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Viscosity peaks at the cholesteric-isotropic phase transitions

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In this work, the effective viscosity of the cholesteryl myristate and cholesteryl nonanoate liquid crystals is studied as a function of temperature at the region of their cholesteric-to-isotropic phase transition, where blue phases are found. Using a change of scale it is shown that the viscosity peaks that characterize these phase transitions are shape invariant, which suggests that large-scale fluctuations on the two-point correlation function give an important contribution to the observed viscosity. The consequences of this fact are investigated and, from the experimental data, the critical exponents associated with the diverging two-point correlation function are calculated. The results found for both compounds are essentially the same, being also in good agreement with the known values of the corresponding critical exponents of nematic-isotropic phase transition.

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I. INTRODUCTION

During the last years, some experimental data [1–3] have revealed that the effective viscosity measured along the nematic-isotropic phase transition of a sample submitted to free-fluid-flow conditions (i.e., without an externally induced order) presents abrupt changes. A typical example is shown in Fig. 1, where viscosity data of a MBBA [N-(p-methoxybenzylidene)-p-butylaniline] sample is used to illustrate this phenomenon. To understand the origin of these changes it is enough to consider that after the phase transition new conditions for the transport of momentum between adjacent shear planes are found and, consequently, viscosity changes must be observed. Using this sound argument and the conjecture that the effective viscosity observed on a nematic liquid crystal sample submitted to free-flow conditions would correspond to a minimum at given conditions, Jadzyn and Czechowski (JC) [2,3] have suggested an explanation for changes in viscosity like those observed in Fig. 1. Under high-shear-rate conditions, the peak observed in Fig. 1 would result from a change from the viscosity of the isotropic phase (η_{iso}) to the smallest Miesowicz's coefficient, η_2, of the nematic phase. Figure 1 also displays the Gähwiller [4] measurements of the orientated viscosities of the MBBA. For this compound, comparison of these experimental data seems to confirm the above consequence of the JC assumption. During the nematic-isotropic phase transition, the effective viscosity of a free-flow sample jumps from the isotropic viscosity to the value of the viscosity given by Miesowicz's η_2 coefficient, causing a peak in the measured effective viscosity. The physical origin of this conjecture is easily understandable: as η_2 describes the viscosity of a nematic sample in which the director is aligned along the fluid flow direction, this phenomenon arises from the orientation assumed by the director due to the fluid flow gradients and, as is largely known, it must correspond to the configuration in which the director assumes, at each point, the flow alignment angle [5]. However, as this angle is only attained at high shear rates, the JC conjecture must have an asymptotic character; only at such a limit would the effective viscosity actually arrive at η_2. Consequently, if we start from low shear rates, a plot of the effective viscosity as a function of the shear rate would reveal how the viscosity approaches such a limit.

Nevertheless, a more complex and interesting situation is exhibited by certain cholesteric materials (N^*), which are characterized by the nonalignment of the molecular axis that exhibits a helical twisted structure, with a finite helical pitch. For some of these compounds a direct passage from the isotropic (I) phase to N^* phase is not observed, but a concentrated sequence of blue phases (BP's) with a very high viscosity [6–8] is found in the narrow interval containing this phase transition. The richness of this situation encourages research on the connections between the BP's viscosity and such a succession of phase transitions. Here, at least two aspects of this phenomenon will be detached. First, all these transitions are first-order phase transitions presenting a latent heat that puts them in the class of phase transitions known as weak first-order phase transitions [9,10]. Second, the complete transition from the cholesteric to the isotropic phase, in

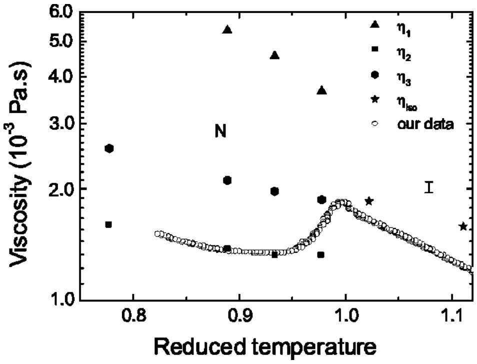

FIG. 1. MBBA viscosity as a function of the reduced temperature. The solid line represents the effective viscosity measured on a nonoriented sample. The dots represent the measurements for the viscosity of the orientated sample [4]. According to these data at the phase transition the viscosity jumps from the isotropic viscosity, at the isotropic phase, and assumes the value of the η_2 Miesowicz's coefficient, at the nematic phase.

