Dynamics at the Nematic-Isotropic Phase Transition in Aerosil Dispersed Liquid Crystal

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Photopyroelectric high resolution ac calorimetry has been used to study the nematic-isotropic phase transition in octylcyanobiphenyl liquid crystal incorporating an aerosil soft gel. We have found that the sample is not in thermodynamic equilibrium in the two phase coexistence region, as shown by the frequency dependence of the double peak in the specific heat and by its thermal hysteresis. The results suggest that the dynamics of the system becomes slower as it is cooled over the transition temperature. An explanation for the formation of a nematic glassy phase in liquid crystals with quenched disorder based on the similarity of these results with the ones obtained in other disordered materials is attempted.

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It is well known that quenched random disorder (QRD), which is present in many real systems, has a strong impact on phase transitions. After the argument by Larkin *et al.* [1], which shows that long range translation order cannot be present in 3D systems with QRD, the essential ingredients for the physical description of disordered systems with discrete symmetry have been included in the random field Ising model (RFIM). This has stimulated an extensive research activity on diluted antiferromagnets in external fields (DAFF), which seemed to be prototype RFIM systems. It is now clear [2], however, that, if DAFFs are cooled in the low temperature phase with no applied field, quasi-long-range order is established but the system is not in thermodynamic equilibrium. The slow dynamics has been attributed to the limitations imposed by the static random field induced fluctuations over the dynamic thermal ones, which leads to an activated dynamics and to a divergence of the relaxation time. Similar conclusions have been obtained for superconductors with QRD [3,4] and superfluid helium in restricted geometries [5].

These concepts have recently been extended beyond second order phase transitions and, in particular, to vitrification and crystallization of liquids [6]. It has been proposed that in any liquid two ordering mechanisms compete: density ordering, which leads to crystallization, and a bond ordering, due to the anisotropy of the intermolecular potential, which favors local symmetry. This means that, upon cooling, islands of locally favored structures, with long but finite relaxation times, are randomly distributed in a sea of a normal liquid. This is equivalent to a symmetry breaking random field against density ordering and the resulting phase, in analogy with DAFF systems, is called Griffiths-like phase [7]. An important role in deciding whether the system undergoes crystallization or vitrification is played by the energy barriers between the local favored structures and the equilibrium low temperature phase [8]. If these barriers are sufficiently high, then the relaxation time increases and the system is frozen in a glassy state.

The experimental counterparts of these ideas are the recent results showing the role of structural heterogeneity, arising from the interplay between the orientational and translational degree of freedom, in the relaxation dynamics of liquid crystals and supercooled liquids [9].

Liquid crystals in low density thixotropic gels made of quartz nanoparticles (aerosil), hereafter called filled nematic (FN), have recently emerged as promising systems to investigate QRD [10]. These systems exhibit a rich variety of first and second order phase transitions, and the disorder strength can be easily tuned to very low values adjusting the aerosil concentration. It has been recently shown that QRD has a striking effect on the weakly first order nematic-isotropic (NI) transition. A double peak structure of the specific heat c_p [10–12] in the two phase coexistence region, associated with the NI transition, has been recently found in FN, which indicates that the transition takes place in two steps. It has been proposed that this behavior is due to the variation of the disorder strength in the coexistence region which causes a crossover from an initial random dilution (RD) regime, in which the coupling with the aerosil is weak, to a random field (RF) one, in which the strength of the coupling increases and induces distortion of the director field. Moreover, it is argued that, since this mechanism is not related to any specific liquid crystal property, it could be universal for any first order transition in the presence of QRD.

Another characteristic of FN is that, contrary to what happens in DAFF, they do not seem to suffer the problems arising from slow dynamics at phase transitions, as demonstrated by extensive studies at the smectic*A*-nematic one [13]. Turbidity measurements and simulations [14,15], on the other hand, have shown that memory effects and glass-like behavior are present in the nematic phase of FN. This last feature resembles that of DAFF systems and has been attributed to pinned topological defects.

One may ask, at this point, if the similarities among the experimental results obtained in different systems (DAFF, superconductors, and confined liquid helium) and the role of structural heterogeneity envisaged in the theoretical description of glass transition can help in understanding the NI transition in FN. This unified description of the physics of different systems with QRD would give some

indications on a possible universal behavior at the weakly first order phase transitions in disordered materials. A consequence of this could be the presence of slow dynamics at the NI transition in FN, an aspect which has not been investigated in Ref. [11]. In this view the onset of a sort of a nematic Bragg phase below the NI transition follows in a very natural way.

