Delta\omega)^{\alpha}]$. Figure 3 shows the results for the fitted empirical exponent $\alpha(T)$. It confirms the expectation of the crossover between

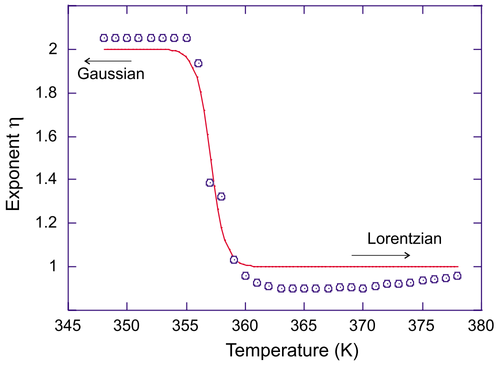

FIG. 3. (Color online) The values of exponent α obtained from a three-parameter fit (○). The values of $\alpha=1$ and 2 are evidently approached far from the transition point. The solid line is the best fit by the crossover function, which we then use as the fixed value for $\alpha(T)$.

the Lorentzian regime in the high-temperature isotropic phase and the Gaussian regime in the nematic phase. To reduce the freedom of multiparameter fitting, we choose a fixed form to the variable exponent $\alpha(T)$ so that it describes the fundamental crossover between $\alpha=1$ and 2, as shown in the plot $\alpha(T)=1.5-0.5\tanh[(T-T^{*})/m]$. The closest fit is achieved with $T^{*}=357.1$ K and the width of temperature crossover $m=1.62$ K. Note that (as we shall see below) the actual critical point of the transition is about a degree higher $T_c=358$ K. This discrepancy is natural since the crossover from the diffusive to the slow-relaxation regime occurs only when the local nematic mean field grows sufficiently strong to slow down the molecular rotation rate. With this choice of $\alpha(T)$, we only have two fitting parameters $\bar{\nu}_Q$ and $\Delta\omega$, which are obtained as functions of temperature. The quality of line fits is very good in the relevant sections of all spectra, as in fact shown by error bars in Fig. 4.

IV. NEMATIC-ISOTROPIC TRANSITION

Having established the rules of analysis of our DNMR signal, we then fitted the Pake pattern to all the spectra. The first fitting parameter $\bar{\nu}_Q$, gives the magnitude of the nematic order $S(T)$. In this case, it is defined as the time average of orientational motion of individual rodlike units. There is an effective averaging of the output signal over the sample volume, but in the NMR experiment, it takes place after the field of the tensor order parameter $Q_{ij}(\mathbf{r})$ is established at every point at each temperature. In this sense, our analysis is based on the assumption[10] that the scalar value of S is uniform throughout the polydomain director texture in the sample. This assumption has been strongly supported by our measurements. If the magnitude of the nematic order S varied in space (e.g., across domain boundaries or in disclination cores), then our clean double-peak Pake pattern would not be observed deep in the nematic phase. This alone is a very important observation, making a stark contrast with the classical Schlieren texture of a disclination-coarsening nematic liquid having heterogeneous order-parameter field.

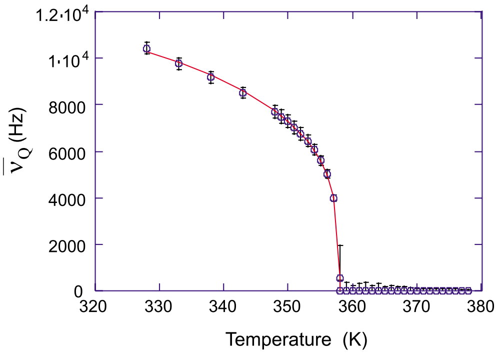

FIG. 4. (Color online) Plot of the average quadrupolar coupling constant $\bar{\nu}_Q$, obtained from a two-parameter fit of NMR spectra.