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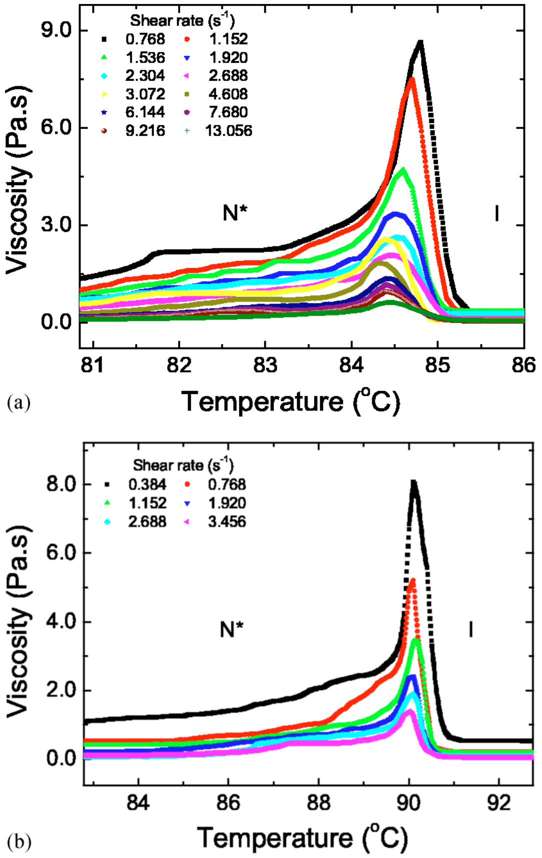

FIG. 2. (Color online) The non-Newtonian viscosity behavior of the myristrate and nonanoate samples when submitted to different shear rates. At both samples the temperature ranges stepwisely from the isotropic to the cholesteric phase and the peak corresponds to the isotropic-cholesteric phase transition. These experimental data reveal the high non-Newtonian character of these viscosity peaks, indicating that as the shear ratio increases the viscosity peaks diminish.

the cholesteryl nonanoate (myristate), comprises a sequence of four (two) weak first-order phase transitions tightly compressed in a narrow temperature range, which is inferior to 1 °C [8,11]. From the first of these aspects follows the well-established fact that at the neighborhoods of a weak first-order phase transition, pretransitional effects, characterized by large fluctuations on the correlation length ξ, would be observed [9,10] [ξ diverges according to the rule given in Eq. (3), below]. Consequently, as the viscosity results from the transport of momentum between different shear planes, distant points will become correlated and viscosity peaks, characterizing such a phase transition, would be induced. The second point reinforces the presence of these fluctuations, widening the temperature interval in which they would be found. Hence, such peaks would have a structure completely different from those characterized by JC. That is, the observed viscosity would have a contribution determined by the fluctuations on the correlation length, which would, concomitantly, have a temperature interval enlarged by the set of quasicontinuum phase transitions occurring there. The investigation of the simultaneous occurrence of these phenomena is the main aim of this work. The structure of these viscosity peaks will be studied, and it will be shown that, at least along the shear rate interval that we have investigated, the region presenting scale invariance (characterizing a critical behavior) is broadened along an unusual temperature interval. So this result is enough to lead us to assert that at this region the observed viscosity must have an important contribution coming from the fluctuations in the correlation length that accompany the sequence of weak first-order phase transitions.

To obtain the experimental data the following procedure has been adopted. While the shear rate was maintained constant, the temperature of samples of cholesteryl myristate and cholesteryl nonanoate, now on named myristate and nonanoate, has been step wisely changed from the isotropic phase to the N^* phase. After attaining the N^* phase, another value of the shear rate was chosen and, starting again from the I phase, a new sequence of viscosity measurements was performed. The thermotropic samples, investigated in this work, were purchased from the Aldrich Chemical Company Ltda. The myristate and nonanoate compounds were purified twice by recrystallization from ethanol. MBBA was used as obtained. The N^*-I and nematic (N)-I transition temperatures were determined by a polarized-light microscope coupled to a charge-coupled-device (CCD) digital camera and equipped with a hot stage (HS1) that furnishes an accuracy of 0.01 K. Viscosity measurements were determined by means of a Brookfield Cone/Plate rheometer model LVDV-III, calibrated with standard oil of known viscosity [12]. The sample temperature was controlled by a Heto circulating temperature bath, stable within 0.01 K. A rate of ~ 8 mK s^{-1} was used during the experiments. The results of these measurements are shown in Figs. 1 and 2, respectively.