In this Letter we investigate the dynamics of the NI transition in FN using an experimental setup which allows high resolution structural and thermal characterization of the samples. The two-steps nature of the transition is confirmed, as shown by the two peaks in c_p in the coexistence region. This double feature is frequency dependent and shows hysteresis between cooling and heating runs. The frequency dependence of the two peaks is not the same, and this is probably related to the crossover mentioned above between RD and RF with decreasing temperature. The results show that the system is not in thermodynamic equilibrium and a qualitative description of the observed behavior in analogy with other disordered materials is attempted.

The FN we have used consists of a soft gel of hydrophilic hydrogen bonded aerosil particles of an average diameter of 7 nm dispersed in octylcyanobiphenyl (8CB) with a concentration of 0.05 g/cm^3. The sample was 30 μm thick. Data have been obtained with the photopyroelectric-based ac calorimetric setup described in Ref. [16] which simultaneously allows the determination of the sample thermal parameters (specific heat, thermal conductivity, and thermal diffusivity) and optical investigation of the sample texture during each temperature scan (1 mK/ min). As in any ac calorimetric measurement, only the qualitative behavior of the effective thermal parameters in the coexistence region can be obtained [17]. Nevertheless, the specific heat data reported in Fig. 1

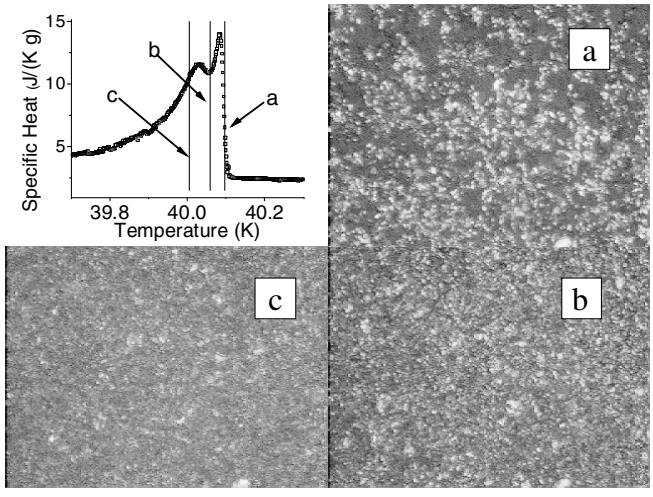

FIG. 1. The 8CB FN specific heat vs temperature, obtained on cooling, with polarizing microscopy images corresponding to the temperatures indicated in the graph.

clearly show that the transition takes place in two steps. For any c_p value, we have recorded the corresponding polarizing microscopy image, and three of them have been reported in Fig. 1. When cooling, the onset of the coexistence region and therefore the nucleation of nematic domains [Fig. 1(a)] correspond to the steep increase in c_p. As the temperature is decreased across the high temperature peak (HTP) region, the domains grow in number and the existing ones are distorted, as shown in Fig. 1(b), to form a coarse grain (CG) texture. In the low temperature peak (LTP) region, new nematic domains continue to nucleate and the existing ones are broken into smaller ones, giving rise to a transition from a CG to a fine grain (FG) texture, as shown in Fig. 1(c).

Although the modulation frequency of the heating source in our experiment is much larger than the one used in Ref. [10] ($f \approx 30$ mHz), the double peak feature in c_p is present in both cases. Moreover, the image sequence is consistent with the proposed crossover from RD to RF. The CG texture, in fact, implies that the coupling with the aerosil is weak (RD) and rather large domains, much larger than the average pore size, can therefore nucleate. The transition from CG to FG, on the other hand, can be explained assuming that the increase of the disorder strength and of the elastic distortion imposed by RF effects break existing domains into smaller ones and reduce the size of new ones nucleating in this region. It should be noted that this justification of the LTP is different from the one given in Ref. [11], where it is stated that the grain size of the domains does not change as the system evolves over the LTP. In any case, this is the temperature region in which the presence of topological defects, pinned to disorder sites [18], becomes relevant and the main characteristic of a glassy phase is established.