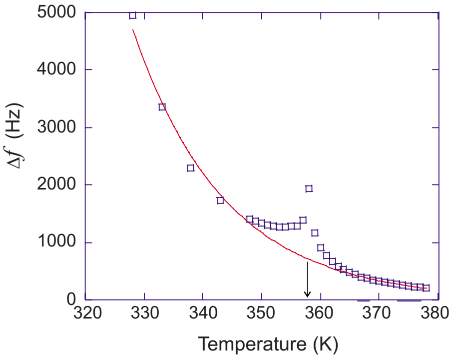

FIG. 5. (Color online) Plot of the frequency width $\Delta f \equiv \Delta\omega/2\pi$, obtained from a two-parameter fit of NMR spectra. The solid line is a base line fit for a polymer approaching its glass transition.

Figure 4 shows the fitted values of $\bar{\nu}_Q$ against temperature. It is clear, as it was visually apparent from the shape of NMR peaks in Fig. 2, that the nematic order arises in a critical fashion. The plot shows the very small errors of the rather stringent fitting of each spectrum. The fit to the order-parameter data suggests the variation $S\propto|T-T_c|^{0.22}$, with the critical point $T_c=358.01$ K. Importantly, the line-shape fitting gives values $S=0$ above T_c unambiguously, indicating that no supercritical or paranematic effects take place in our system. Due to our preparation, the system we study is close to true criticality.

The second evidence for the critical transition is found in the behavior of our second fitting parameter, the distribution width $\Delta\omega$, which is proportional to the correlation time of orientational motion of mesogenic groups. Figure 5 shows the increase in $\Delta\omega$ on cooling the elastomer network. There are clearly two separate effects; the overall increase, representing the slowing down of molecular motion on approaching the structural glass transition in a polymer network, and the pronounced peak around the nematic transition. The solid line in Fig. 5 shows the fit of the base line to the Vogel-Fulcher exponential $\Delta\omega\propto\exp[A/(T-T_\beta)]$, with $A=3200$ and $T_\beta=120$ K. It is not unexpected to find the cut-off temperature T_β to be so much lower than the ordinary polymer glass transition $T_g\approx300$ K in our material. The latter represents the α relaxation or freezing of the polymer backbone motion. Our experiment probes the motion of side groups, that is, β or even γ relaxation, which freezes at much lower temperatures. Importantly, this base line increase is continuous across both the Lorentzian and the Gaussian regimes on both sides of the nematic transition.

The characteristic peak of $\Delta\omega$ peak around the transition has been analyzed, with the base line polymer dynamics taken out. On both sides of T_c, the peak can be fitted by power law $|T-T_c|^{-b}$, using the value $T_c=358.01$ K from the analysis in Fig. 4 and returning the same exponent $b=0.5$ on both sides of T_c. On the one hand, our accuracy in resolving the temperature near the critical point, as well as the errors in the NMR spectra fitting, do not permit us to make a definite conclusion on the values of critical exponents of this transition (the same applies to the $|T-T_c|^{0.22}$ fitting of the order parameter). On the other hand, our main point—that the nematic-isotropic transition in this system has become continuous and fluctuation driven—seems well justified. Regarding the peak in $\Delta\omega(T)$, we suggest that this behavior represents the growth of correlations of critical fluctuations near the transition point. As the size of correlated nematic fluctuations increases near the critical point $\xi \propto |T-T_c|^{-\nu}$, the time for (collective) reorientation of rodlike units within this volume increases accordingly. Curiously, the provisional exponent we obtained from the best fit is very close to the mean field $\nu=1/2$, which connects with the earlier discussion of the mean-field approximation and the AT line.

V. SUMMARY

A detailed study of DNMR in polydomain nematic elastomers suggests that the structure of this state is analogous to random-anisotropy spin glass. The local order parameter was found to be homogeneous throughout the system in spite of the director correlations being short range. Our analysis suggests that the transition from the isotropic phase is of continuous critical nature. Since this transition (quadrupolar order with weak quenched random-anisotropy field) has not been studied with renormalization group, we cannot assign any particular significance to the critical exponents. However, the fact that we see an apparent critical behavior in a system that undergoes a first-order transition in its pure state is of remarkable importance. This could be the first experimental study that confirms the prediction of such an effect. Secondary findings of this work, on the continuous change between the Lorentzian and Gaussian NMR line shape and on the continuous slowing down of β relaxation of polymer side groups on cooling the elastomer, are also of great interest in their respective fields.

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