II. SCALE INVARIANCE OF THE CHOLESTERIC-ISOTROPIC PHASE TRANSITION PEAKS

In Fig. 2 details of the N^*-I phase transition regions are detached. The first fundamental difference between these data and the corresponding ones of the MBBA, presented in Fig. 1, is that soon after the phase transition peak, at the N^* phase, the effective viscosity is not smaller than the viscosity observed in the I phase before the beginning of the phase transition. Indeed, it does not matter how intense the shear rate is; for both compounds, the viscosity of the N^* phase is always greater than the viscosity of the I phase. Of course, this is in contradiction with what is known about the behavior of the usual nematic-isotropic phase transitions; when coming from the isotropic phase and entering in a nematic phase the coefficient η_3 would be a "continuation" of the isotropic viscosity and, at least just after the transition, it would be expected to find $\eta_2 < \eta_3$. Probably, the nonobservation of a viscosity decrease is due to the fact that for cholesterics a global uniform orientation (the essence of the concept of Miesowicz's coefficients) is senseless and, at least as long as the shear rate does not destroy the cholesteric helix axis, the above limit cannot be η_2.

Another intriguing aspect of Fig. 2 is that the height of the peaks seems to be very sensible to the value of the shear rate; as the shear rate increases, the height of the peaks diminishes. If the JC conjecture can be applicable to the N^*-I phase

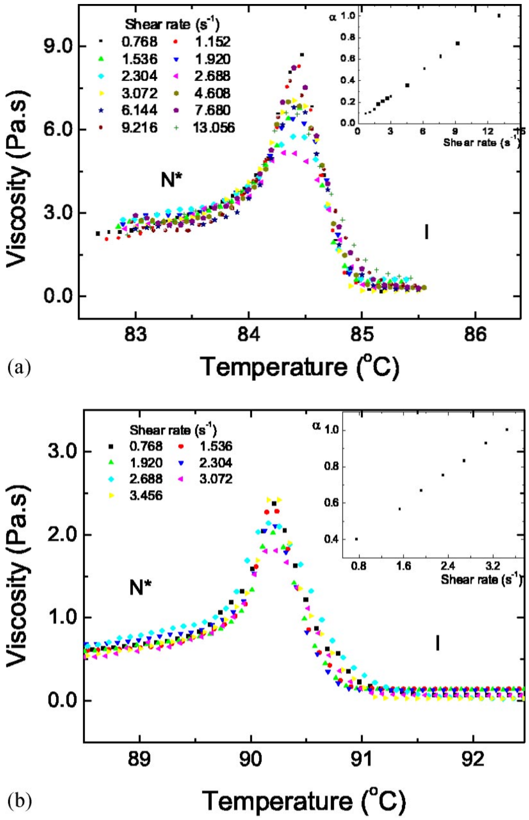

FIG. 3. (Color online) Results obtained with the rescaling of the experimental data of the myristate and nonanoate peaks at the cholesteric-isotropic phase transition. The original data points, which have been put on detailed in Fig. 2, have been rescaled in such a way that the distance between the distance curves, defined in Eq. (1), become the shortest. The results obtained indicate that, save a multiplicative number, all these curves have the same singular behavior. This is a strong signal that these peaks have an important contribution coming from the unbounded fluctuations that characterize the critical behavior of the N^*-I phase transitions.

transition of these compounds, there would be a minimum gap for these peaks, which would correspond to the minimum jump in the values of the viscosity during that phase transition. The data observed in these figures do not reveal the existence of such a minimum gap, indicating that the shear rate used in this experiment is not enough to arrive at such an asymptotic region. In order to look for a rule connecting the different shear rates and the corresponding viscosity intensity observed in these peaks, the data points of the N^*-I phase transition region have been submitted to a change of scale and the results are exhibited in Fig. 3, where an important aspect of these peaks is revealed; their shape becomes invariant. That is, along the N^*-I phase transition region, each equal shear rate viscosity curve has been multiplied by a number α, chosen in such a way that the "distance"