Figure 2 shows c_p vs T data upon heating and cooling where hysteretic behavior is clearly evident. It must be pointed out that the two curves in Fig. 2 have been shifted so that the onset of the two phase coexistence region (approximately 220 mK wide) on the isotropic side coincides. This was done to eliminate the temperature downshift associated with sample contamination in subsequent runs, which may have overshadowed any hysteresis in the HTP. The important issue, evident in the results, is the hysteresis in the relative temperature position of the two peaks, as well as in their magnitude. The LTP, in fact, is, upon heating, about 20 mK closer to the HTP than upon cooling. This hysteresis is also responsible for the difference in the peak values of c_p.

Hysteresis is usually found at first order phase transitions and indicates that the system is not in thermodynamic equilibrium in the transition temperature region. Its origin is in the energy barrier between metastable states and the equilibrium one, which, in some materials, increases so much with decreasing temperature, to induce the formation of a glassy phase. Such an increase is reflected in the

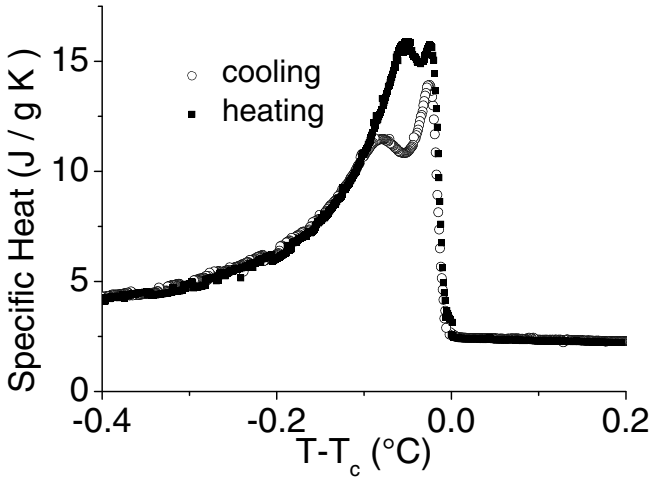

FIG. 2. The 8CB FN specific heat vs temperature at 19 Hz. The curves have been horizontally shifted to align the onset of the coexistence region on the isotropic side.

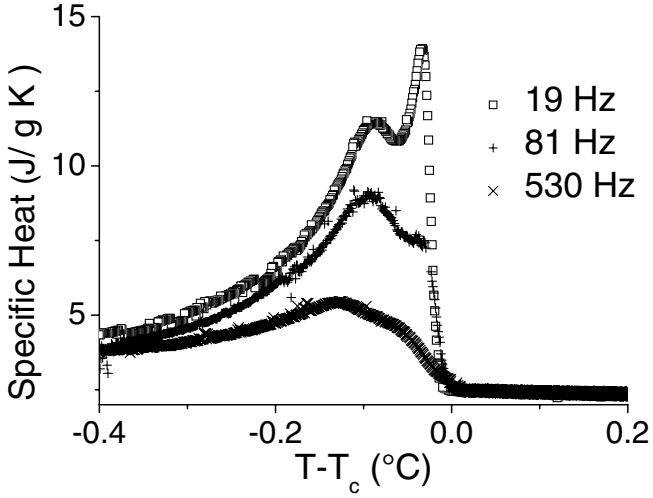

FIG. 3. The 8CB FN specific heat vs temperature at different frequencies, all obtained on cooling. The curves have been horizontally shifted to align the onset of the coexistence region on the isotropic side.

increase of the relaxation time and therefore of the hysteresis effect. The results in Fig. 2 show that the hysteresis of the LTP is larger than the HTP one. The data can be interpreted as due to an increase of the relaxation time, with decreasing temperature with the sample becoming slower when the disorder strength increases.

Another distinctive feature of first order transitions in pure materials is a frequency dependent c_p in ac calorimetry [19]. It has been attributed to the partial phase conversion in one heating cycle in the two phase coexistence region. This is due to the slow dynamics of the system at the transition and should not occur in the zero frequency limit. The presence of QRD can produce two competing effects: on one side it decreases the correlation length, with a decrease of the relaxation time τ, while, on the other hand, it can enhance energy barriers between domains nucleating at slightly different temperatures, which, in turn, can increase τ. The relevance of the latter effect becomes progressively more important with decreasing temperature when the disclination lines, associated with the domain walls, are pinned to defects and therefore RF effects come into play, while the first prevails when the disorder strength is small and therefore the system is in a regime of RD. At any temperature the dynamics depends on which one of these two effects dominates in the coexistence region and, if the disorder strength changes with temperature as in FN, a crossover between the two regimes can occur. We should therefore expect a different frequency dependence of the two peaks.