$$\Delta = \sum_{j=1}^{N} [\alpha v^i(j) - v^s(j)]^2 \tag{1}$$

between the given curve v^i and a standard one v^s (the curve with the highest shear rate) is the shortest. In this equation the upper indexes i and s have been used to indicate each viscosity curve, while the index j runs over all N data points of a fixed curve. The result of this procedure was surprising: as is revealed in Fig. 3, all viscosity curves have coalesced in a unique curve. Furthermore, at least in the interval of shear rates that have been analyzed, the law connecting the scale factor α and the shear rate seems to be linear, not indicating any kind of saturation, which would be a signal of the minimum gap mentioned above. That is, the shape invariance of the viscosity peaks of these compounds under a linear shear rate scaling law implies that for sufficiently high shear rate the height of a peak can be made as small as wanted and, therefore, it can become less than the difference between the viscosity coefficients of the two phases. Consequently, it even being true that JC explain the viscosity behavior of some compounds, as shown in Fig. 1, the same argument seems not to be applicable to explain the peaks observed on the myristate and nonanoate samples. Below, at the end of this work, this result will be reconsidered and this apparent contradiction with the results found on nonanoate and myristate discussed.

III. FLUCTUATIONS IN THE VISCOSITY PEAKS

According to the theory of critical phenomenon the fluctuations accompanying a continuous phase transition can dominate the physical scenario and make the functions associated with correlations between different points become divergent. That is, as the viscosity results from the transport of moment between adjacent shear planes it is function of a two-point correlation function and, consequently, along a continuous phase transition it can present a singular behavior. Nevertheless, the transitions described here are not continuous, but quasicontinuous (weak first order), which have as one of the characteristics the properties identified above [10,13,14]. To make it clear, let us remember that at the neighborhoods of a continuous phase transition the connected two-points correlation function $G_c^2(r)$ has a behavior given by [15]

$$G_c^2(r) = \langle \phi(0)\phi(r) \rangle \approx e^{-r/\xi}, \tag{2}$$

where $\langle x \rangle$ represents a statistical mean of the random variable x over all particles of the sample separated by a distance r and where

$$\xi = |T - T_c|^{-\nu}, \tag{3}$$

T is the temperature, T_c is the critical temperature, ν is a critical exponent, and $\phi(r)$ is any function defined at the point r. So, as one has $\nu > 0$, when $T \to T_c$ the correlation between different points diverges and, no matter their distance, they are connected. To deduce the behavior of the viscosity in such conditions remember that the viscosity η can be defined as [16]

$$\eta = \frac{1}{VkT} \int_0^\infty \langle J(0)J(t) \rangle dt,$$

where J is given by [16]

$$J(t) = \sum_{j\neq i}^{N} z_{ij}F_{ij}^{x}(t),$$

z_{ij} is the distance, perpendicular to the shear plane, between the particles i and j, and F_{ij}^{x} is the component of the force between them along the direction x. In the above equations we have made use of the fact that a liquid crystal is a dense fluid to discard the "kinetic" term of J [16]. As consequence of this definition, it is immediately obvious that the viscosity involves interactions between different particles and, at the neighborhoods of a critical point, it would be given by an average over two-points correlation function, as given by Eq. (2) [15]. Hence, around a critical point,

$$\eta = \frac{\rho^2}{kT}\int_V \int_0^\infty J(0)J(t)g(\vec{r})e^{-r/\xi}g(\vec{r})dtd^3r, \tag{4}$$

where, as usual [17], the homogeneity of the system has been used to convert the discrete double sum into an integral over the position of the corresponding particles, which have the probability $g(\vec{r})$ of staying separated by the distance $\vec{r}$. Making the change of variables $x_i \to \xi\overline{x_i}$ it is straightforward to show that the viscosity will be transformed as

$$\eta \to \xi^3\overline{\eta}, \tag{5}$$

where $\overline{\eta}$ express the nonsingular viscosity term in terms of the new variable $\overline{\vec{r}}$. So

$$\eta = \overline{\eta}|T - T_c|^{-3\nu}. \tag{6}$$

This equation reveals that around a critical point the behavior of all viscosity curves presents the same divergent term $|T - T_c|^{-3\nu}$. Hence, the scale invariance observed in Fig. 3 can be easily explained. In the neighborhoods of these phase transitions all the viscosity curves will share the same critical exponent ν and differ by a multiplicative shear-rate-dependent term $\overline{\eta}$.

According to Eq. (6) we have

$$\nu = -\frac{1}{3}\frac{\ln(\eta) - \ln(\overline{\eta})}{\ln|T - T_c|}. \tag{7}$$

So, as the temperature approaches the critical point T_c, a plot of the above equation as a function of $|T - T_c|$ would converge to ν. Figure 4 exhibits this plot for both compounds, myristate and nonanoate. The agreement in the curves and values obtained for ν reveals a consistency with the idea that both peaks can result from the same basic fundamental phenomenon, the critical behavior of the set of the weak first-order phase transitions present around the N^*-I phase transition. For both cases our data points suggest that $\nu \simeq 0.25$, in good agreement with the known value of the corresponding critical exponent of the nematic-isotropic phase transition [10]. It is important to emphasize that the myristate and nonanoate compounds present a set concentrated blue phases, in the narrow domain of the temperature, near the isotropic phase [18].

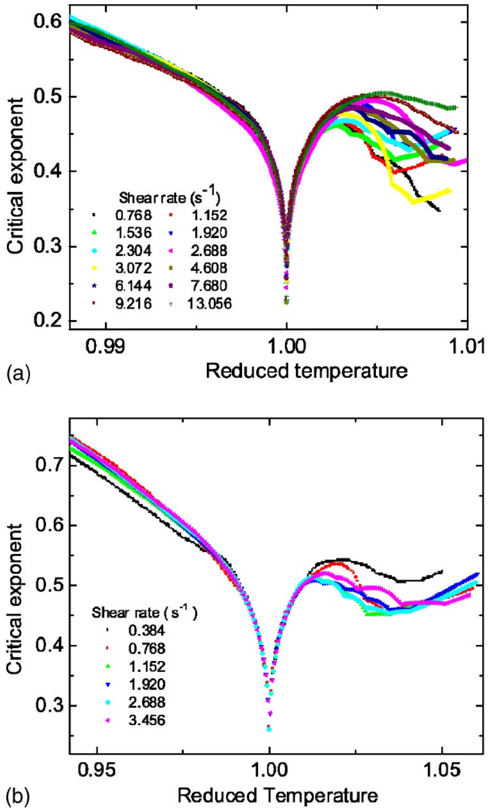

FIG. 4. (Color online) Critical exponents ν obtained with the use of the application of Eq. (7) at the data shown at Fig. 3. As the shape of the peaks are scale invariant we have used $\overline{\eta}=1$. Both graphs coherently indicate a critical exponent at the region of $\upsilon = 0.25$. This result is in good agreement with the known values of this critical exponent for the N^*-I phase transition.

IV. CONCLUSION

Before ending this work, we would like to stress that the relevant rheological problems that can be envisaged by the conditions of the experiment that we have described are not exhausted by the present work. Some other interesting problems remain to be understood and, some of them will be now mentioned. First, it is known that when the chirality of the cholesteric mixture is increased, the first-order phase transition line, which separates the blue phase (BP_{III}) from the I phase, ends at a critical point that borders a supercritical region, where strong fluctuations in the optical activity have not been observed [19–22]. This result has been interpreted as a sign that the BP_{III} and I phases possess the same macroscopic symmetries. This immediately suggests new questions about the rheology of these phases: how is the absence of chiral fluctuations reflected in the viscosity data? What is the rheological behavior of these materials in the supercritical region? Of course, this work has not answered these questions but, at least, our results are enough to highlight their importance. Furthermore, another important question arises from our results. It has been established that the divergence in ξ leads to the formation of viscosity peaks that, in the measured shear rate interval, are scale invariant. Nevertheless, these same peaks seem not be detectable in the

MBBA compound, for which the same arguments apply. We believe that there are two main cooperating reasons for it. The first one was detailed in the Introduction: the existence of tight, compressed sequence of weak first-order phase transitions (blue phases) clearly reinforces and enlarges the temperature interval in which the viscosity peaks are observable, making them more apparent for the myristate and nonanoate than for MBBA. Nevertheless, we understand that there may also be another reason. It is a experimental fact that when compared with myristate and nonanoate the MBBA presents, for the same shear rate, a small effective viscosity ($\sim 10^2$ smaller) and, as we have observed above, the JC hypothesis has an asymptotic character and, surely, the viscosity observed in the MBBA is close of the corresponding asymptotic value. Consequently, when we realize that these two reasons work together, it is concluded that to observe in the MBBA the same scaling rules that we have observed in the viscosity peaks of the myristate and nonanoate, it would be also necessary to decrease the shear rate applied to the sample to a very small value.

To sum up, in this work the nature of the viscosity peaks observed during the N^*-I phase transition of myristate and nonanoate liquid crystals has been studied. It has been found that their shape is scale invariant, a characteristic result associated with the critical behavior of the two-point correlation functions of this phase transition. The critical exponent associated with these peaks has been calculated, and it was found that they present good agreement with the value of the corresponding critical exponent of the nematic-isotropic phase transition.

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