The results reported in Fig. 3 show that a frequency dependence of the two peaks in c_p is, indeed, present and that it is stronger in the HTP than in the LTP. These data, combined with the increase of the relaxation time with decreasing temperature deduced from Fig. 2, lead to the conclusion that the dynamics of the LTP is slower than the HTP one. The experimental setup we have used in the present work does not allow measurements over a frequency range wider than the one shown in Fig. 3. Because of this limitation, it would not be meaningful to attempt any more quantitative analysis of the vs frequency observed trend. However, the c_p frequency dependence confirms that the system is out of equilibrium.

The results can be explained as follows. The increase of the disorder strength in the LTP region causes the CG to FG transition. In the FG state any further rearrangement of the director inside the domains is opposed by the constraints due to the pinning of topological defects imposed by QRD [18]. This results in an increase of the energy barriers among metastable states and the equilibrium one, in an increase of the relaxation time τ. The system can therefore eventually fall into a kind of a Bragg nematic glass phase as suggested by the results reported in Ref. [20]. This hypothesis is consistent with what has recently been found in Monte Carlo simulation [18] where it has been shown that the origin of memory effects in the nematic phase of FN is the pinning of very long disclination lines. It should be noted that our interpretation of the results is very similar to the ones used to explain the glassy properties of the antiferromagnetic phase in DAFF and the Bragg phase in superconductors.

The results we have obtained are the experimental evidence of the common features between what has been experimentally found and theoretically predicted in different samples and transitions. The nucleation of nematic domains in an isotropic sea in the coexistence region, and the subsequent structural heterogeneity, closely resembles the locally favored structures invoked in Ref. [16] and therefore a Griffiths-like phase. In this respect, because of the pinning of the topological defects in the LTP region,

QRD can be seen as an amplification factor for the energy barriers among nucleated domains which can eventually lead to the formation of a glassy phase. Fortunately, the increase of the disorder strength in the coexistence region with decreasing temperature and the crossover from RD to RF greatly helps in widening the temperature range where the Griffiths-like phase can exist and gives a unique experimental opportunity to look at the evolution of the dynamic behavior associated with it.

We believe, on the basis of the description of our experimental results, that in all cases where QRD is strong enough and pinning of disclination lines in FN, domain walls in DAFF, and vortex lines in superconductors and superfluid helium become relevant, an increase of the energy barriers among metastable states and the equilibrium one occurs, therefore leading to a low temperature glassy phase.

The situation seems to be completely different at the second order NA phase transition in FN [13], in which no hysteresis and frequency dependence has been found in x rays and calorimetric measurements. This could be somehow surprising if one considers that this is supposed to be a transition between nematic and smectic Bragg glass phases. A possible explanation could be the freezing of the distribution of topological defects in the nematic phase, which is not significantly altered by the appearance of the smectic order. This accounts for the proposed decoupling of the smectic and nematic order parameter which drives the transition toward the 3D XY universality class but could have a little effect on the experimentally accessible dynamics of the system. This is probably much slower than the one at the NI transition, where the glassy nematic phase is formed from an isotropic liquid.

Regarding the proposed universality of the double peak structure of c_p, we believe that this feature is strictly related to the existence of the crossover from RD to RF behavior. This is, in fact, what comes out from the experimental data in 8CB FN in which the concentration of aerosil is varied. At large concentrations, nematic domains nucleating at any temperature in the coexistence region experience RF effects, and there is a single broadened peak in c_p. At very low concentrations, on the other hand, there is again a single peak in c_p which is, in this case, weakly affected by rounding if compared to pure materials. It should be noted, moreover, that the crossover from RD to RF does not depend on the aerosil concentration only, but it is also material dependent. It has been shown, in fact, that if the LC becomes stiffer, then the crossover takes place at a larger concentration [12]. This is, of course, a general conclusion and does not apply to LC only.

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